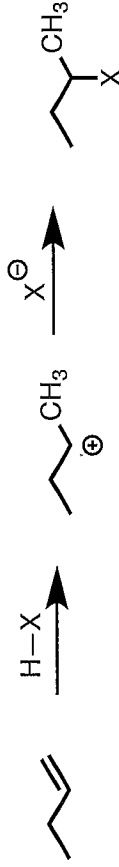


Chapter 4: Reactions of Alkenes

In an addition reaction the C=C pi bond is broken and two new sigma bonds are formed in its place.

There are a variety of different mechanisms that can result in an addition reaction. The most common mechanistic pathway is called *Electrophilic Addition*. The starting material is often an alkene or an alkyne, where the pi bond is acting like a nucleophile. Rate order equations, stereochemical outcomes, and reactivity of the starting material are all dependent upon the starting material and reagent combination so it is difficult to generalize.

Example 1:

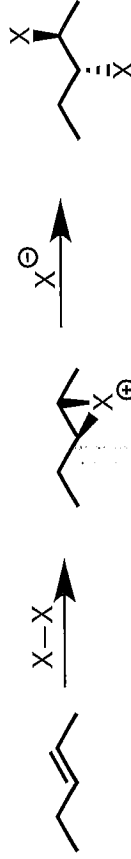


The alkene acts as a nucleophile and accepts a proton
Add one hydrogen
Form a carbocation

The nucleophile attacks the carbocation

- The pi bond breaks as it forms a new sigma bond to hydrogen.
- One carbon of the alkene adopts a proton and the other carbon adopts a positive charge (carbocation)
- Recall that carbocations can rearrange; it is at this step that a rearrangement might occur
- The nucleophile that results from the first step (X⁻) attacks the carbocation and forms the second new sigma bond

Example 2:



- The pi bond breaks as it simultaneously forms two new sigma bonds to make a cyclic intermediate
- This cyclic intermediate is highly strained and very reactive
- The nucleophile that results from the first step (X⁻) attacks the most substituted site of the cyclic intermediate and breaks open the three membered ring and forms the final sigma bond.

A Note About Syn and Anti:

The terms syn and anti are used to discuss the spatial relationship between groups. We use these terms differently than cis and trans because syn and anti refer to the reaction process or the mode of addition.

Syn addition: two groups are added to the same face of the pi bond

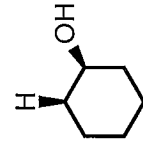
Anti addition: two groups are added to opposite faces of the pi bond

How to recognize this in the product:

Syn = both groups up (both wedged) or both groups down (both dashed, or "hatched")

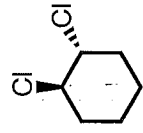
Anti = one group up (wedged) and one group down ("dashed" or "hatched")

In chair cyclohexanes it is possible to denote up / down oriented without a dash or wedge to indicate direction.



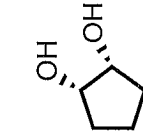
syn

H and OH



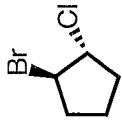
anti

Cl and OH



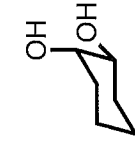
syn

OH and OH



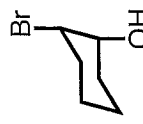
anti

Br and Cl



syn

OH and OH



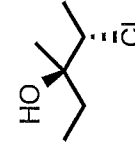
anti

Br and OH



syn

C-C and
C-C of the
ring

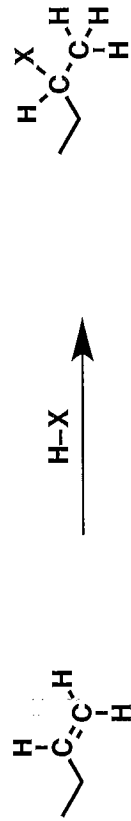


anti

OH and Cl

Addition of Hydrogen Halides To Alkenes

General Reaction:



X = halide

Major product

Typical acids: *HCl*, *HBr*, *HI*

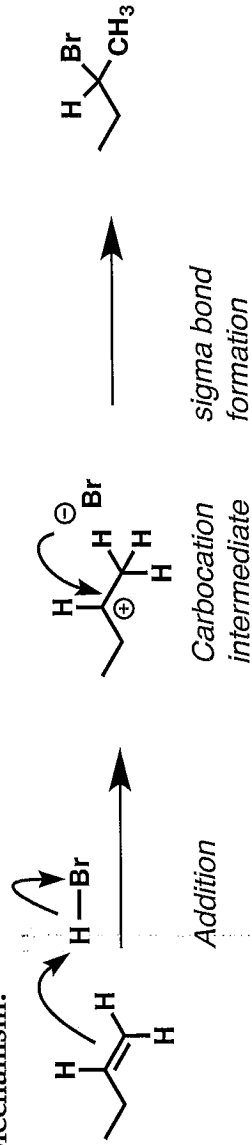
“Markovnikov”
selectivity

Minor product
“anti-Markovnikov”

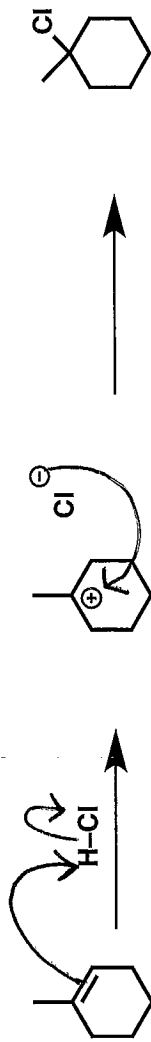
Mechanism Basics Box:

- Acids (HX) include HCl, HBr, and HI
- First step is protonation of alkene to give a carbocation, with the pi bond acting as a base
- Rearrangements may occur to give a more stable carbocation intermediate
- The final step is addition of X⁻ to carbocation, which may occur from either face of the cation
- Net effect is addition of HX across double bond with X at the “most substituted” position (“Markovnikov” selectivity)
- The rate-determining step is formation of the carbocation

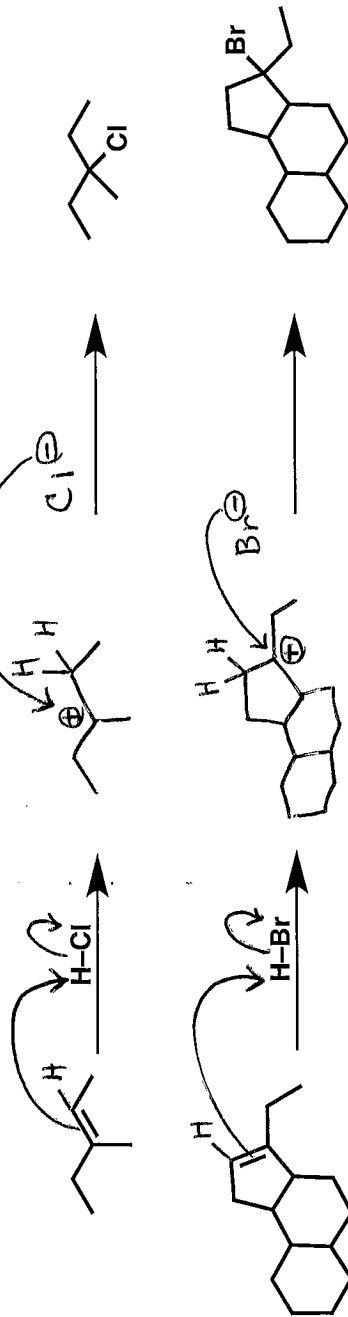
General Mechanism:



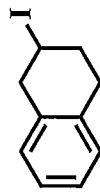
Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediates).



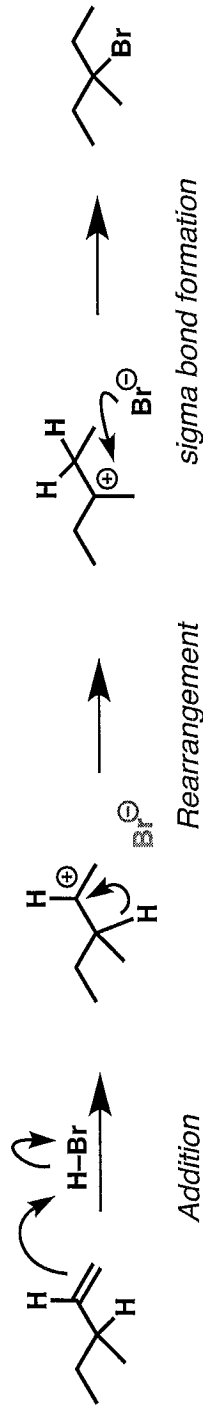
Why not this?



comes from 2° site

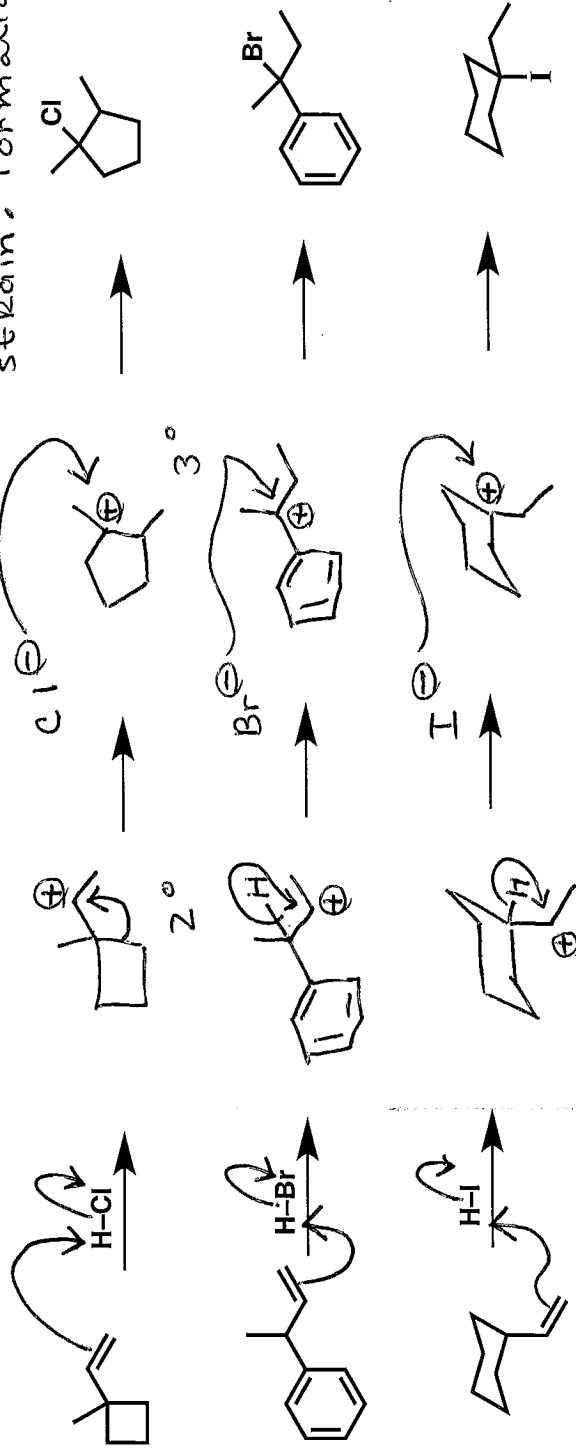
allylic 2° site

Advanced Examples - Addition With Rearrangement



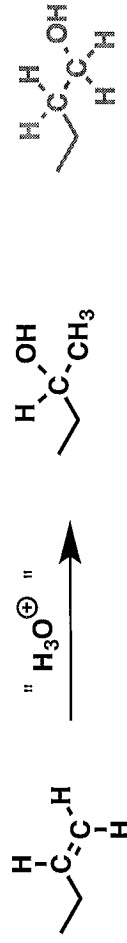
Complete the mechanism by following the pattern (draw arrows and intermediates).

Ring expansion alleviates ring strain. Formation of 3° carbocation.



Acid-Catalyzed Addition of Water And Alcohols To Alkenes

General Reaction:



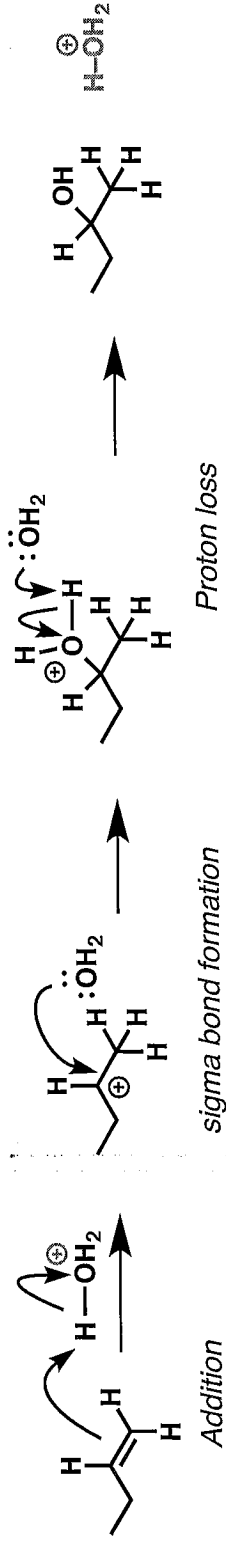
Aqueous acid often written H_3O^+ or $\text{H}_2\text{O} / \text{H}_2\text{SO}_4$

"Markovnikov" product (major)

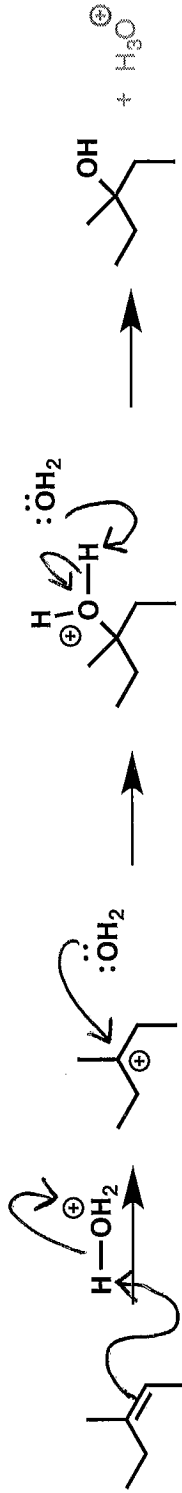
Mechanism Basics Box:

- See mechanism box for addition of HX to alkenes
- Mechanism is same as for addition of HX, except for final deprotonation step
- Rearrangements may occur to give a more stable carbocation
- Use of alcohols instead of water produces ethers
- Rate determining step is formation of a carbocation intermediate

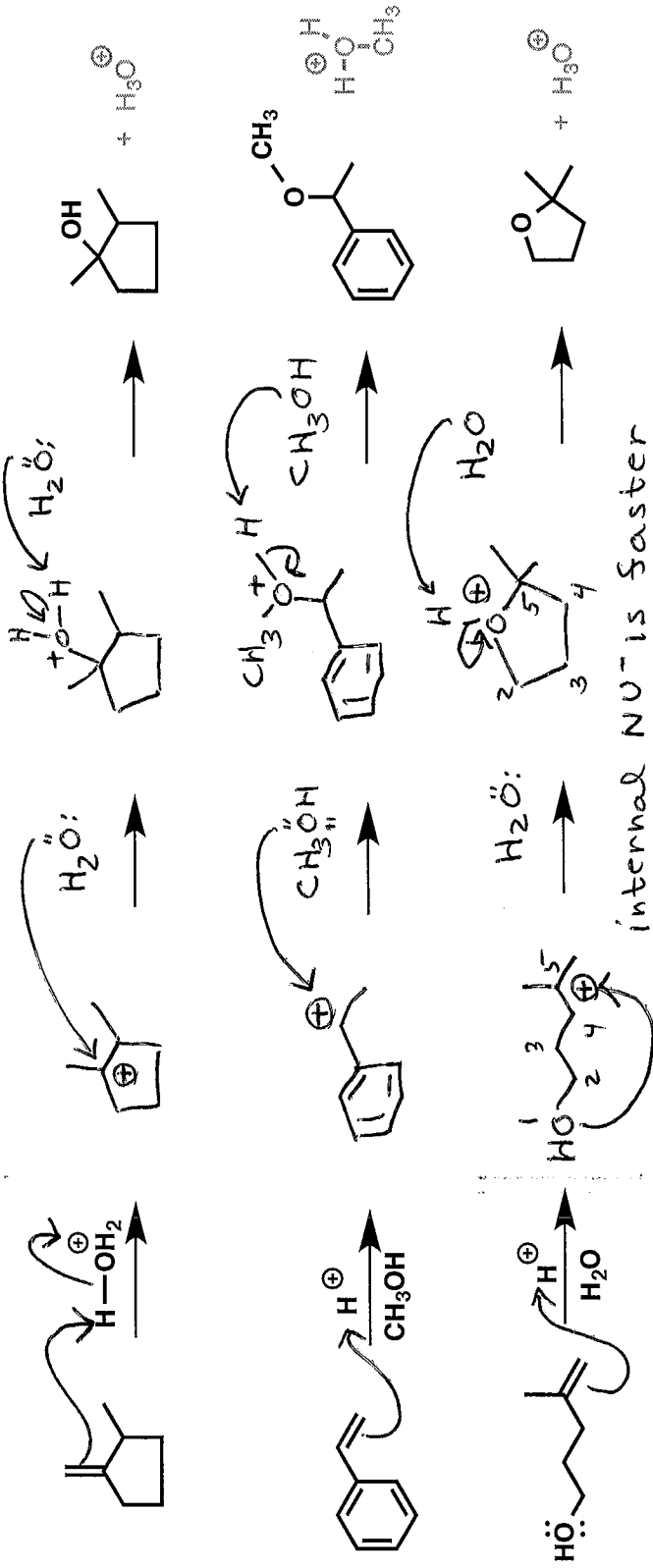
General Mechanism:



Fill in the missing arrows.



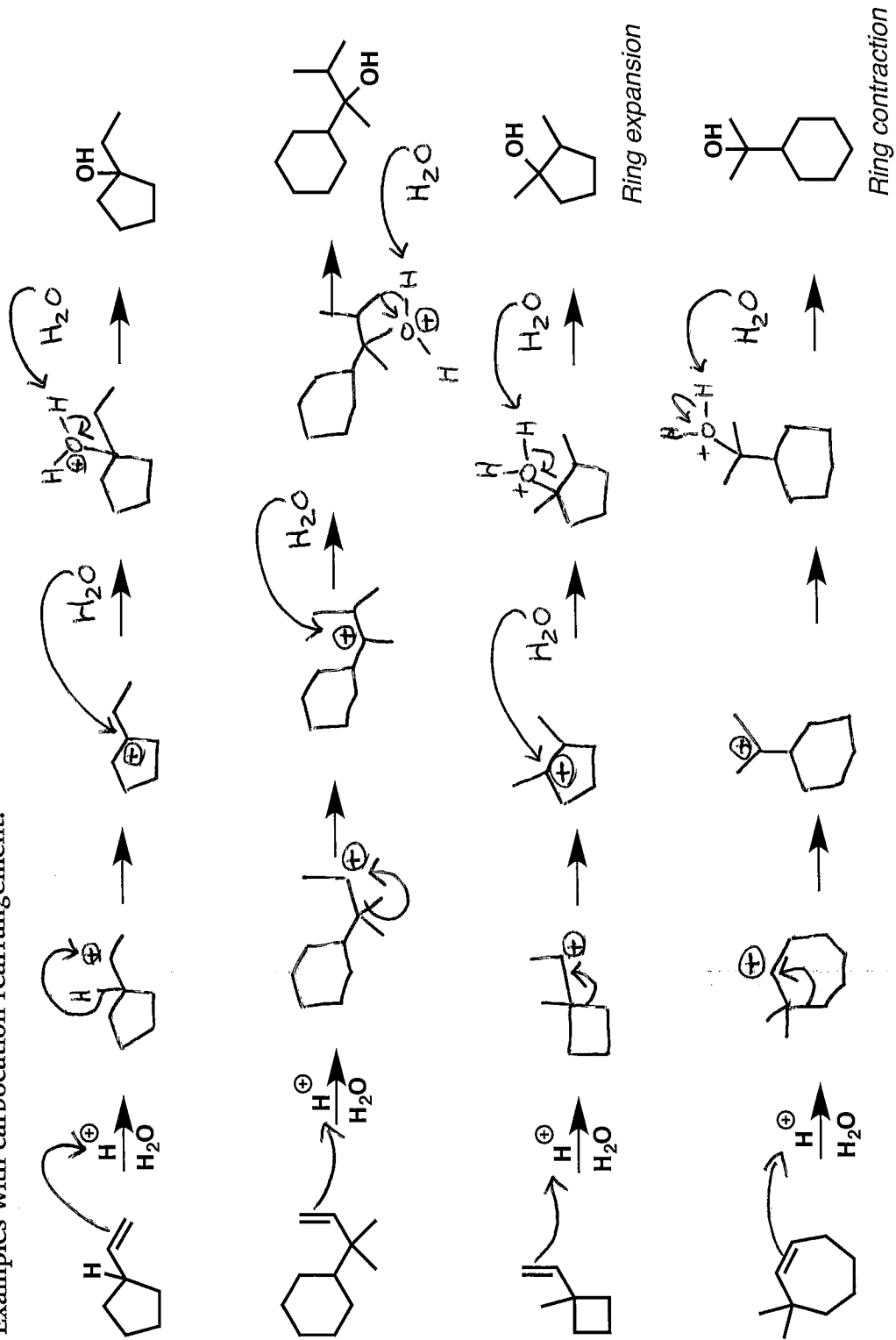
Complete the mechanism by following the pattern (draw arrows and intermediate)



internal NU⁻ is faster

H₂O and CH₃OH act very similarly; both are alcohols.

Examples with carbocation rearrangement.



Halogenation of Alkenes

General Reaction:



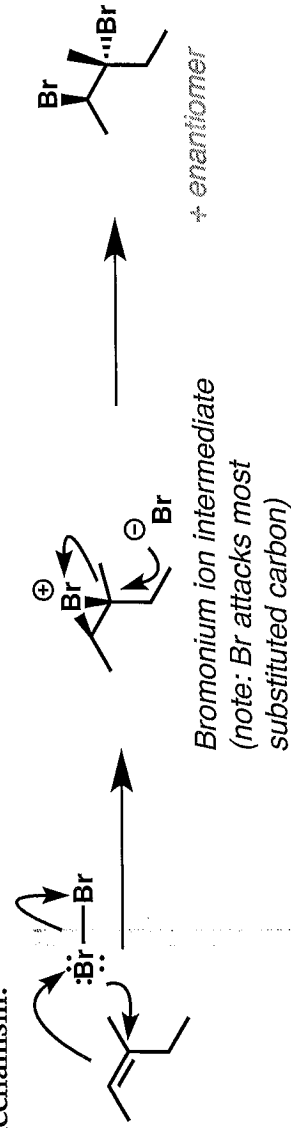
Can use Cl_2 , Br_2 , I_2 as well as mixed halides such as BrCl and IBr

"vicinal" dihalide (1,2-dihalide)
"anti" addition

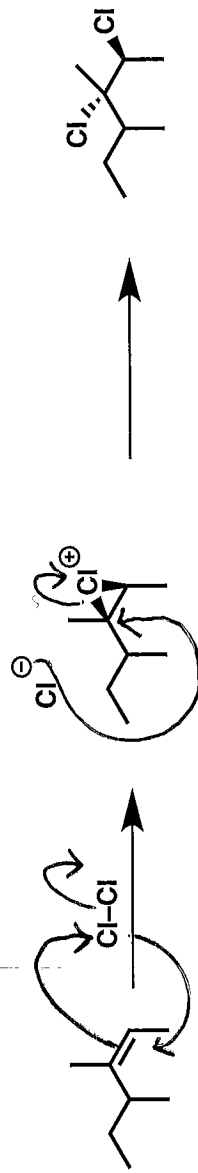
Mechanism Basics Box:

- Halogens include Cl_2 , Br_2 , I_2 as well as mixed halides such as BrCl and IBr
- Reaction proceeds through a 3-membered "halonium" ion intermediate
- Halonium is then attacked from backside by halide nucleophile at most substituted carbon
- Stereochemistry of final products is "anti"
- Rearrangements (e.g. hydride and alkyl shifts) do **not** occur

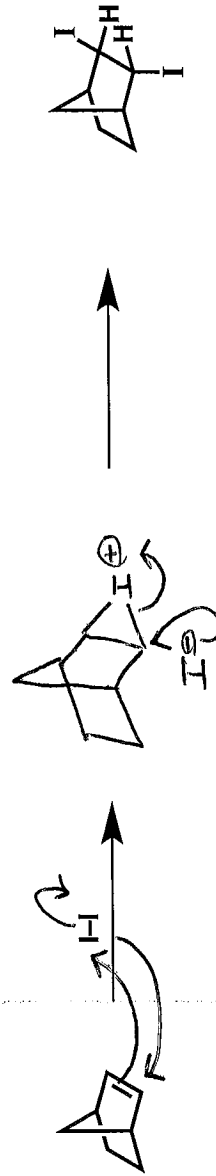
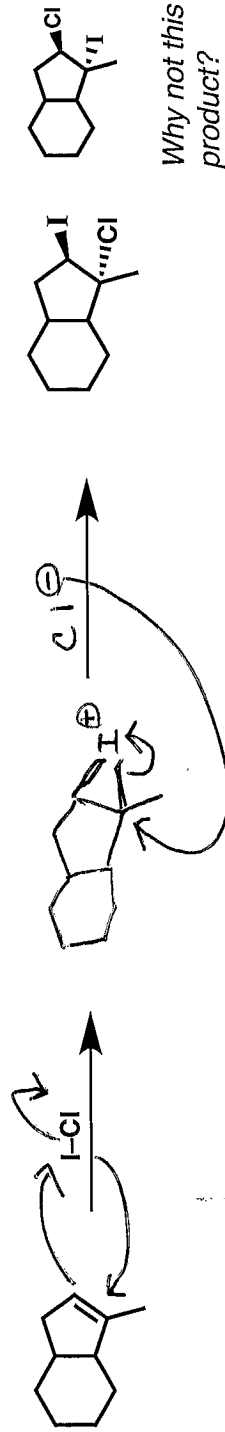
General Mechanism:



Fill in the missing arrows.

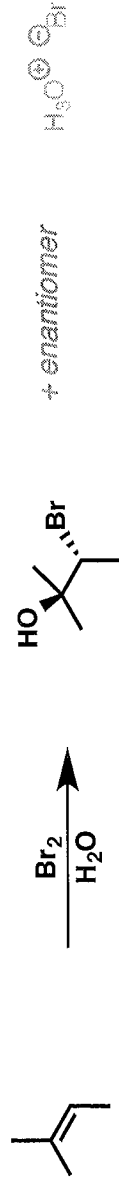


Complete the mechanism by following the pattern (draw arrows and intermediate)



Halohydrin Formation From Alkenes

General Reaction:



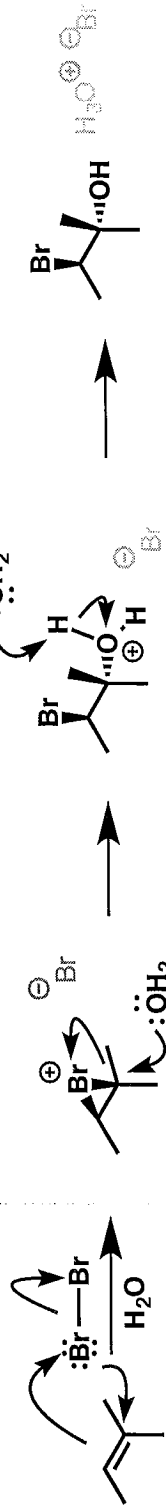
Can use Cl_2 , Br_2 , I_2 as well as "halonium" sources NBS and NCS

A "halohydrin" ("bromohydrin" in this case) "anti" addition

Mechanism Basics Box:

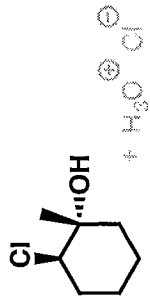
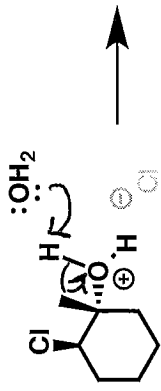
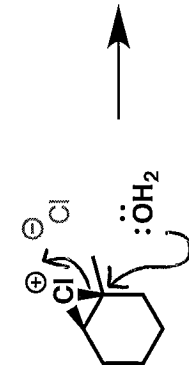
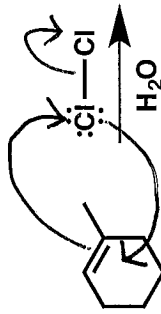
- Reaction proceeds through a 3-membered "halonium" ion intermediate
- Source of halogen can be Cl_2 , Br_2 , I_2 as well as *N*-bromosuccinimide (NBS)
- Halonium is then attacked from backside by nucleophilic solvent at most substituted carbon ("Markovnikov")
- Stereochemistry of final products is "anti"
- Rearrangements (e.g. hydride and alkyl shifts) do **not** occur
- Use of alcohol such as CH_3OH as solvent results in an "ether" product

General Mechanism:

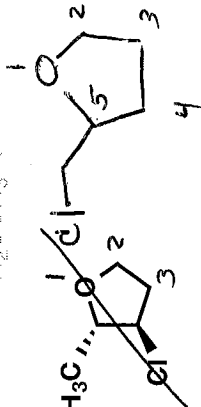
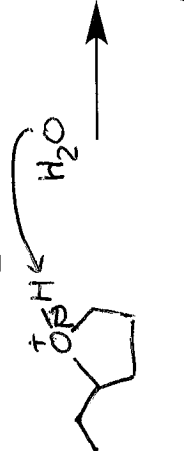
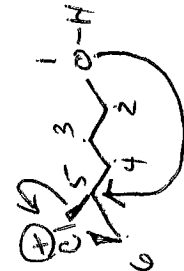
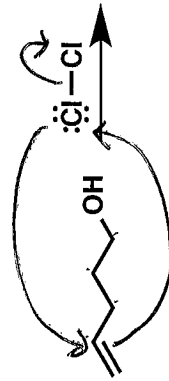
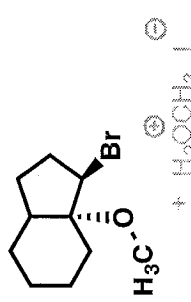
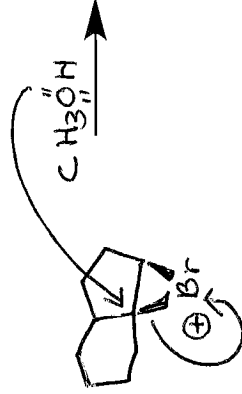
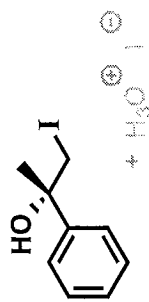
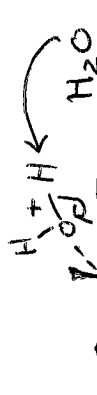
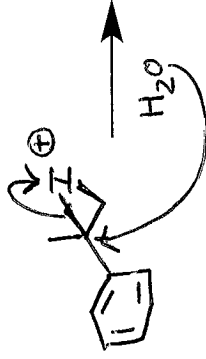


H_2O attacks most substituted carbon of bromonium ion ("Markovnikov")

Fill in the missing arrows.



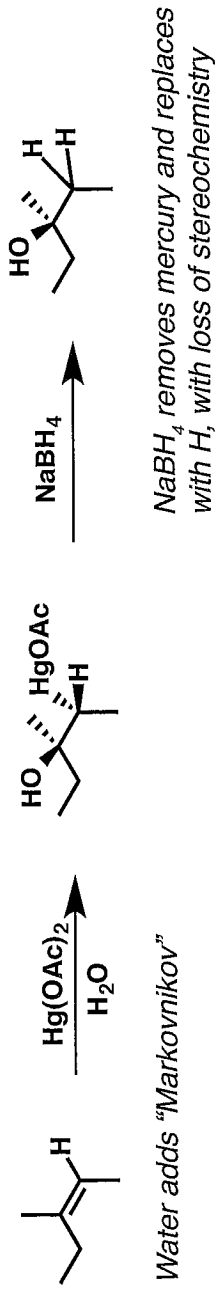
Complete the mechanism by following the pattern (draw arrows and intermediate)



WRONG

Oxymercuration of Alkenes

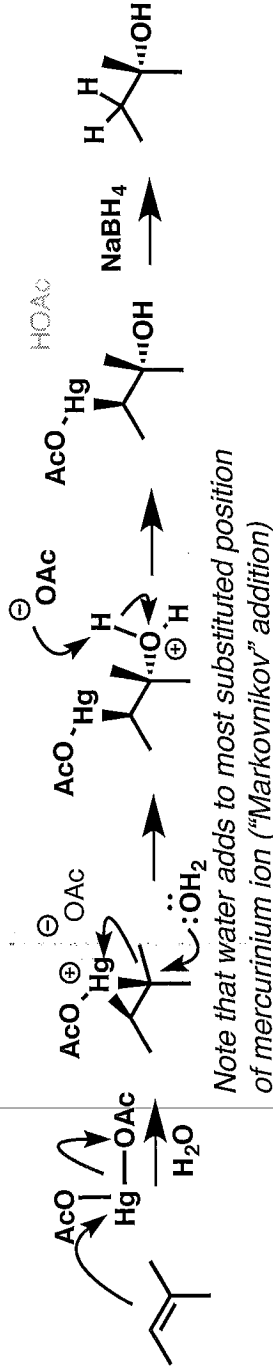
General Reaction:



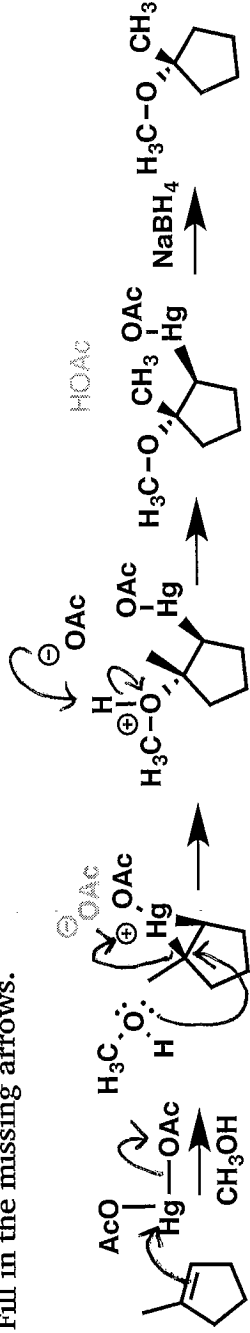
Mechanism Basics Box:

- Reaction proceeds through 3-membered "mercurinium" ion intermediate
- Solvent (water or alcohol) attacks most substituted carbon ("Markovnikov")
- Attack occurs from backside ("anti" addition)
- With water as solvent, product is an alcohol
- With alcohol as solvent, product is an ether
- Rearrangements (e.g. hydride and alkyl shifts) do not occur
- Purpose of NaBH₄ is to replace Hg with H
- Mechanism for NaBH₄ step is complex - generally not covered - but results in loss of stereochemistry at that center

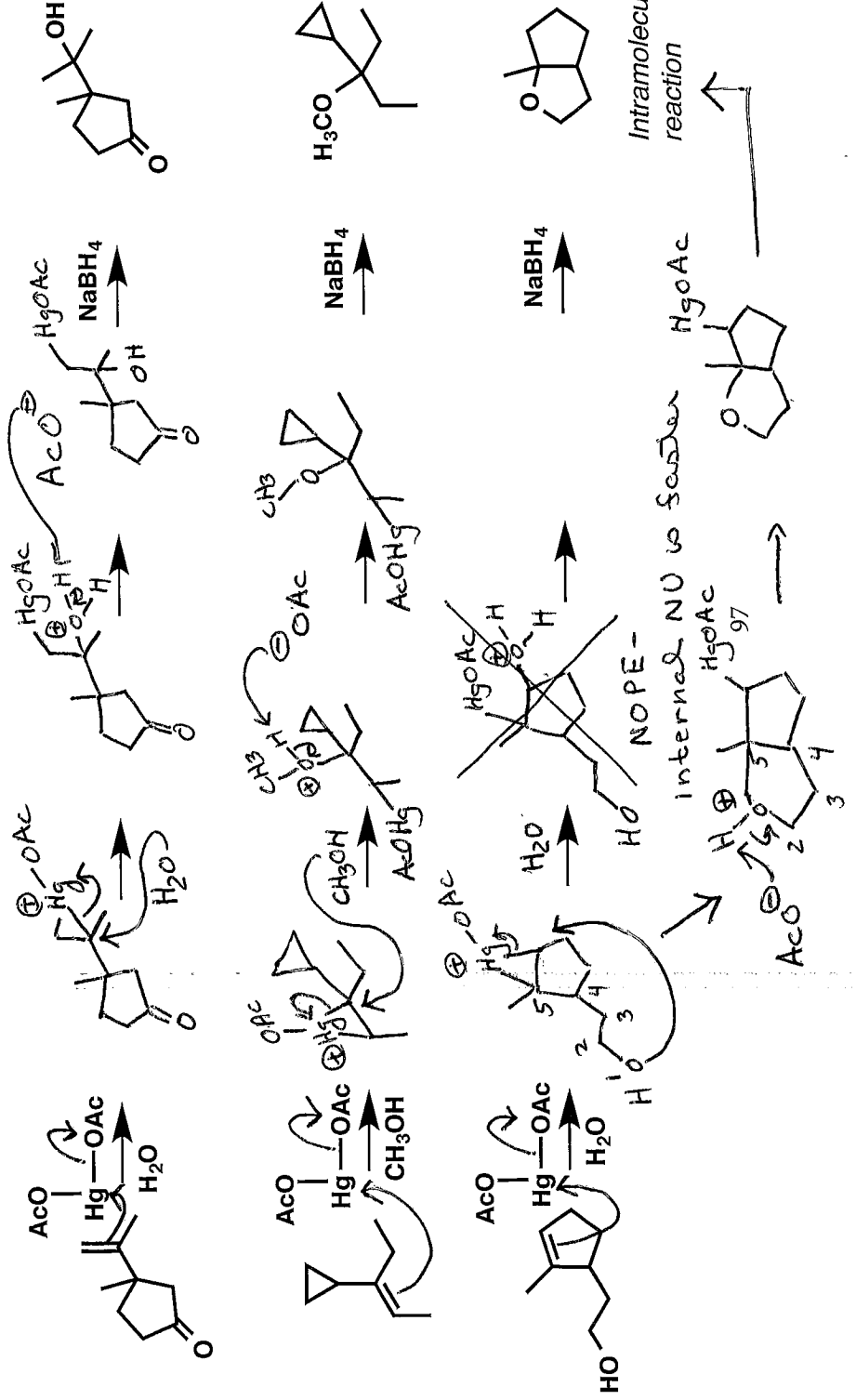
General Mechanism:



Fill in the missing arrows.

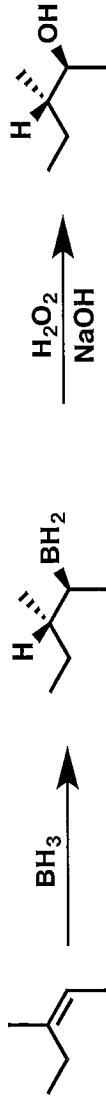


Complete the mechanism by following the pattern (draw arrows and intermediates).



Hydroboration-Oxidation of Alkenes

General Reaction:



Could also use $\text{BH}_3 \cdot \text{THF}$, B_2H_6
9-BBN, Sia_2BH

“anti-Markovnikov” regiochemistry
“syn” stereochemistry

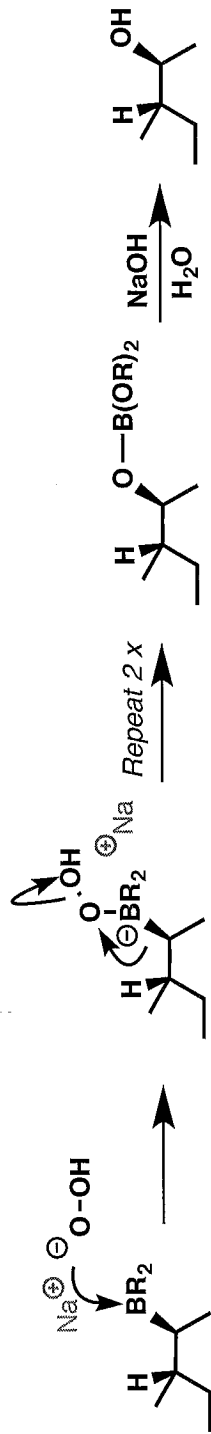
Mechanism Basics Box:

- “Borane” can be BH_3 , B_2H_6 , “ R_2BH ”, 9-BBN, catecholborane - all work the same way
- Initial reaction forms C-H on most substituted carbon and C-B on least substituted carbon
- Stereoselectivity of reaction is “syn” (H and B add to same face)
- Addition of $\text{NaOH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ results in replacement of B by O with retention of configuration
- “Hydrolysis” step involves breaking of B-O and then protonation of O-
- BH_3 can do up to 3 hydroboration reactions
- Solvent is usually tetrahydrofuran (THF) or ether

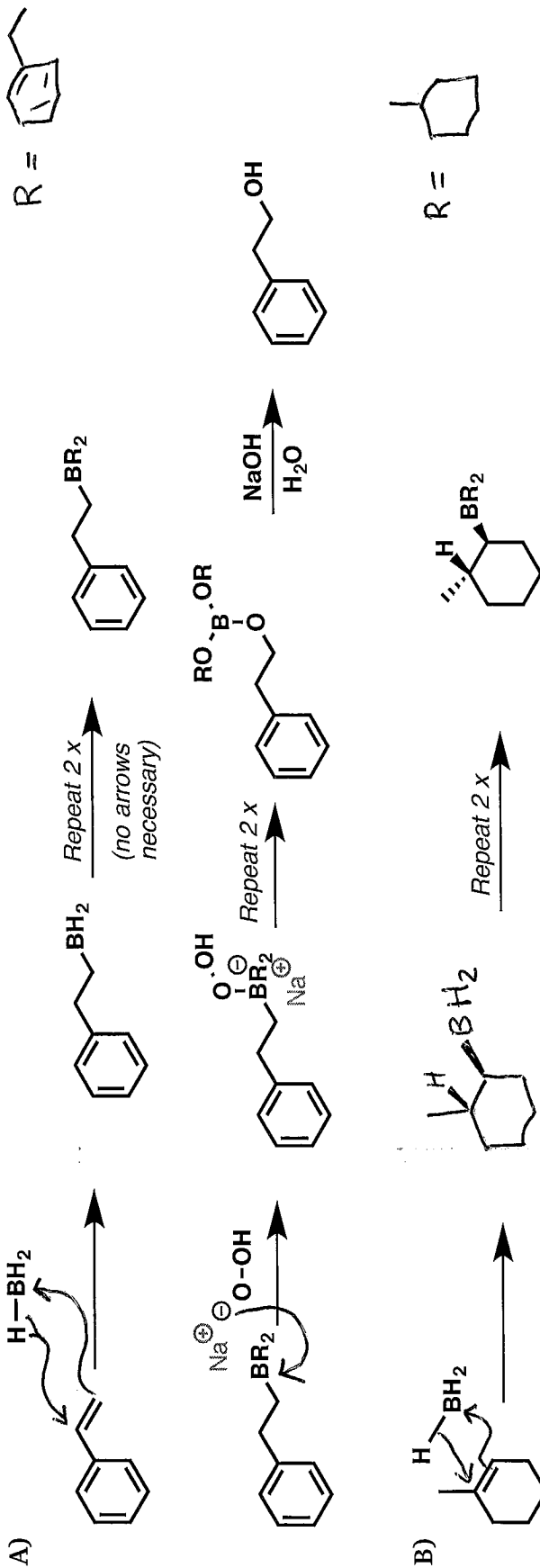
Mechanism Step 1: Hydroboration



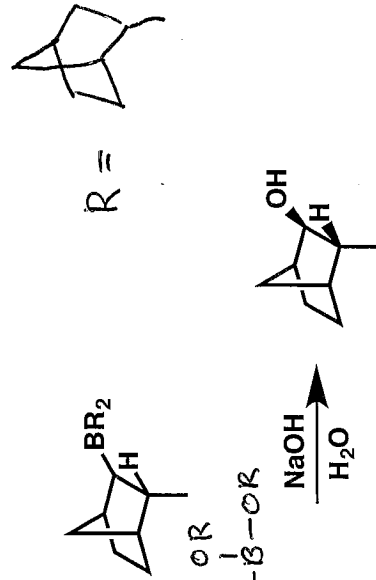
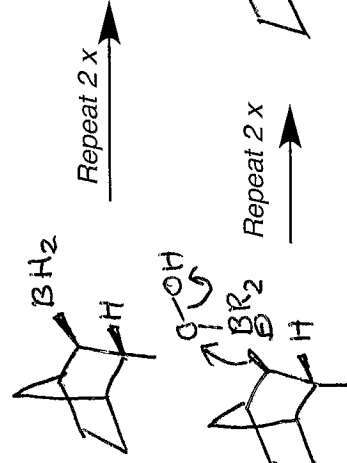
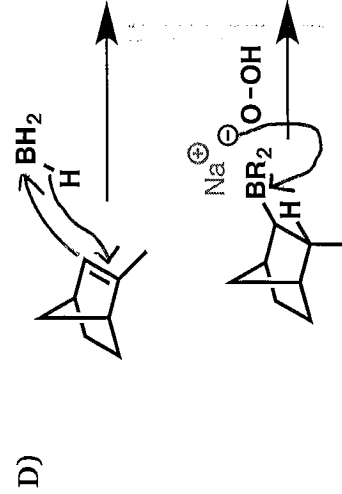
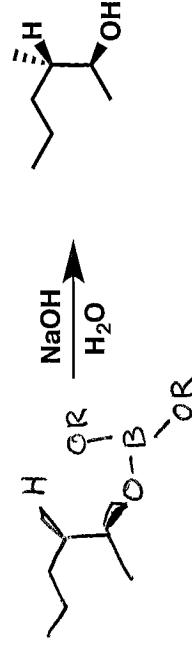
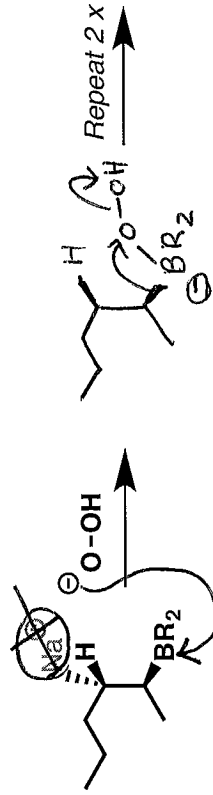
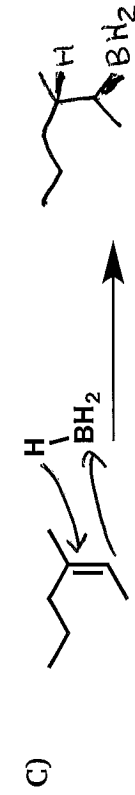
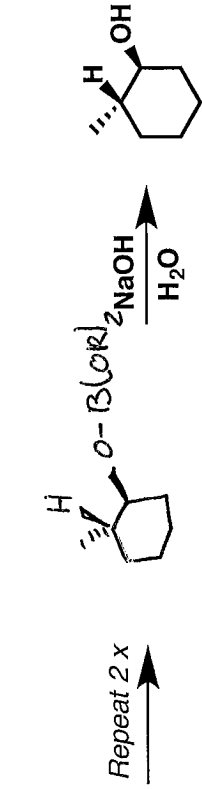
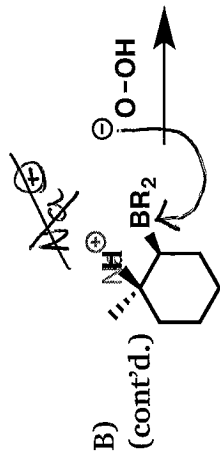
Mechanism Step 2: Oxidation



Complete the mechanism by following the pattern (draw arrows and intermediate).

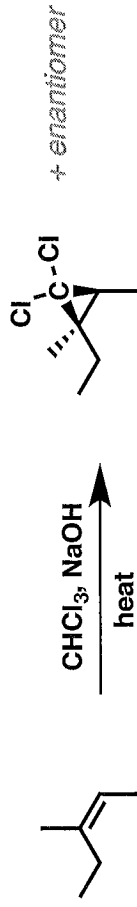


syn addition



Cyclopropanation of Alkenes

General Reaction:

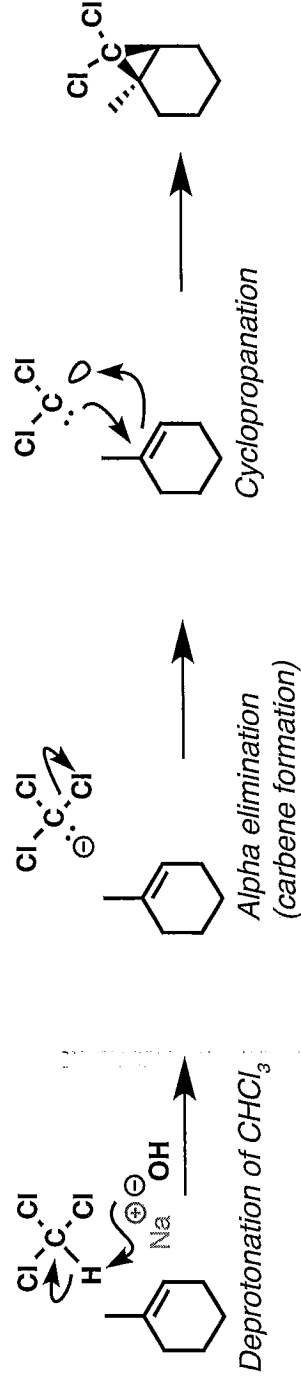


Syn stereochemistry

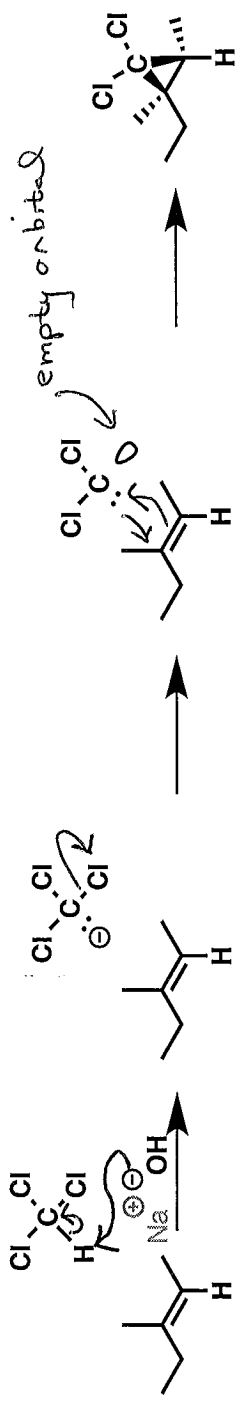
Mechanism Basics Box:

- Treatment of chloroform (CHCl_3) with strong base leads to deprotonation and then loss of Cl^- , forming a carbene intermediate (“dichlorocarbene”)
- Carbene is a short-lived highly reactive intermediate, which does a concerted reaction (“cycloaddition”) with the alkene to produce the cyclopropane
- Rate determining step is “alpha-elimination” to form the carbene intermediate

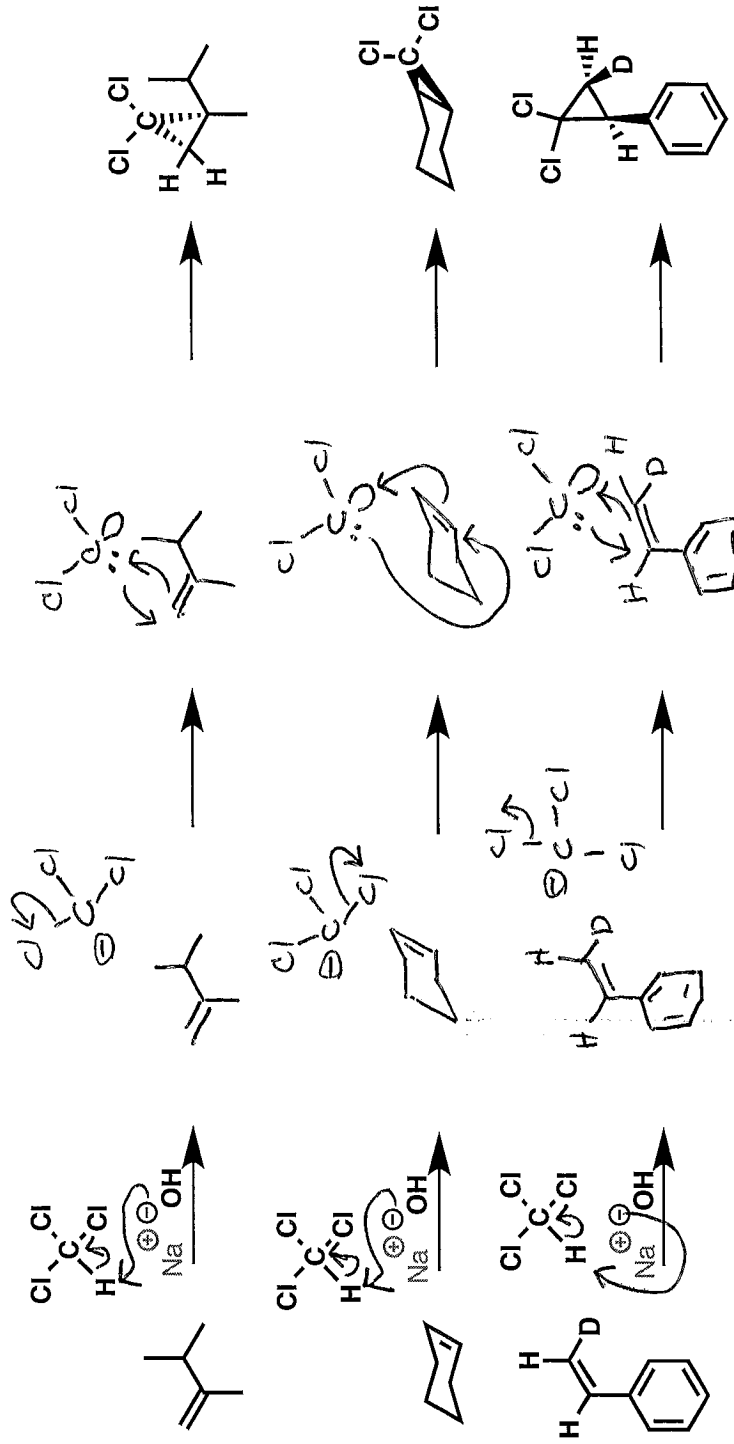
General Mechanism:



Fill in the missing arrows.

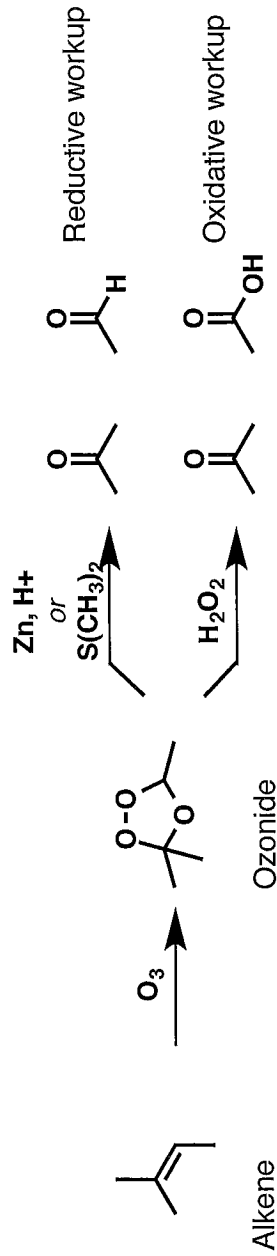


Complete the mechanism by following the pattern (draw arrows and intermediates).



Ozonolysis of Alkenes

General Reaction:

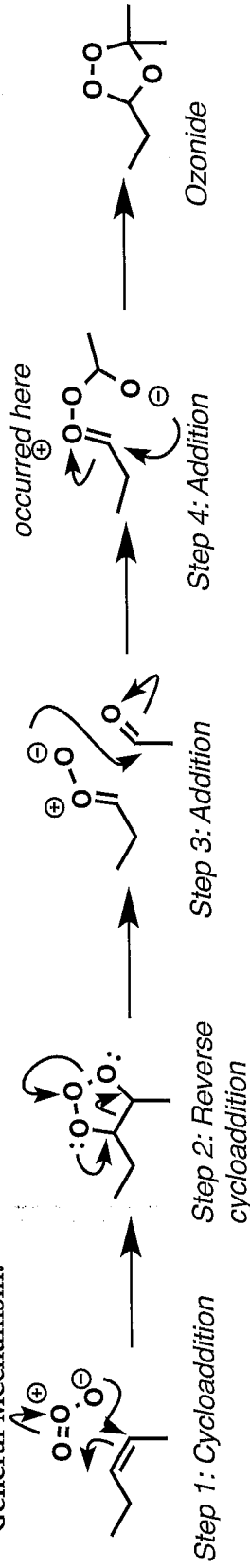


Only the mechanism of the first step is covered here

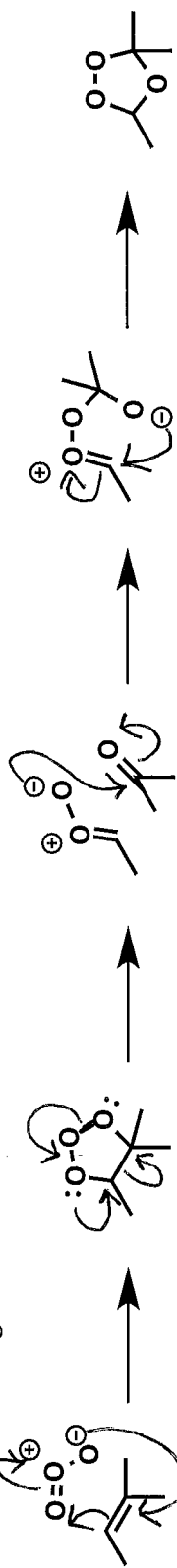
Mechanism Basics Box:

- In the first step, ozone (O_3) performs a cycloaddition with the alkene, forming a "molozonide" intermediate
- This is unstable and breaks down in a "reverse cycloaddition", breaking the C-C bond
- Two consecutive additions of oxygen to carbonyls (C=O) leads to formation of the ozonide
- Reductive workup (with Zn or DMSO, mechanism not shown) preserves C-H bonds
- Oxidative workup (H_2O_2 , mechanism not shown) oxidizes aldehydes to carboxylic acids

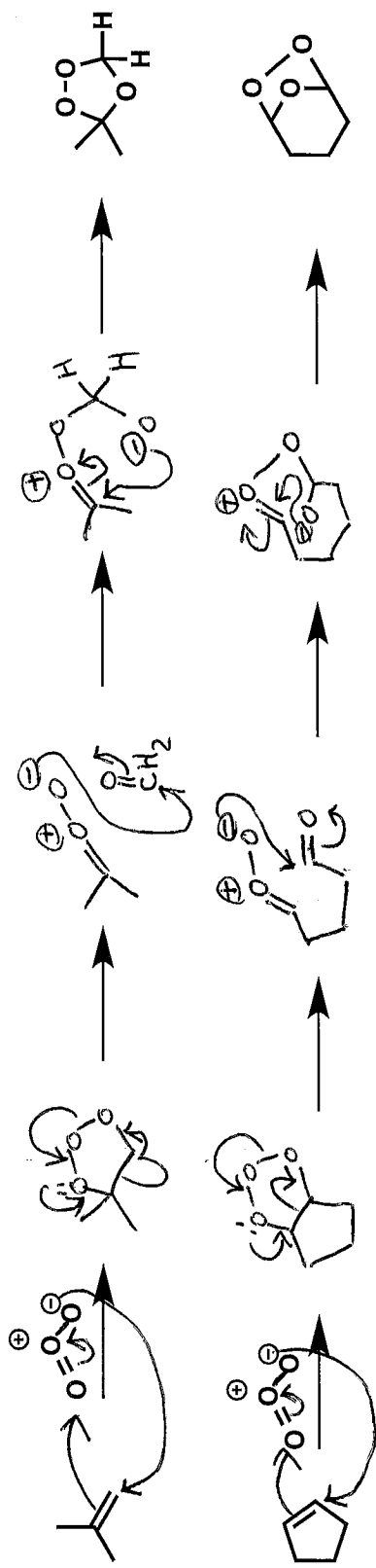
General Mechanism:



Fill in the missing arrows.

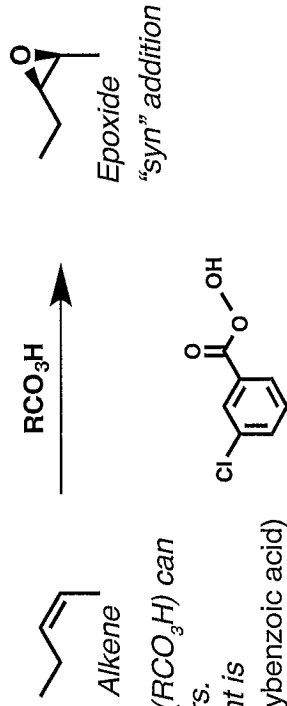


Complete the mechanism by following the pattern (draw arrows and intermediates).



Epoxidation of Alkenes

General Reaction:

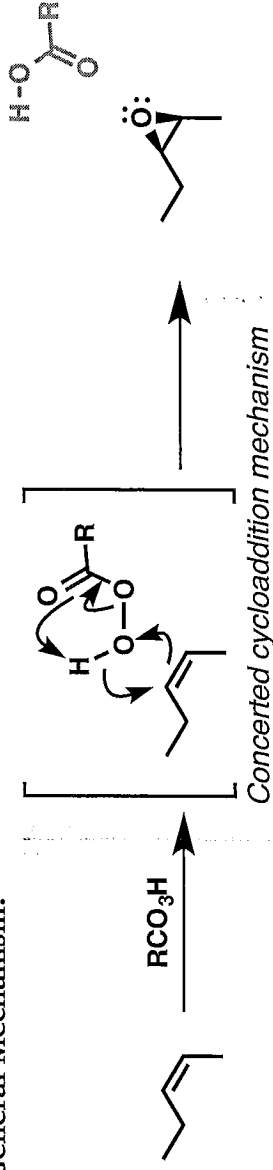


The R of the peroxyacid (RCO_3H) can be CH_3 , CF_3 , Ph, or others. A commonly used reagent is *m*-CPBA (m-chloroperoxybenzoic acid)

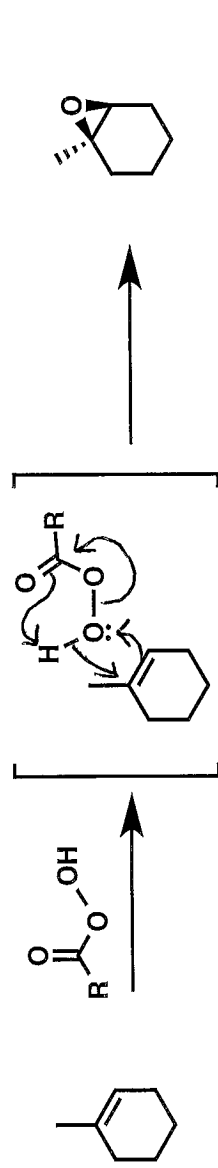
Mechanism Basics Box:

- Reaction occurs in one step (concerted reaction)
- Stereochemistry of addition is always *syn*
- The reaction is stereospecific - the geometry at the double bond is preserved
- Peroxyacids (RCO_3H) have a weak O-O bond
- Common examples of peroxy acids are *m*-chloroperoxybenzoic acid (*m*-CPBA) and methylperoxybenzoic acid

General Mechanism:



Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediate)

