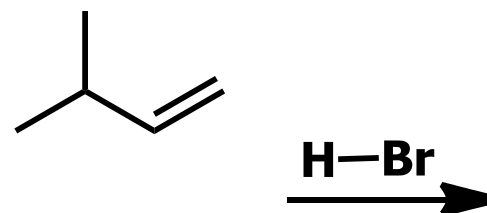
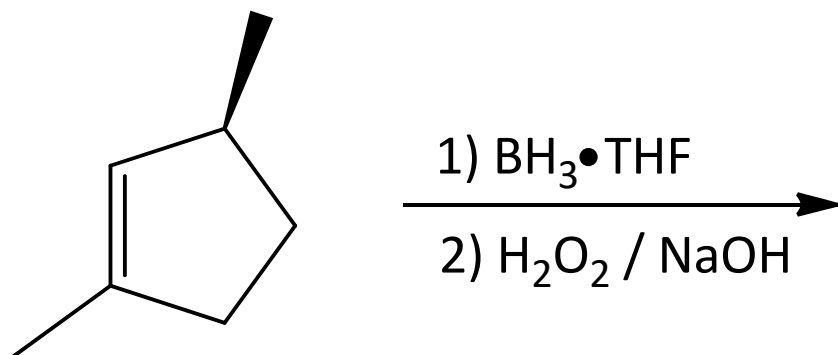
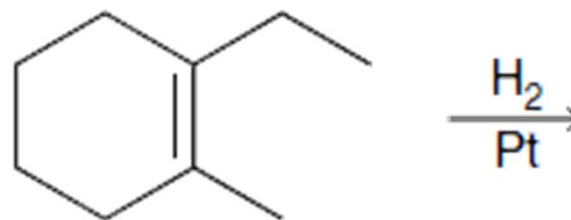
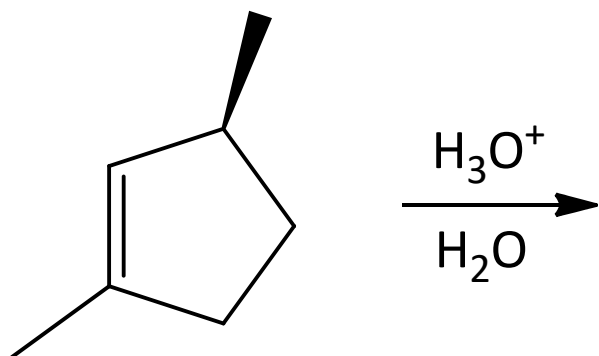


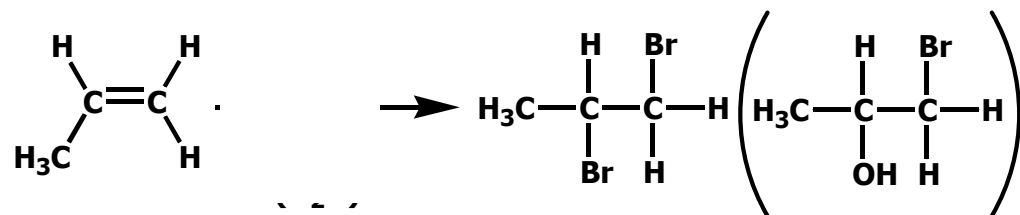
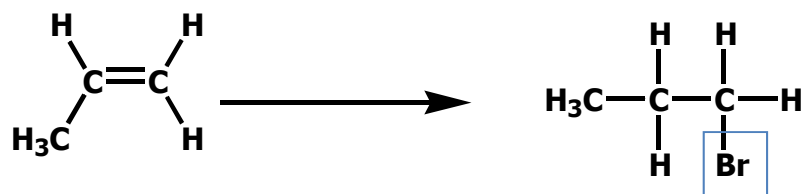
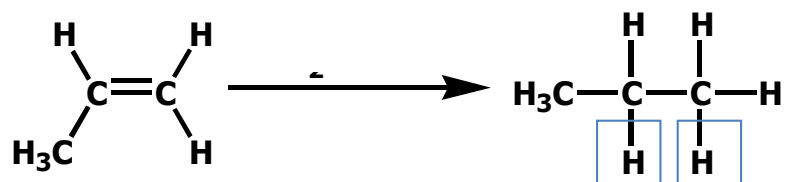
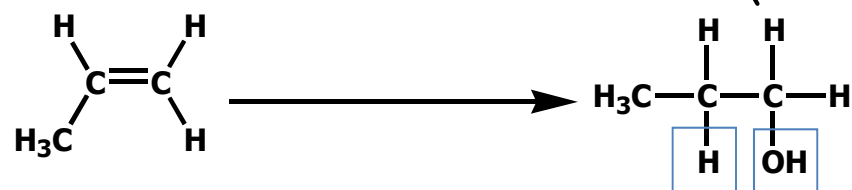
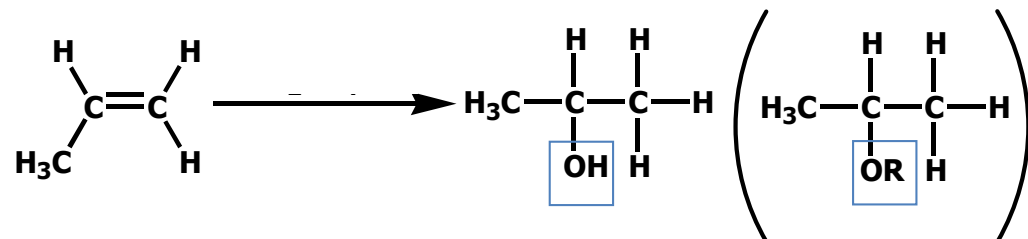
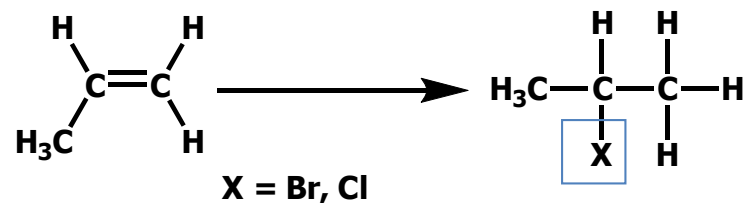
Chapter 8 part 4:

Halogenation/Halohydrins formation

- Today Hydrogenation Halogenation/Halohydrin formation



Addition Reactions:

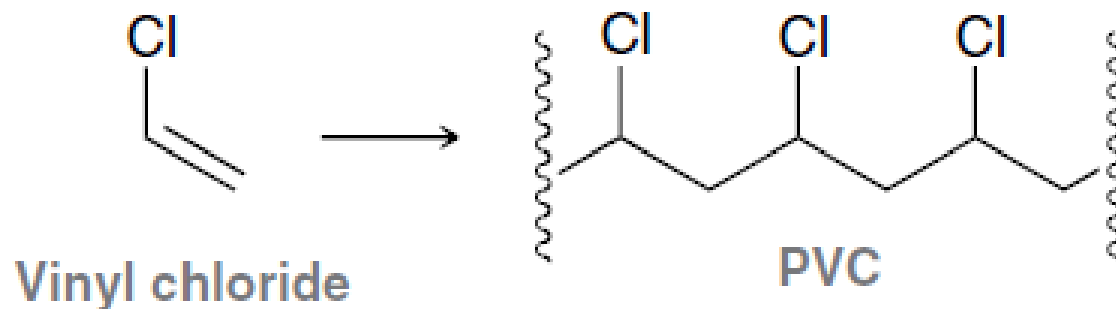


Halogenation

- Halogenation involves adding two halogen atoms across a C=C double bond.

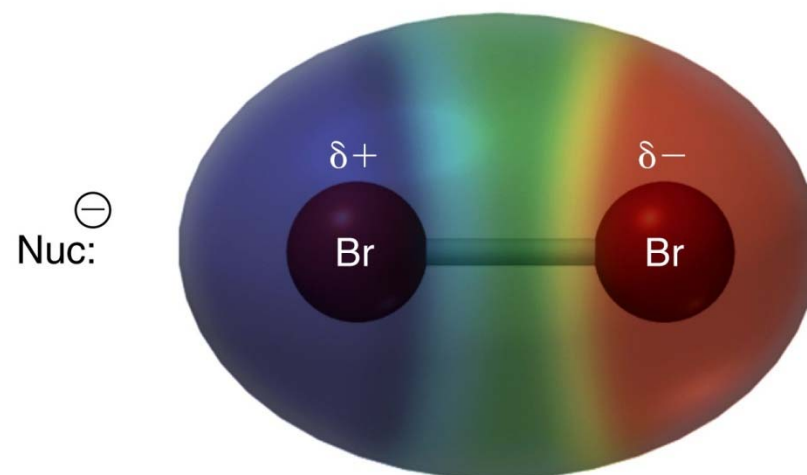


- Halogenation is a key step in the production of PVC.

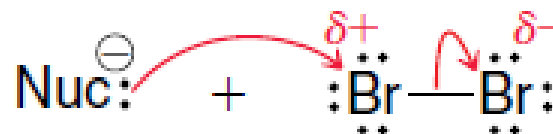


Halogenation

- Let's look at the reactivity of Br_2 . Cl_2 's reactivity is similar.
- It is nonpolar, but it is polarizable. WHY?
- Does the Br_2 molecule have a good leaving group attached to it?



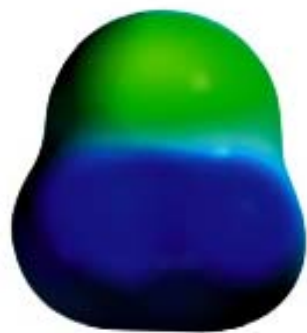
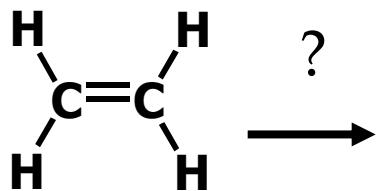
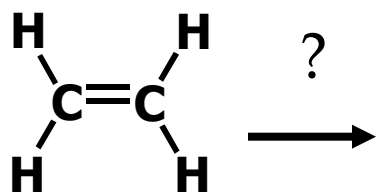
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Addition of Halogens to Alkene

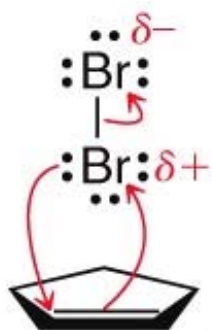
Imagine an alkene attacking Br_2 .

Imagine an alkene attacking Br_2 . You might imagine the formation of a carbocation.



Bromonium Ion

Halogenation

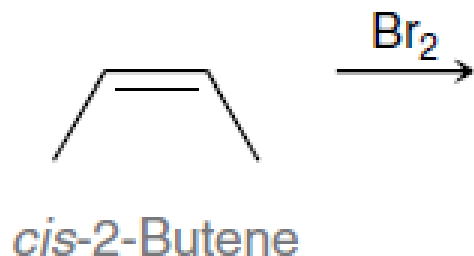


Nucleophilic attack
+
Loss of a leaving group

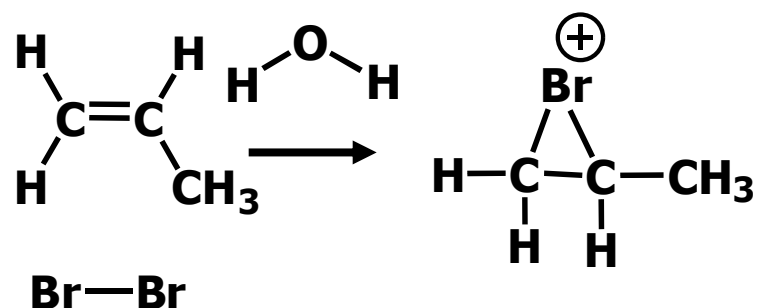


The alkene functions as a nucleophile and attacks molecular bromine, expelling bromide as a leaving group and forming a bridged intermediate, called a bromonium ion

- Only ANTI addition is observed. WHY?



Addition of Halogens in or with Water

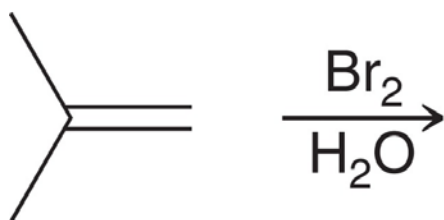


Halohydrins are formed when halogens (Cl₂ or Br₂) are added to an alkene with WATER as the solvent.

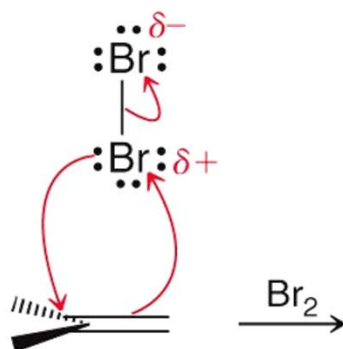
The bromonium ion forms from Br₂ + alkene, and then it is attacked by water.

Halohydrin Regioselectivity

- The –OH group ALWAYS adds to the more substituted carbon

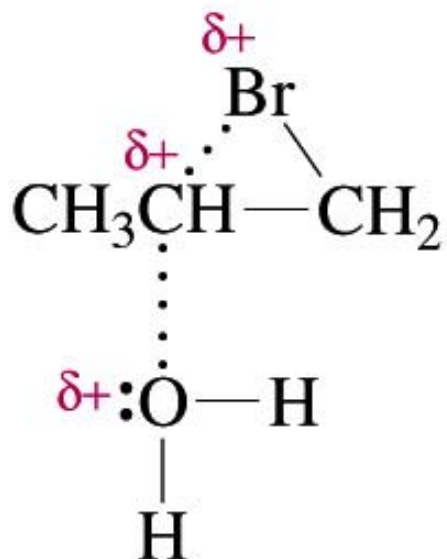


- The key step that determines regioselectivity is the attack of water on the bromonium ion

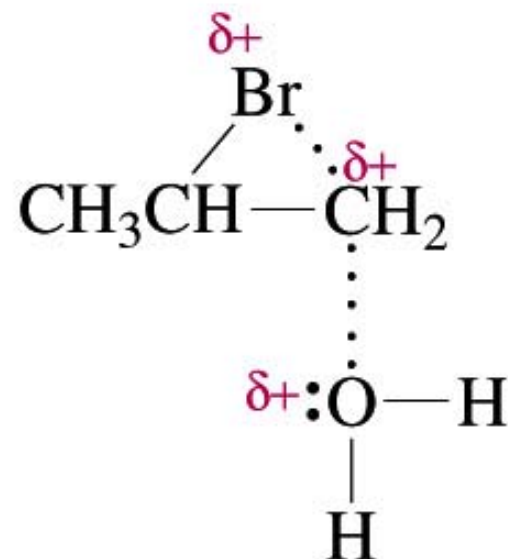


Bromonium ion is captured by water

Consider the transition states ...



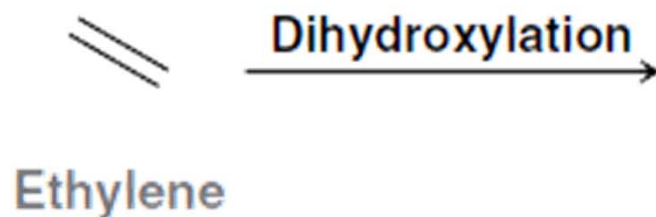
more stable transition state



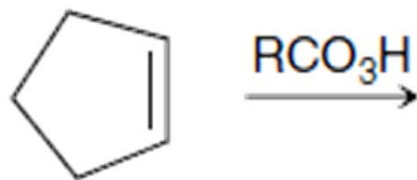
less stable transition state

Anti Dihydroxylation

- Dihydroxylation occurs when two –OH groups are added across a C=C double bond.

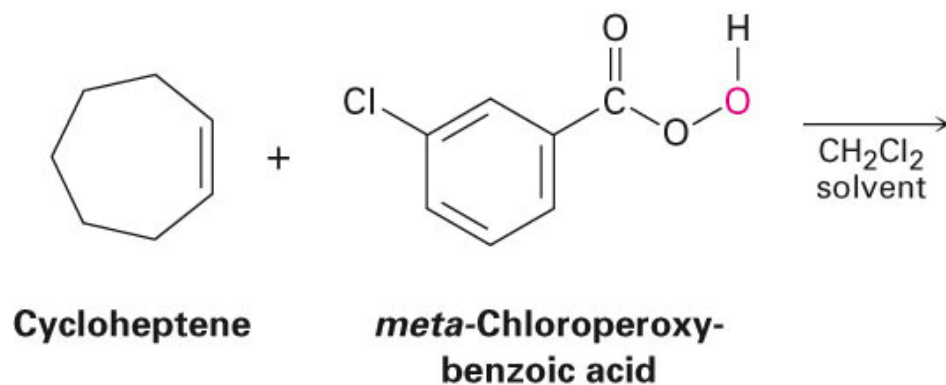


- ANTI dihydroxylation is achieved through a multi-step process.

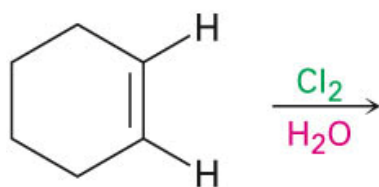


Preparation of Epoxides:

- Treatment of an alkene with a peroxyacid gives an epoxide



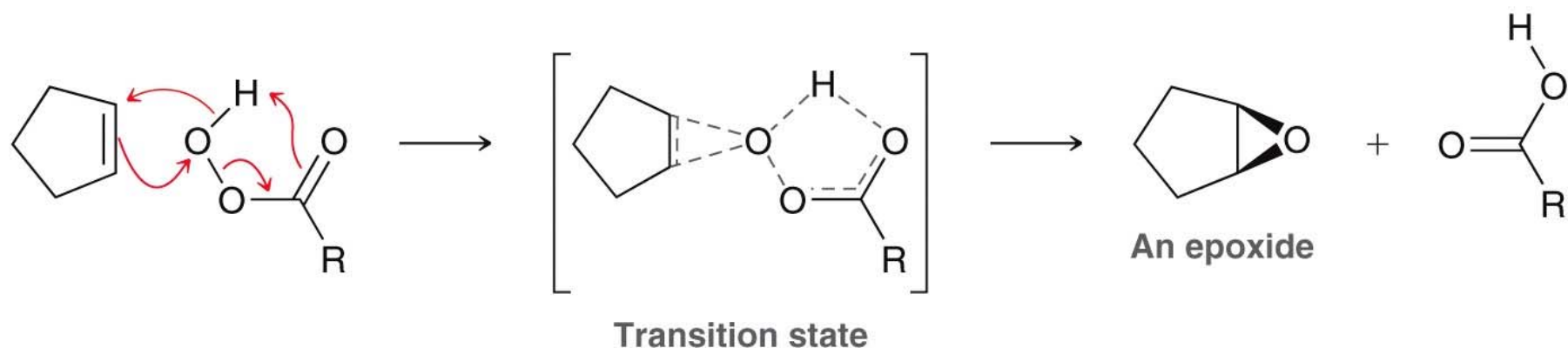
- Treatment of a halohydrin with base gives an epoxide



Cyclohexene

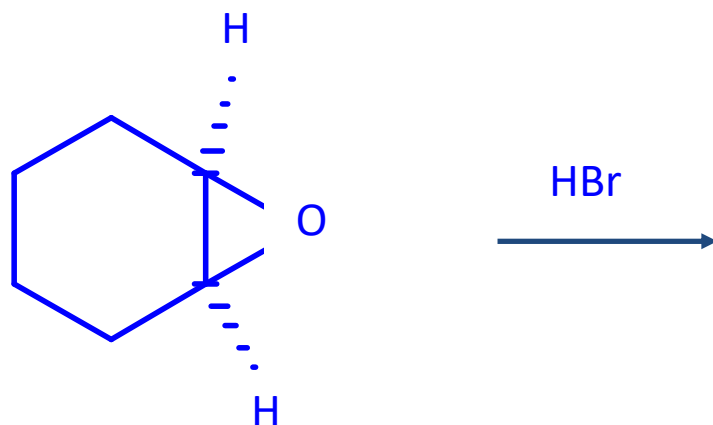
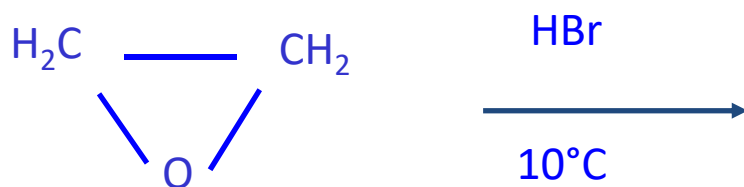
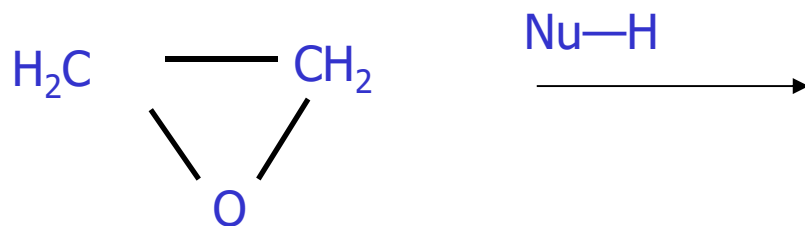
Anti Dihydroxylation

- First, an epoxide is formed



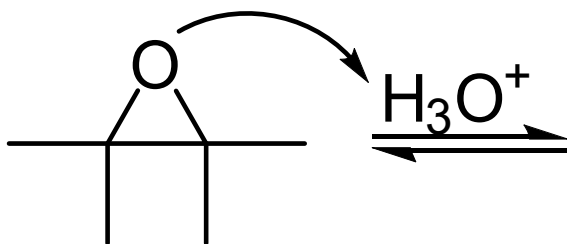
- Replacing the relatively unstable O-O single bond is the thermodynamic driving force for this process
- Is there anything unstable about an epoxide?
- Will an epoxide likely to react as a nucleophile (Lewis base) or as an electrophile (Lewis acid)?

Reactions of epoxides involve attack by a nucleophile and proceed with ring-opening.



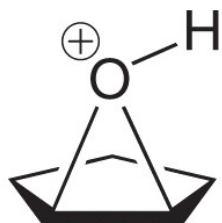
Anti Dihydroxylation

- Nucleophile attacks more substituted carbon of a protonated epoxide
- Inversion of configuration at site of nucleophilic attack
- Water is a poor nucleophile, so the epoxide is activated with an acid



Mild acid reacts with epoxides in water to generate anti 1,2-diols

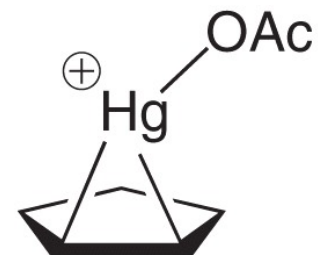
Anti Dihydroxylation



A protonated epoxide



A bromonium ion



A mercurinium ion

For Next Time....

End Chapter 8 on Friday

Exam #2 Wednesday!

Next week Chapter 9

Suggested Homework Problems Chapter 8

1, 2, 5, 9, 12,13, 18, 24, 27, 31, 42-46, 52, 57,62,63

Suggested Homework Problems Chapter 9

1,7,9,13,18,20,32-37, 41,44,52,57