

Alkene Reactions
2- Addition Reactions -
Synthesis of Alcohols

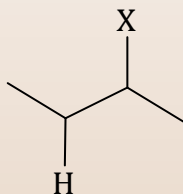
Dr. Sapna Gupta

All Reactions

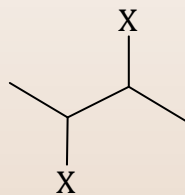
✓ Covered in previous power point.

✓ Covered in this power point.

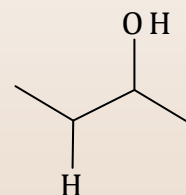
✓ hydrohalogenation



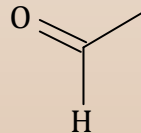
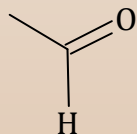
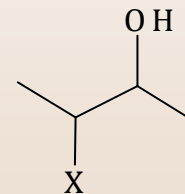
✓ halogenation



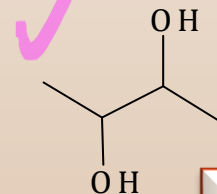
✓ hydration



✓ halohydrin



oxidative cleavage

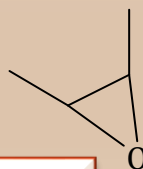


diol

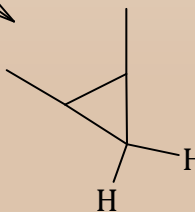
✓ reduction



✓ epoxide



✓ carbene addition



General Mechanism - Review

- The alkene is the nucleophile and the reagent is the electrophile.
- Alkene types: symmetric or asymmetric; terminal or internal.
- Addition can be syn (same side) or anti (on the opposite sides) of the double bonds. In both cases stereoisomers can be formed if chiral center is generated.
- Markovnikov addition (H adding to the carbon with more hydrogens) and anti Markovnikov addition (H adding to the carbon with less hydrogens) can occur.
- Rearrangement of the carbocation is possible in case of S_N^1 or E1 reactions.

All the above can be found the power point preceding this one.

Hydration – Introduction

Hydration of an alkene is also an addition reaction just like we have covered before. The product is always at least one alcohol group. Essentially what we are doing here is synthesizing alcohols.

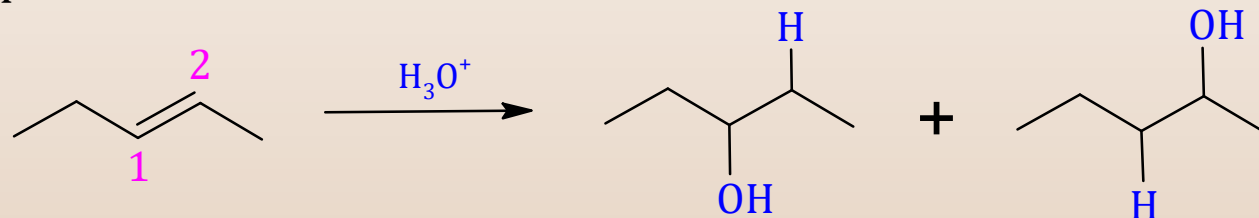
There are many reagents that can carry out hydration. Choice of the reagent will depend on what kind of an alcohol is needed: Markovnikov or anti Markovnikov addition of OH; one or two OH groups on the alkene, syn or anti addition. The kind of product needed will drive what kind of substrate and reagent that can be used.

Below are the reactions we will learn:

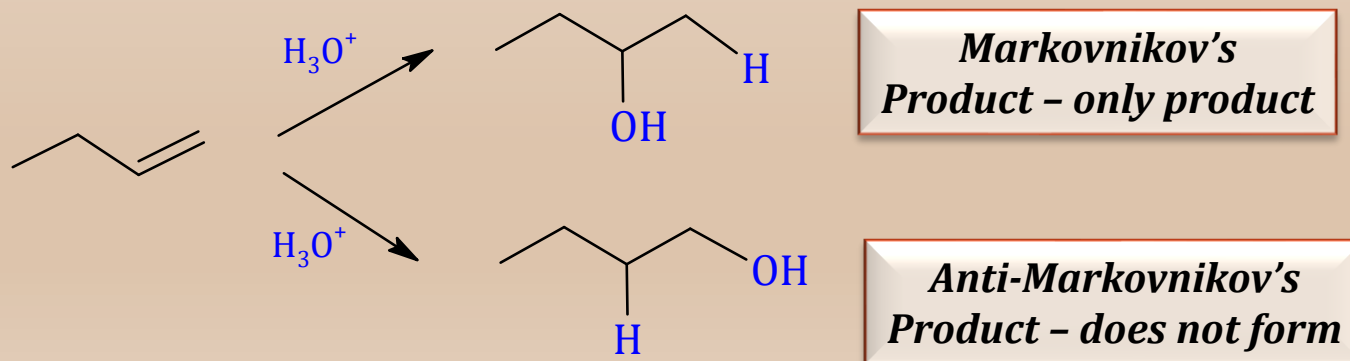
- 1) Hydration - Adding one alcohol:
 - a) Hydration with acid catalysis
 - b) Oxymercuration
 - c) Hydroboration
- 2) Halohydrin formation
- 3) Diol synthesis
 - a) Syn diol
 - b) Anti diol

1a) Addition of H₂O with Acid Catalyst

Hydration of an alkene is the addition of water, H₂O, H-OH to give an alcohol. This reaction is done in the presence of an acid, usually dilute sulfuric acid and phosphoric acid.



- The acidic medium implies that the reaction is via carbocation intermediate.
- HOH adds in accordance with *Markovnikov's rule*.

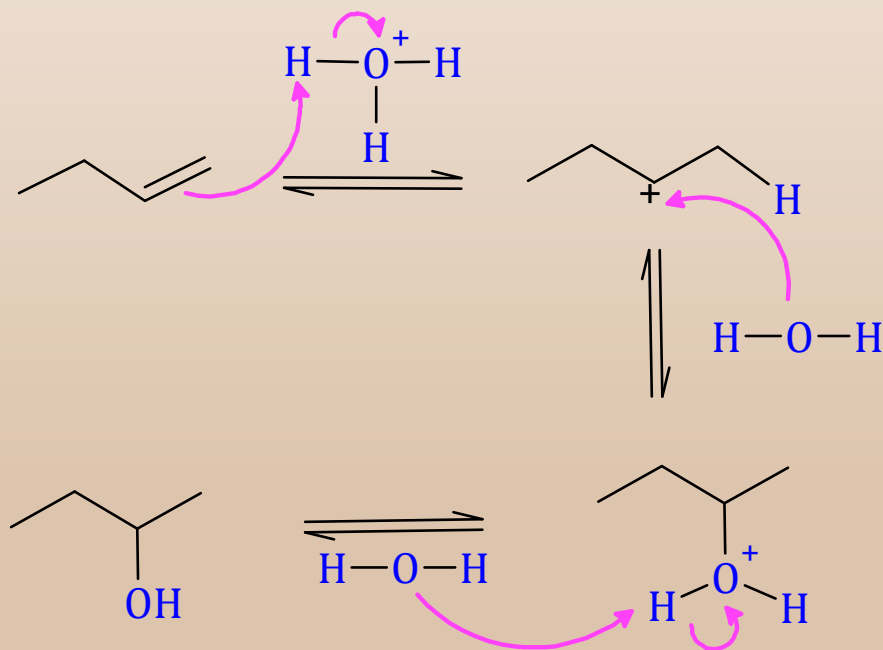


1) Hydration - Mechanism

Mechanism of acidic hydration is similar to addition of HX i.e., via carbocation. This means that the more substituted the carbocation, the more stable it is ($3^\circ > 2^\circ > 1^\circ$), which leads to formation of the *Markovnikov's* product.

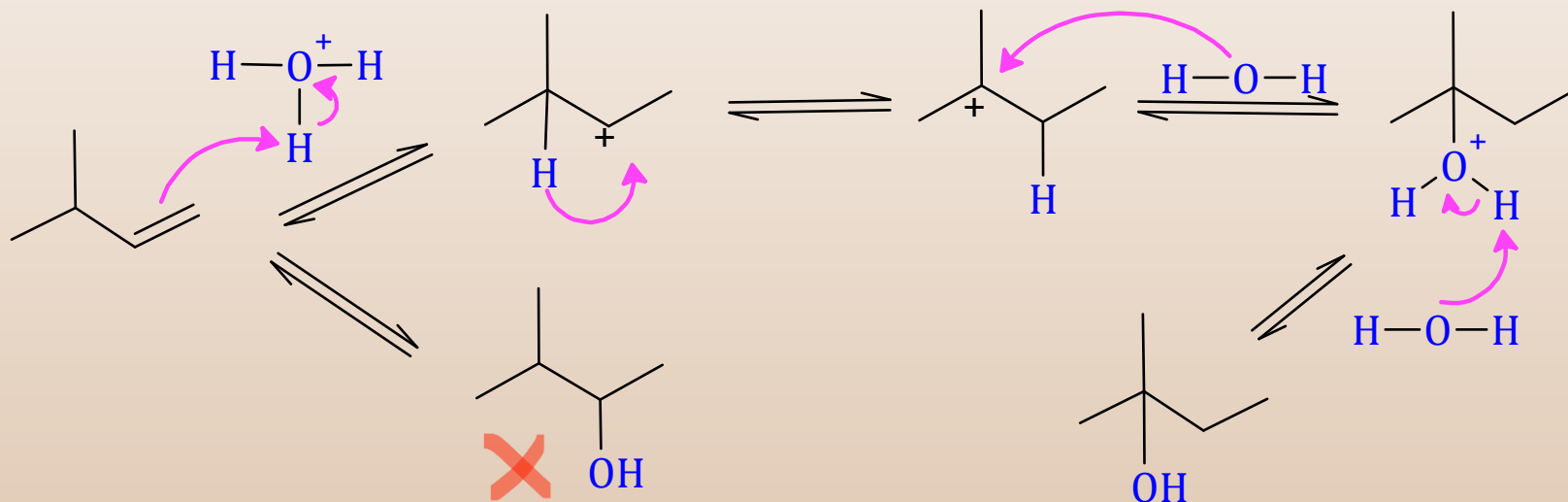
Rearrangement can occur where applicable – see next slide.

- Note: The reaction occurs in equilibrium and can be controlled to go forward or in reverse.



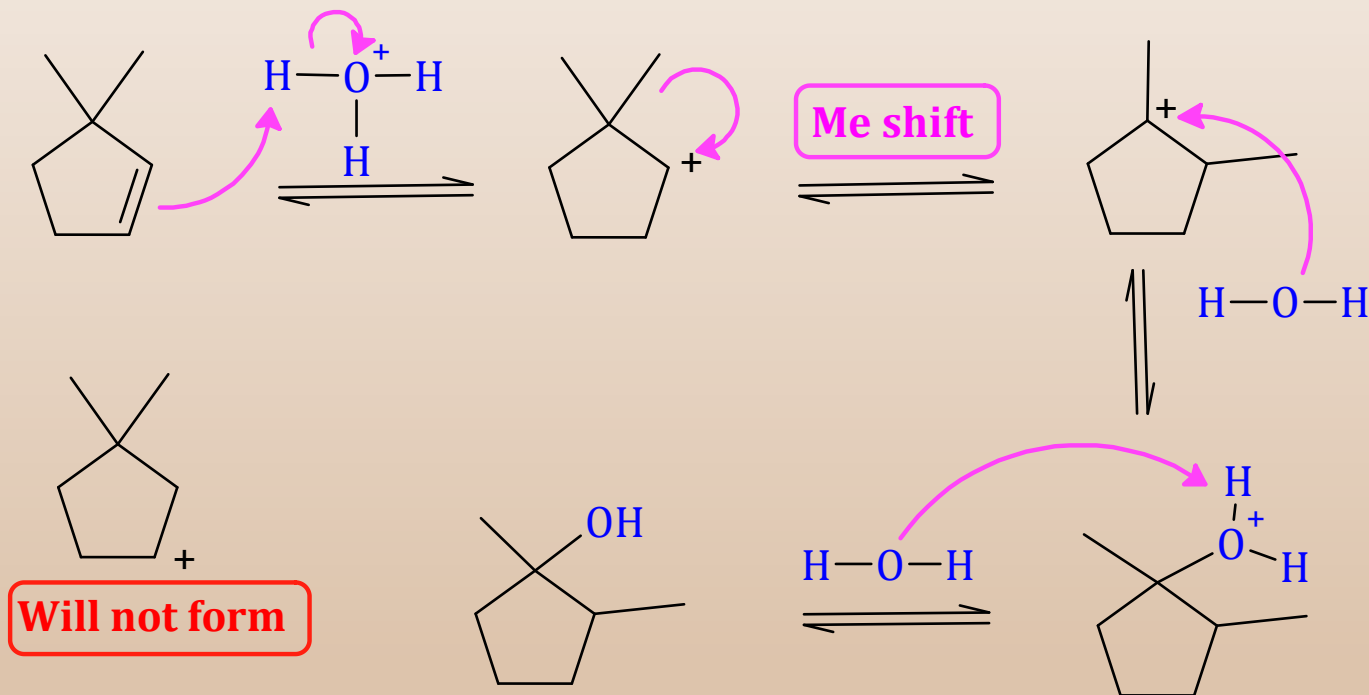
1) Hydration – Mechanism - Rearrangement

Rearrangement can occur where a more stable carbocation can be formed.



2) Hydration – Mechanism - Rearrangement

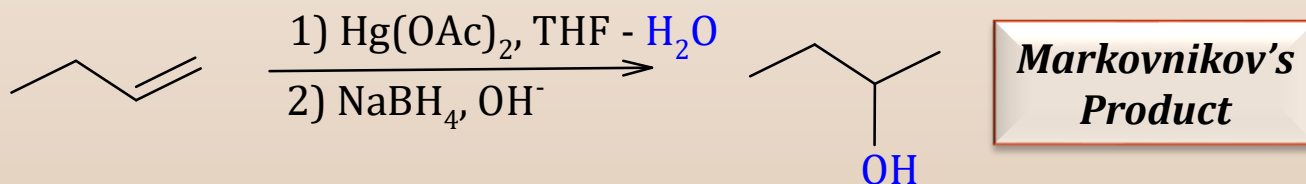
Here is another example of rearrangement. You don't have to write "Me shift", just show the arrow showing the shift. I am just writing it to show you.



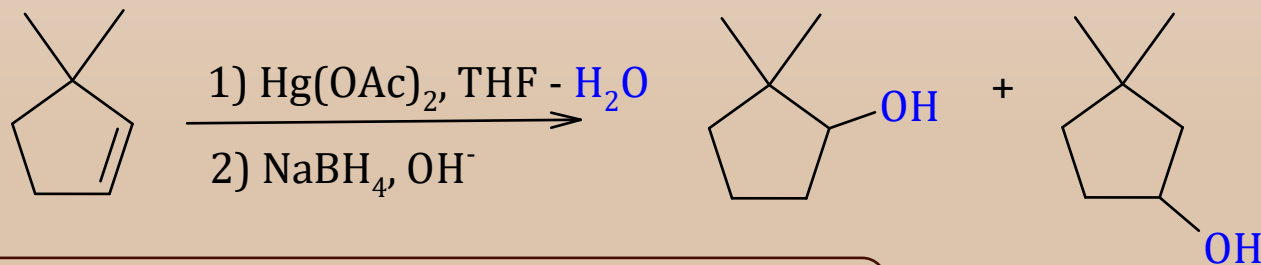
1b) Oxymercuration

Oxymercuration is done to prevent rearrangement because in the acid catalyzed hydration, rearrangement can occur.

- ***The addition is still Markovnikov's addition***
- Reagent is mercury diacetate* $\text{Hg}(\text{OAc})_2$ with water, followed by NaBH_4 and OH^- .



Oxymercuration of 3,3-dimethylcyclopentene shows that the hydration is not specific on the double bond. To avoid multiple products, it is better to do the reaction with a symmetrical substrate.

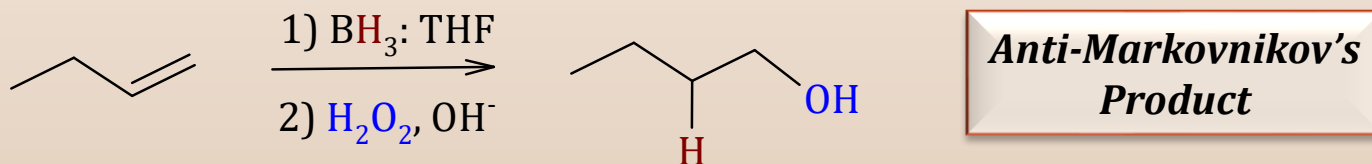


* $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}$ - is acyl (Ac) group and $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{O}$ - is acetyl (OAc) group

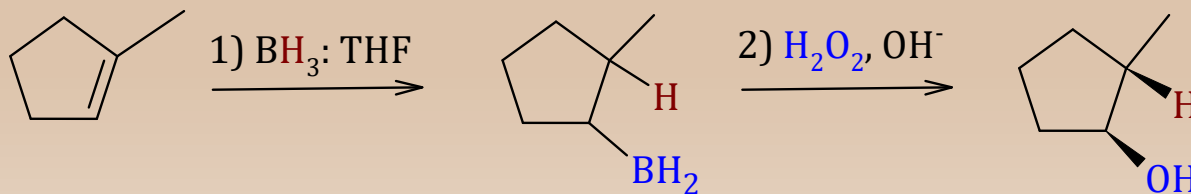
1c) Hydroboration

Hydroboration is carried out in case Anti-Markovnikov's product is needed.

- The reagent needed is a borane reagent for example hydroborane BH_3 :THF – where THF is the solvent that stabilizes the BH_3 . The work up involves a basic wash with hydrogen peroxide ($\text{OH}^-/\text{H}_2\text{O}_2$).
- **The addition is SYN addition** (addition on same side).



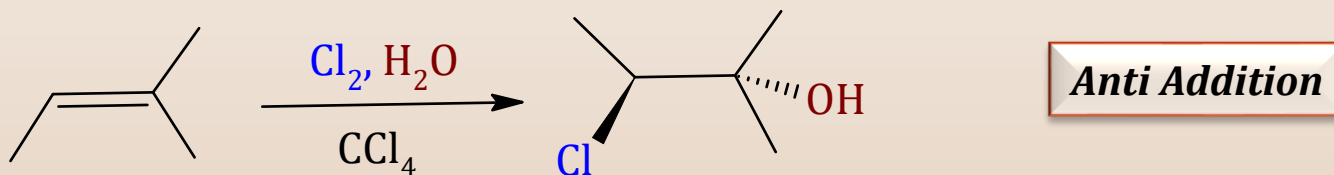
- Borane reagents are Lewis acid (boron has incomplete valence shell), while alkene is the Lewis base in this acid base reaction.
- The transition state involves BH_3 adding across $\text{C}=\text{C}$ which because of the reagent size needs more space. The bulky reagent is thus on the carbon that is less sterically hindered, giving the H on the carbon with less hydrogens.



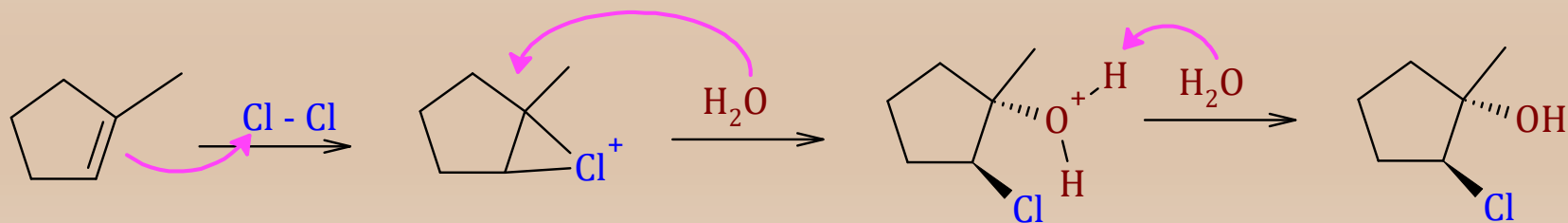
2) Halohydrin Formation

This is the addition of an alcohol and halogen group (HO-X) to an alkene to give a 1,2-halo alcohol, called a halohydrin. **Addition is ANTI.**

- The actual reagent is the halogen, Br₂ or Cl₂, in water in an organic solvent.



- In unsymmetrical alkenes, as shown above, the bromonium ion will have some of its δ⁺ charge density on the more substituted of the two carbons (sort of like a carbocation). The water nucleophile will then react at the carbon with the most δ⁺ charge – i.e. the more substituted carbon. (*NOTE: this is like Markovnikov's addition except the halogen goes to the carbon with more H*).

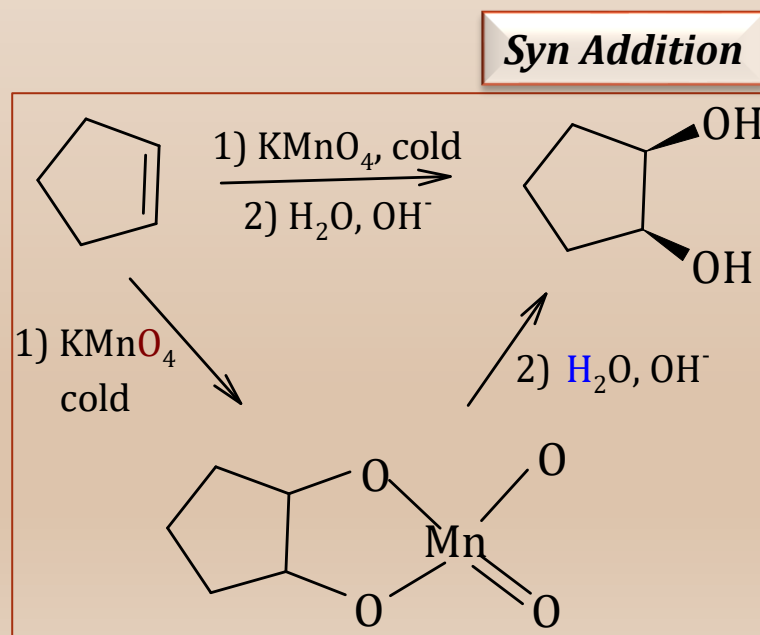
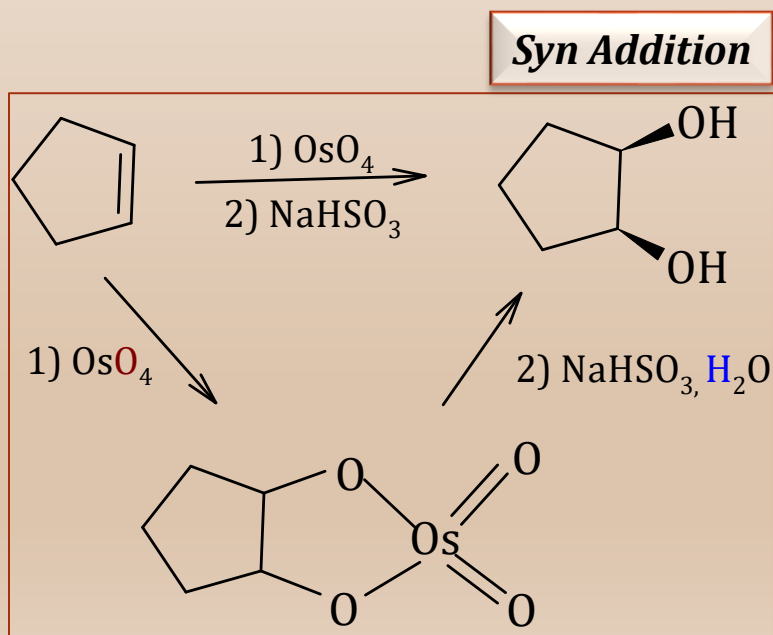


3a) Diol Formation – Syn Addition

Diol formation is when two alcohols are added in 1,2 manner to an alkene. The diol addition can be syn or anti depending on the reagent.

SYN addition reagents:

- Osmium tetroxide (OsO_4) followed by sodium bisulfite treatment.
- Potassium permanganate, KMnO_4 (cold) (**QUALITATIVE TEST**). Note that this reaction has to be done at room temperature (RT) or cool conditions. Higher temperature can change the nature of the products.



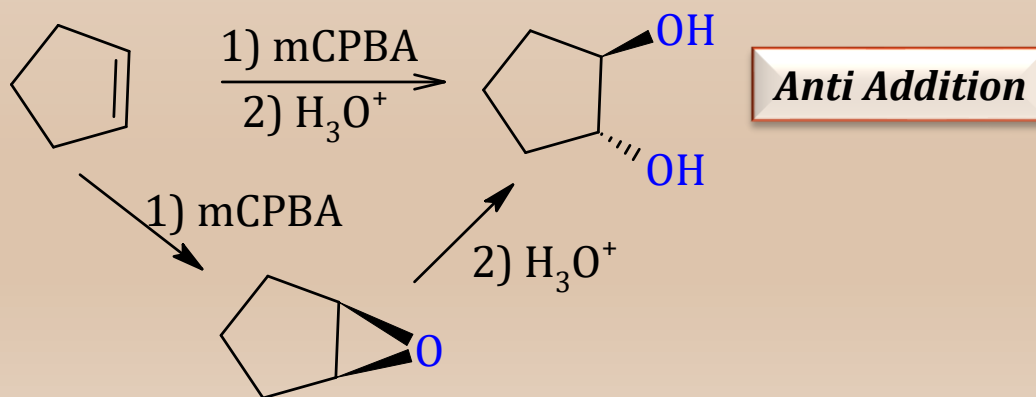
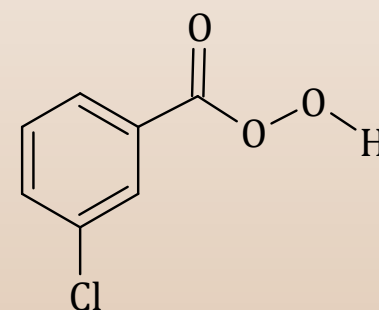
3b) Diols Formation – Anti Addition

Anti addition of OH groups is a two step process.

- First step is epoxidation – formation of a three membered cyclic ether.
- Second is treat it with an aqueous acid or base to open the epoxide.

The reagent used to make an epoxide from an alkene is CH_3COOOH or any peracid (meta perbenzoic acid – MCPBA is a common acid).

- Stereochemistry of **addition of epoxide is ANTI**.
- The epoxide is then treated with weak acid or base to give the **ANTI** diol. (*The mechanism is similar to the bromonium ring opening – slide 11*).

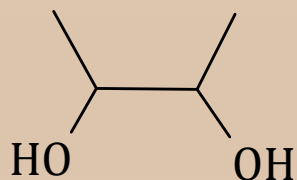
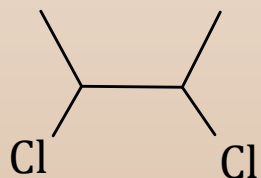


Names of Location of Groups

Below is a summary of the names of the relationship of groups you have learned in addition reactions and I have added two more – vicinal and geminal.

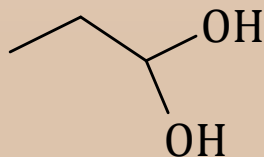
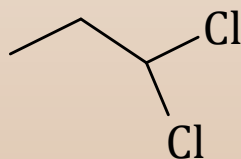
Vicinal/vic

On adjacent carbons
(1,2)



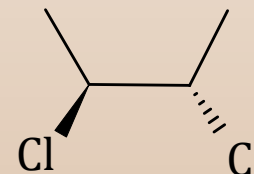
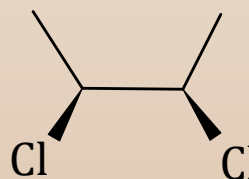
Geminal/gem

On the same carbon
(1,1 or 2,2)



Syn

On the same side



Anti

On opposite sides

Key Words/Concepts

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