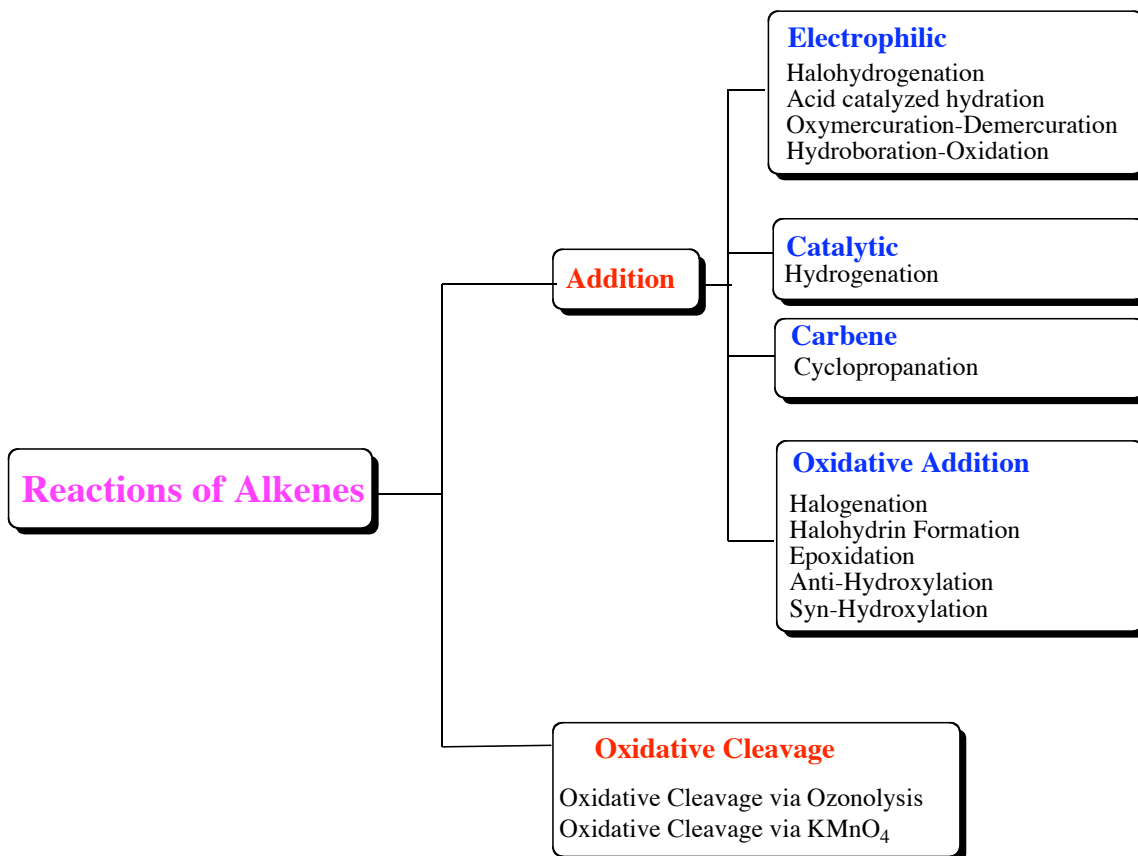
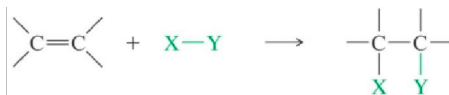


Chapter 8 Notes: Reactions of Alkenes



Reactivity of the Carbon-Carbon Double Bond

A. Since σ bonds are stronger and more stable than π bonds, double bonds tend to react to convert the double bond into σ bonds.



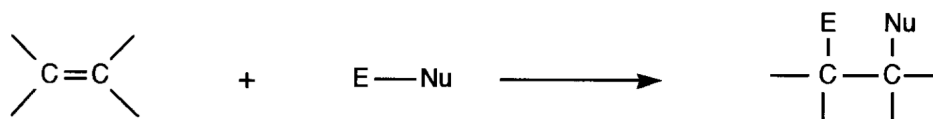
- This is an *addition reaction*
 - Addition reaction—two groups add to the carbon atoms of the double bond and the carbons become saturated
 - Addition reactions are typically *exothermic*
- B. Other types of reactions are *substitution* and *elimination*
- i. Substitution reaction—one fragment replaces another fragment in a molecule
 - ii. Elimination reaction—reverse of addition; one molecule splits into two fragment molecules

Electrophilic Addition to Alkenes

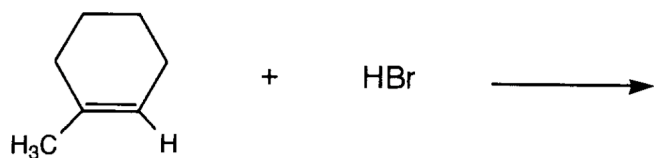
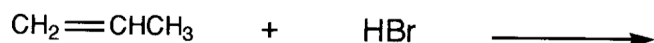
Electrophilic

Halohydrogenation
Acid catalyzed hydration
Oxymercuration-Demercuration
Hydroboration-Oxidation

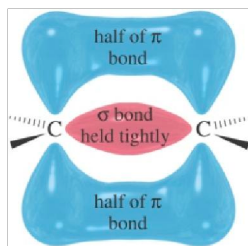
General reaction:



Addition to Unsymmetrical Alkenes: Hydrohalogenation

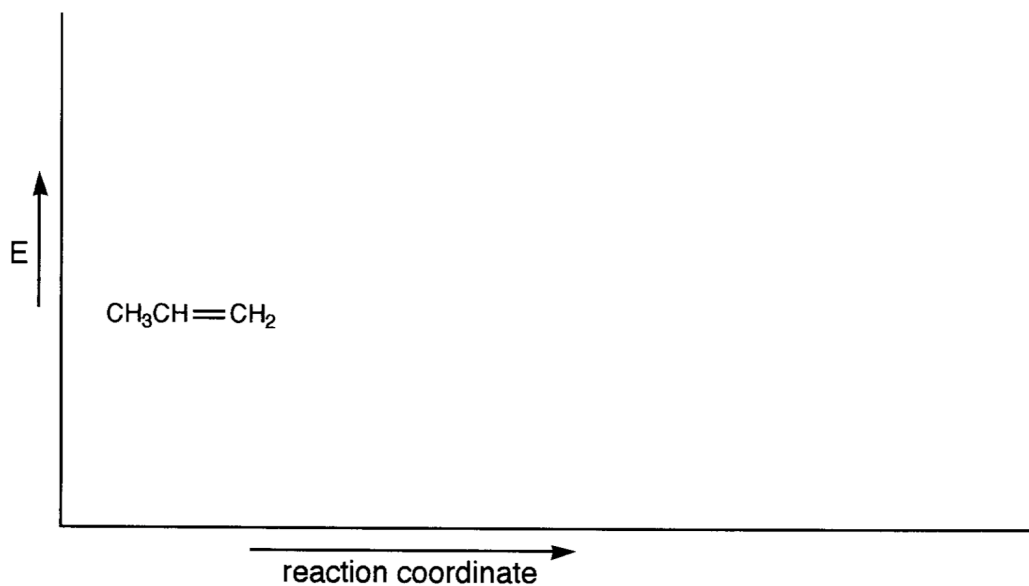


The reaction is regioselective: the product is formed from only one of the two possible orientations of addition.



Markovnikov's Rule: the addition of HX to the double bond of an alkene results in a product with the acidic proton bonded to the carbon which has the greater number of hydrogens.

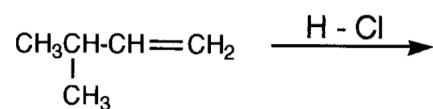
Why? Let's look at RDS of this reaction:



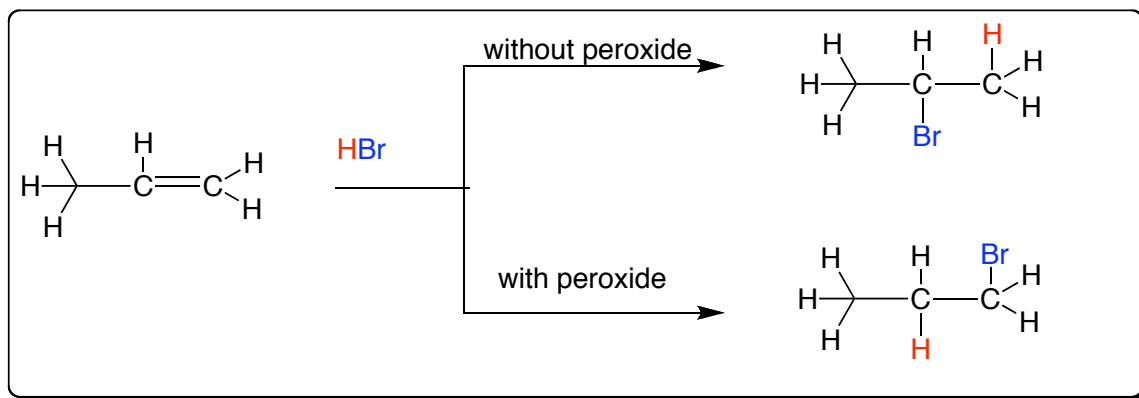
Extension of Markovnikov's Rule: Rearrangement

In an electrophilic addition, E^+ adds in a way that generates the most stable carbocation intermediate.

Example:

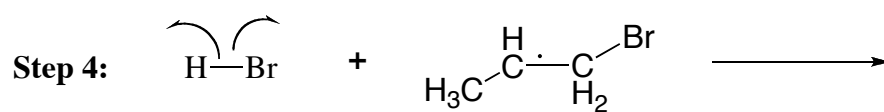
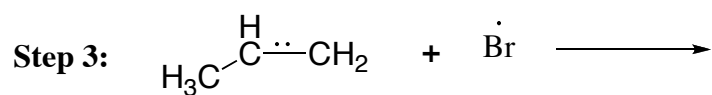
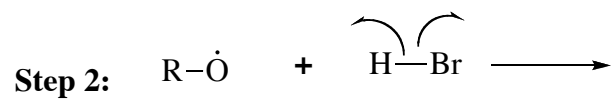
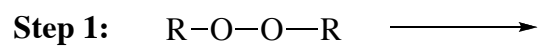


Anti-Markovnikov's Addition: Free Radical Addition Mechanism:



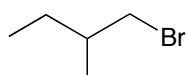
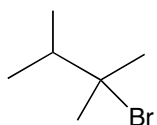
Without peroxide:

With peroxide:



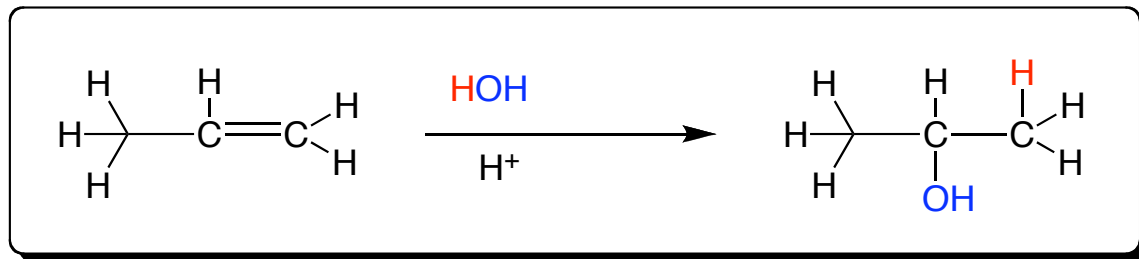
Synthesis problems:

Propose a synthetic routine for the preparation of the following compounds:



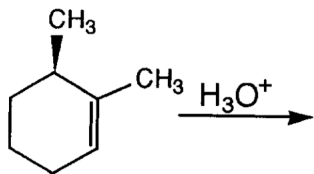
Hydration of Alkenes: Addition of Water Under Acidic Conditions:

Dilute sulfuric acid as a catalyst



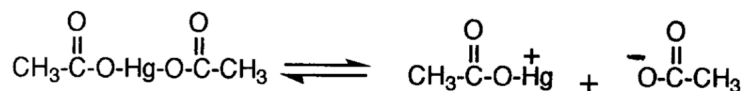
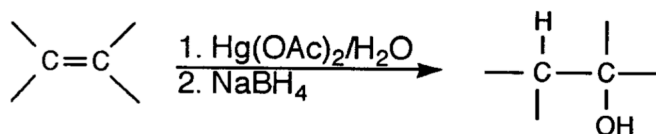
Mechanism:

Example:

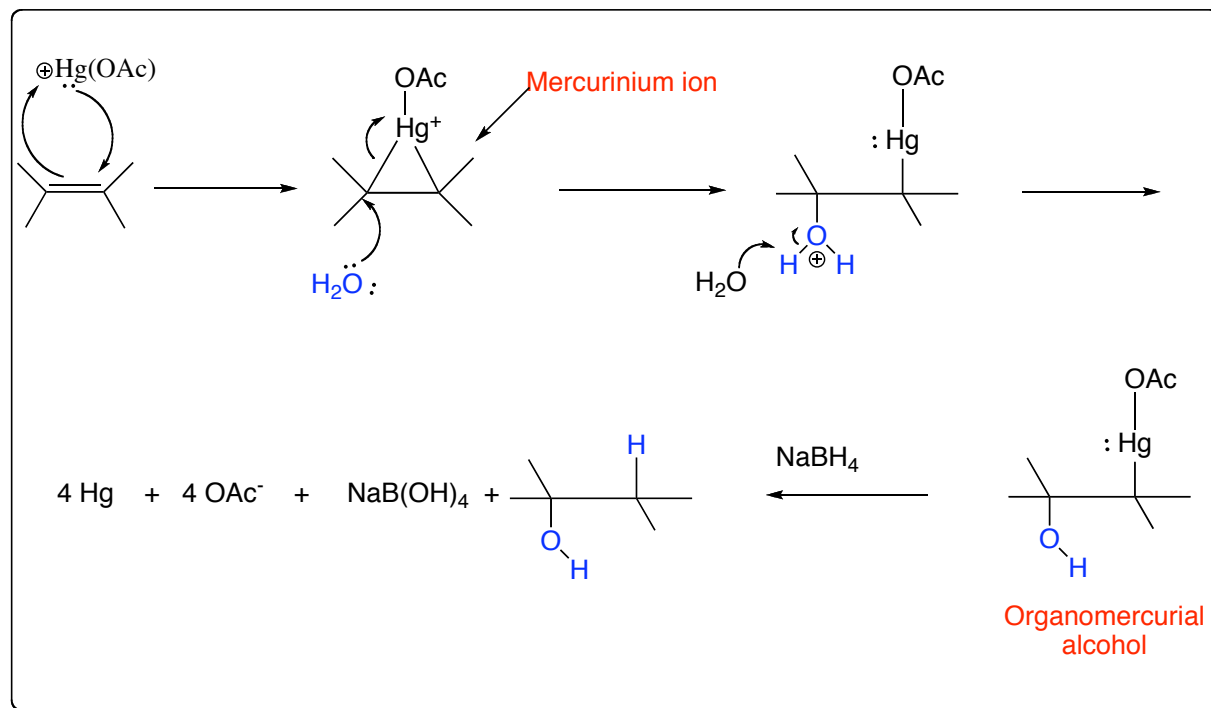


Indirect Hydration: the product is an alcohol, but the addition is done via different mechanism.

Oximercuration/ Demercuration Reaction (obeys Markovnikov's Rule):

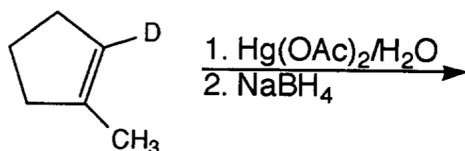


Mechanism:



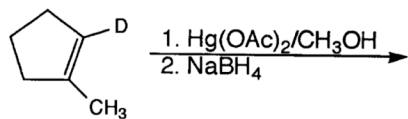
Mercurinium ion has two highly electron-poor carbons, but the one with higher substitution is more electron-positive. Thus attack by water will take place on this side.

Example:



Useful variation of this reaction: instead of water, use an alcohol to form ether.
The mechanism, regioselectivity, and stereochemistry are all the same.

Example:



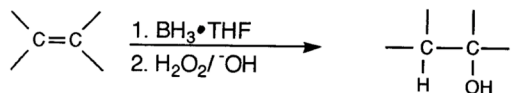
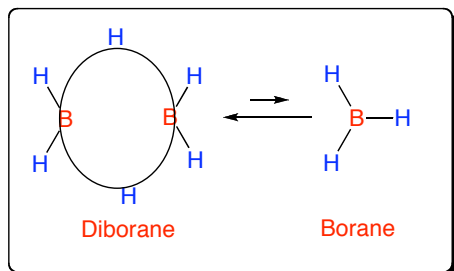
Convert 1-iodo-2-methylcyclopentane into 1-methylcyclopentanol:

Hydroboration Reactions: Anti-Markovnikov Addition

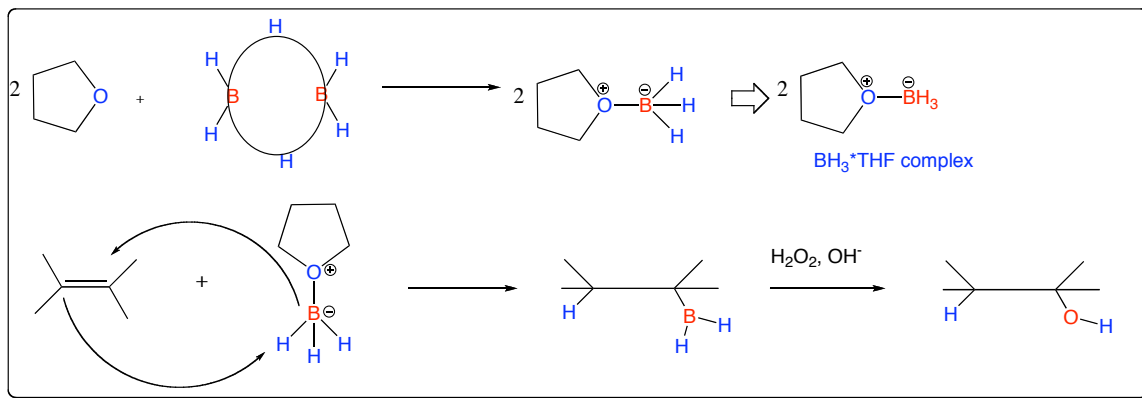
Used when an alkene should be converted into an alcohol via anti-Markovnikov's rule:

Brown (Purdue University): diborane B_2H_6 adds to alkenes with anti-Markovnikov's orientation.

Diborane: compounds with three-centered bonds

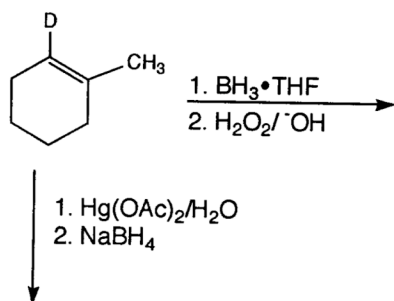


Mechanism:



Addition of borane complex takes place via anti-Markovnikov's rule as boron adds to the less hindered site.

Examples:



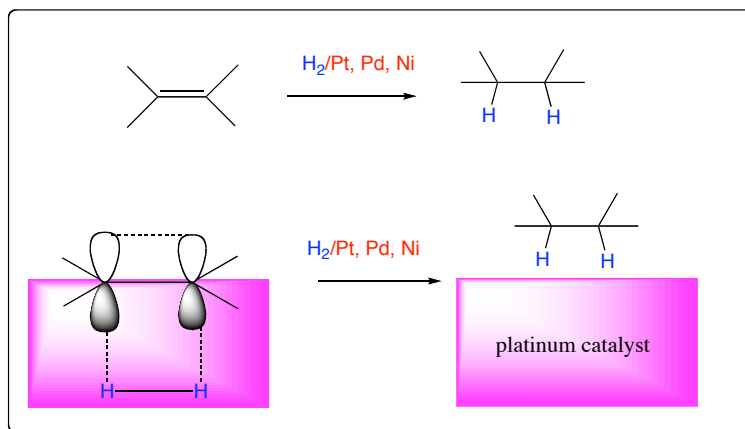
Show how you would accomplish the following synthetic conversions:

1-butene to 1-butanol

2-bromo-2,4-dimethylpentane to 2,4-dimethyl-3-pentanol

**Catalytic Addition:
Hydrogenation of Alkenes:**

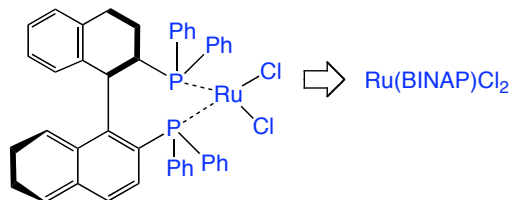
General Reaction:



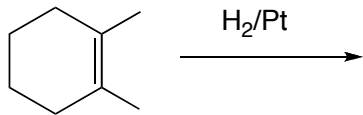
Wilkinson's Catalyst catalyzes the hydrogenation of carbon-carbon double bonds.

Induces production of optically active products from optically inactive starting materials: asymmetric induction or enantioselective synthesis.

The catalyst is chiral, then the transition state is leading to the formation of one enantiomer in large excess.



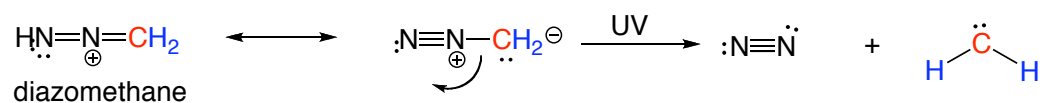
Examples:



**Carbene Addition:
Cyclopropanation of Alkenes**

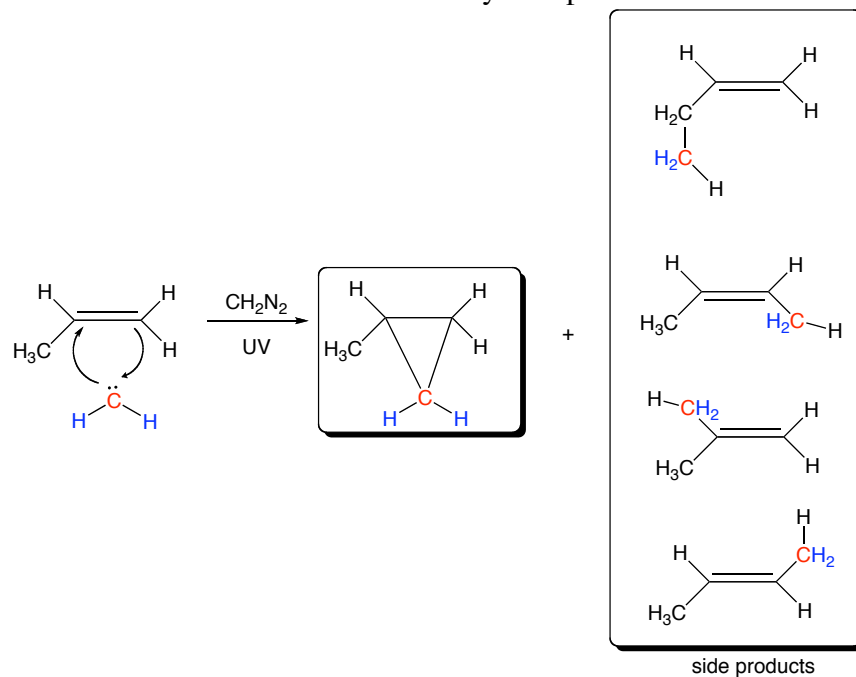
Simplest carbenes: $:\text{CH}_2$ uncharged reactive intermediate.

Diazomethane is the starting material for preparation of carbenes:



Problem with it: highly toxic, highly explosive.

Problem with direct carbenation with diazomethane: many side products are formed.



Example: explain how these products could be produced via reaction of cyclopentene with diazomethane.

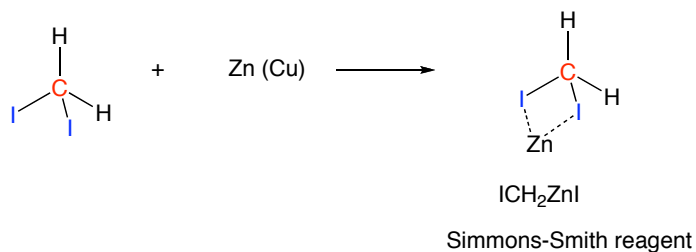


Cleaner cyclopropanation: Simmons-Smith Reaction

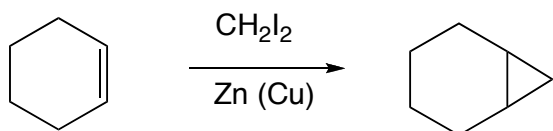
Formation of a carbenoid to form cyclopropane with better outcome.

Why carbenoid: reacts like carbene, but does not have divalent carbon atom.

Simmons-Smith Reagent: mixture of methylene iodide to the zinc-copper couple (zinc dust activated with small amounts of copper).

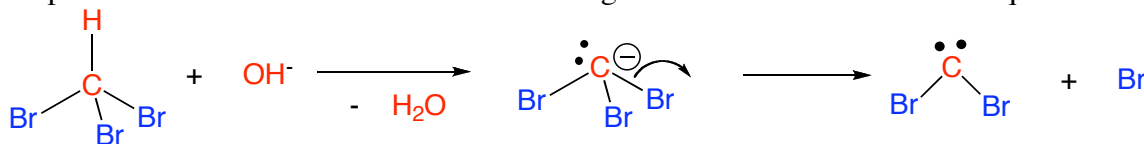


Example:



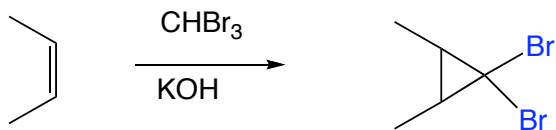
Other cyclopropanation routine:

Preparation of carbenoid from reaction of halogenated haloalkane with 50% aqueous solution of base:



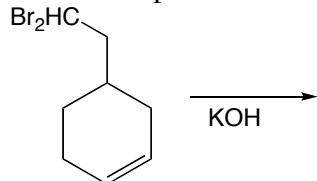
The elimination of hydrohalogen is called an alpha-elimination: both bromine and hydrogen are removed from the same carbon.

Advantages of this reaction: retention of cis- or trans- stereochemistry of the reactants.

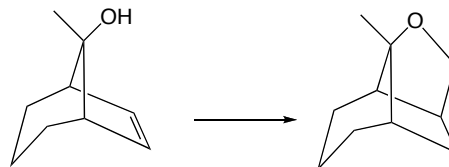


Example:

Predict the product of the following reaction:



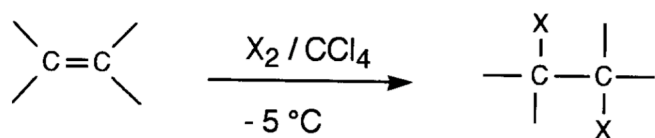
Propose synthetic conditions for the following reaction:



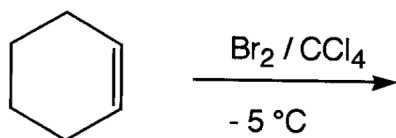
Oxidative Addition

Halogenation
Halohydrin Formation
Epoxidation
Anti-Hydroxylation
Syn-Hydroxylation

Halogenation of Alkenes: X_2 , $X=Br, Cl$, sometimes I).



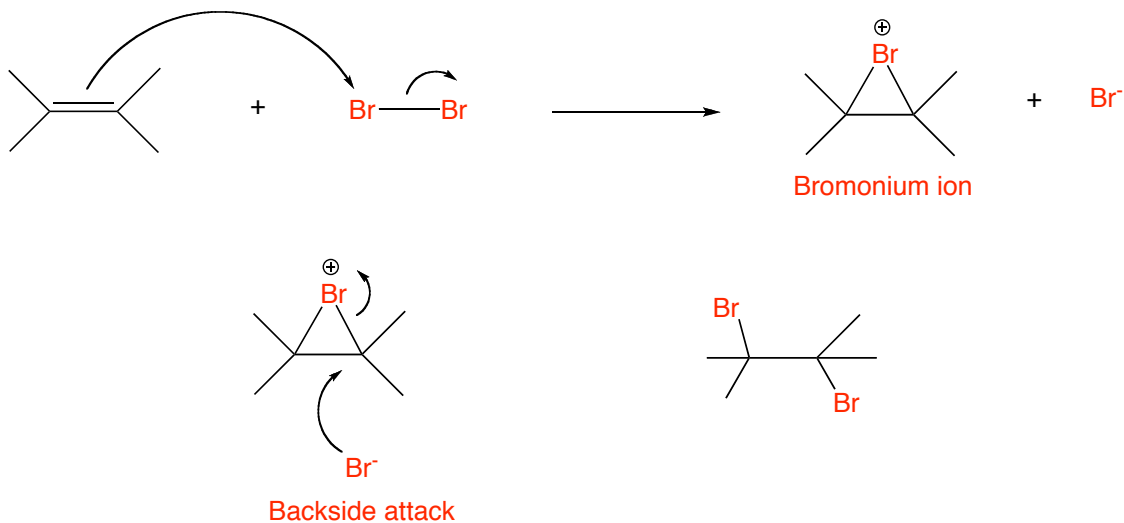
Example:



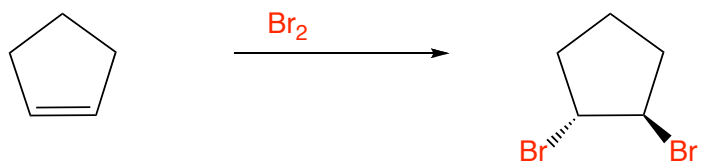
Mechanism:

Halogen is electrophilic and can react with alkene nucleophile producing a halide anion:

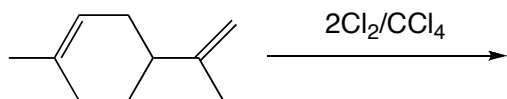
Addition of bromine to alkenes is a stereospecific **anti addition**



Examples:

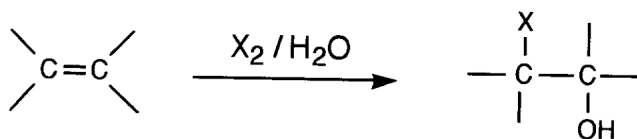


Propose mechanism and the products for the following reactions.



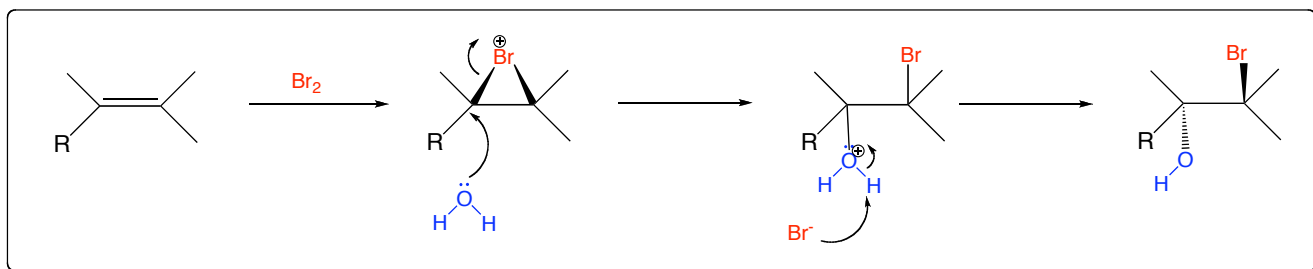
(Z)-3-decene + Br_2 in carbon tetrachloride

Formation of Halohydrins:

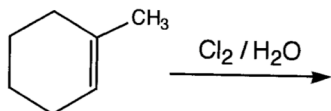


Mechanism: upon formation of halonium ion, water molecule attacks it (from the most sterically hindered side) and the halohydrin forms. The addition is anti, just like in halogenation.

Water molecule will always add to the more substituted carbon: more electron-poor, better electrophile.



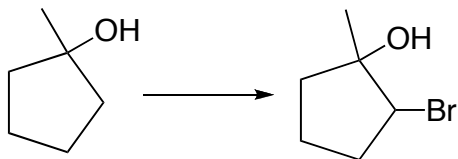
Example:



Convert 3-methyl-2-pentene into 2-chloro-3-methyl-3-pentanol

Predict major product(s) for the following reactions:
Trans-2-butene plus chlorine in water

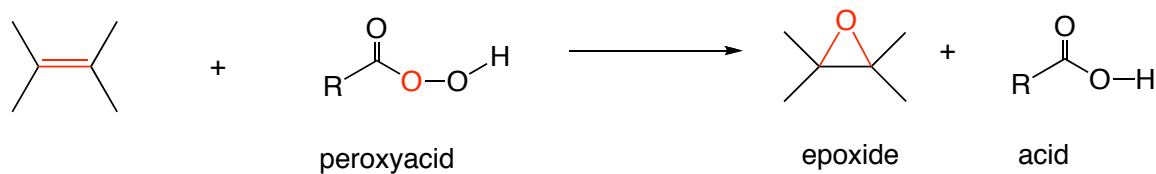
Show how you would accomplish the following transformations:



Epoxidation of Alkenes:

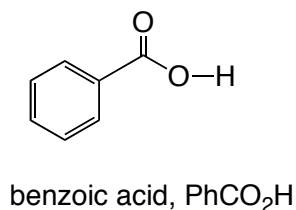
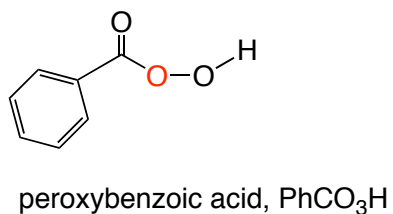
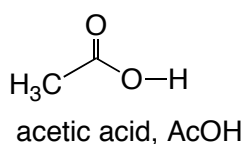
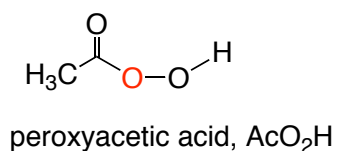
Oxidative addition: carbon is oxidized (REMEMBER: any time you add oxygens to carbon its oxidation state will increase).

General reaction:

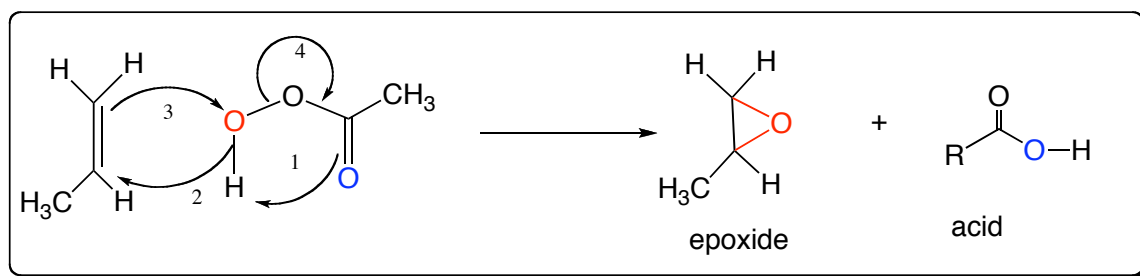


Peroxyacids: contain an extra oxygen within carboxylic acid functional group: $R(CO)C-O-O-H$

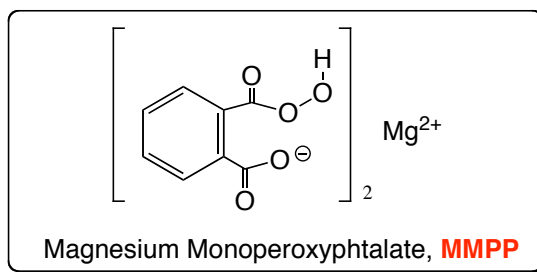
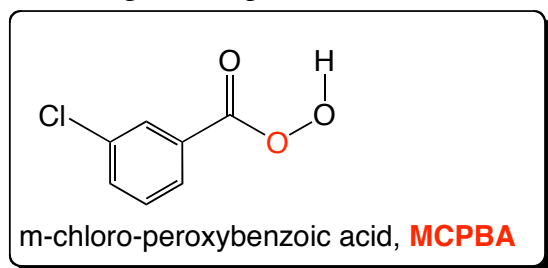
Examples of peroxyacids:



Mechanism: concerted one-step reaction



Great reagent for epoxidation:



The stereochemistry of the epoxide is similar to that of alkene: the reaction is concerted, so there is no rotation to form the opposite stereochemical product.

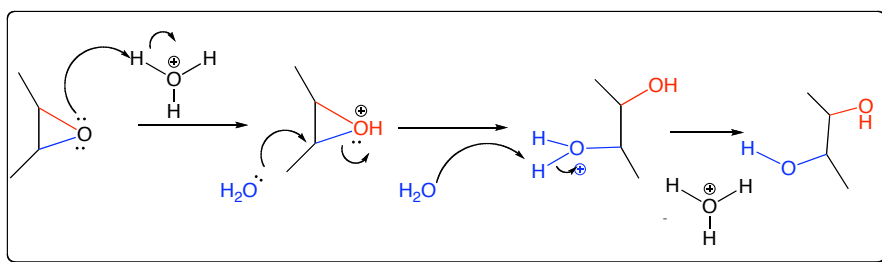
Examples:

Predict the products of following reactions
trans-3-hexene + MCPBA

Z-5-methyl-hept-4-ene + MCPBA

Acid-Catalyzed Anti-Hydroxylation of Epoxides:

Key steps: the reaction takes place under acidic conditions, first step is protonation of epoxide oxygen.



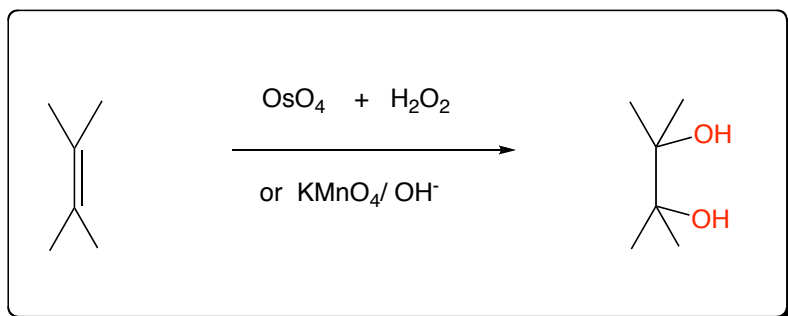
Note: the reaction is stereospecific, the resulting two hydroxy groups end up on different sides of the C-C bond.

Example:

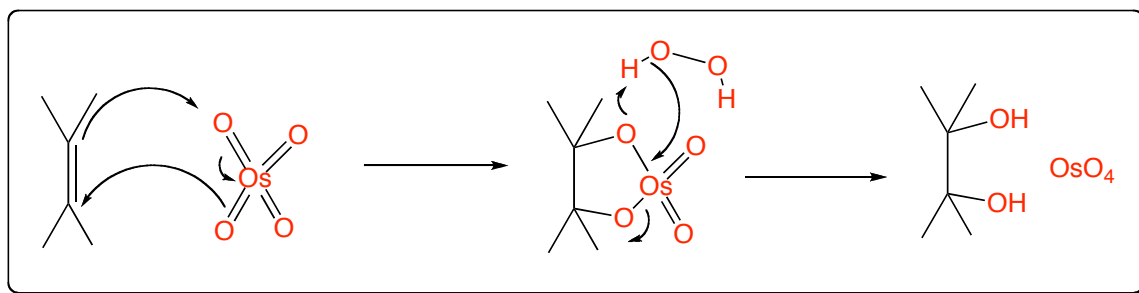
Propose a mechanism for the following reactions: cis-cyclodecene + MMPP in ethanol followed by dilute hydrochloric acid:

Syn-Hydroxylation of Alkenes:

General Reaction:



Mechanism:

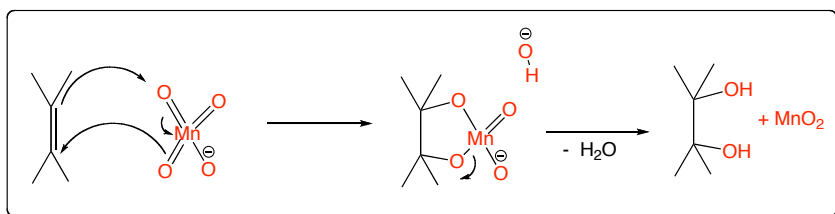


Disadvantages: expensive, toxic, volatile.

Alternative method:

Cold dilute solution of basic KMnO_4

Disadvantage: lower yields



How would you choose a reagent for syn-hydroxylation?

For microscale reactions osmic acid is appropriate: the yields are very important.

For macroscale reactions use KMnO_4 .

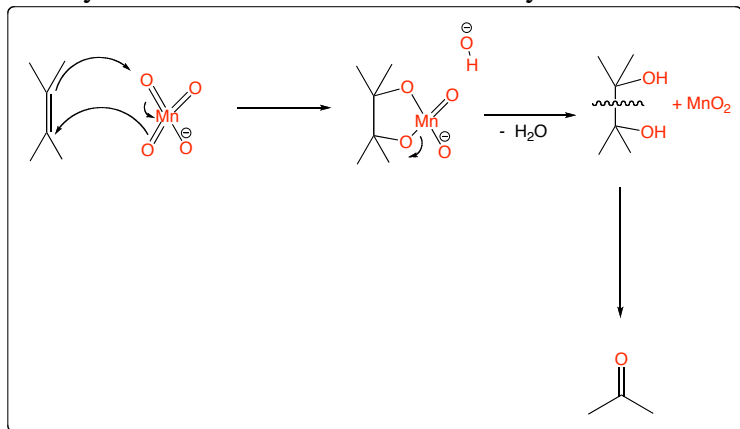
Examples:

Oxidative Cleavage Reactions of Alkenes:

See reaction above: if potassium permanganate solution is concentrated, acidic, or warm, oxidative cleavage is possible.

Products: initially ketone and aldehyde.

Aldehyde is oxidized further into carboxylic acid.

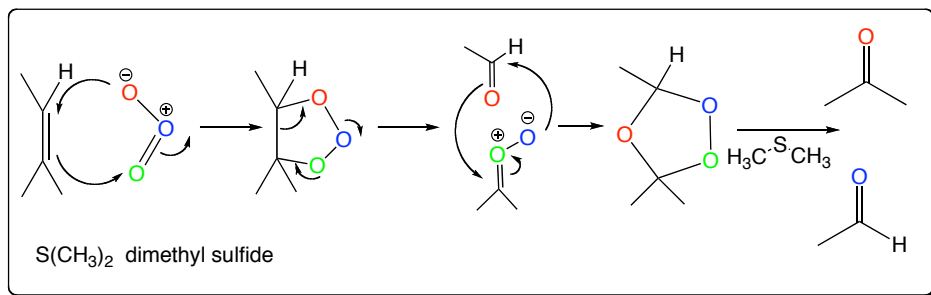


Examples:

Ozonolysis:

Much milder oxidative cleavage reaction.

Both ketone and aldehyde reaction products can be isolated.



When to use which reagent:

If interested in isolation of aldehyde, use ozone.

If carboxylic acid is the desired product, use hot permanganate solution.