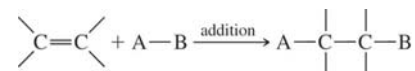
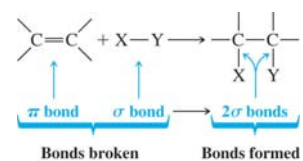


Chapter 8 Alkenes and Alkynes II: Addition Reactions

Additions to Alkenes



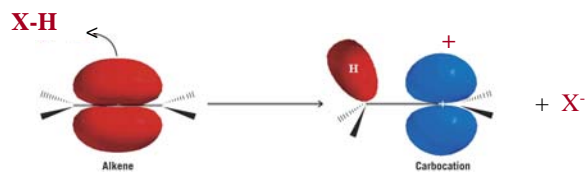
Generally the reaction is exothermic because one π and one σ bond are converted to two σ bonds



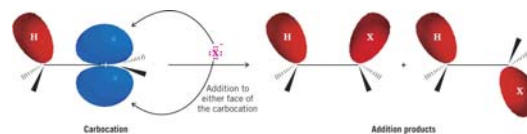
Alkenes are electron rich

The π electrons of the double bond are loosely held and are a source of electron density

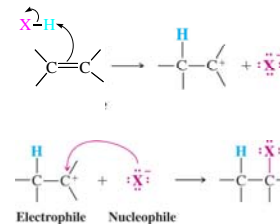
Alkenes are nucleophilic and react with electrophiles such as H^+ from a hydrogen halide to form a carbocation



- ◆ The carbocation produced is an electrophile
 - It can react with a nucleophile such as a halide



In addition reactions the alkene is a nucleophile in the first step and an electrophile in the second

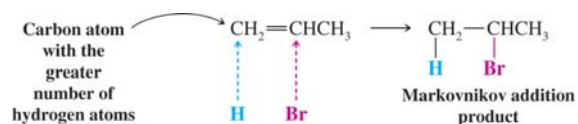


Addition of Hydrogen Halides to Alkenes: Markovnikov's Rule

Addition of HBr to propene occurs to give 2-bromopropane

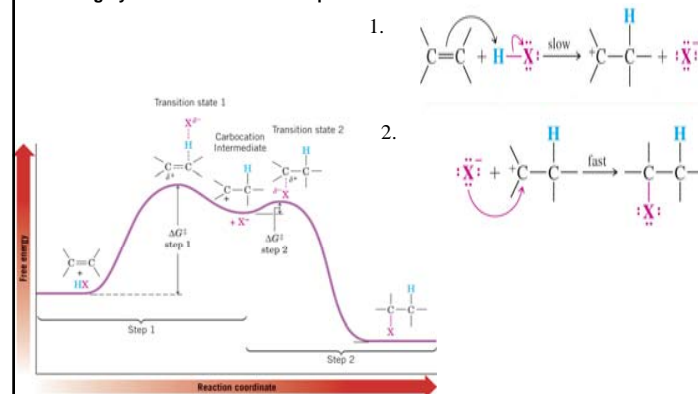


- **Markovnikov's Rule (Original):** addition of HX to an alkene proceeds so that the hydrogen atom adds to the carbon that already has the most hydrogen atoms



Mechanism for hydrogen halide addition to an alkene

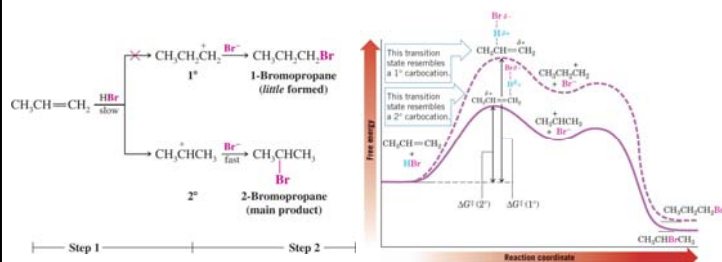
- ♦ The reaction has a highly endothermic first step (rate determining) and a highly exothermic second step



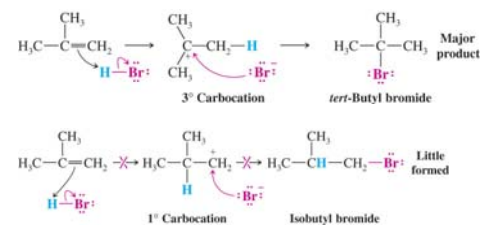
Theoretical Basis of Markovnikov's Rule

Product with the more stable carbocation intermediate predominates

Transition state for the rate determining step (first step) resembles a carbocation and is stabilized by factors which stabilize carbocations



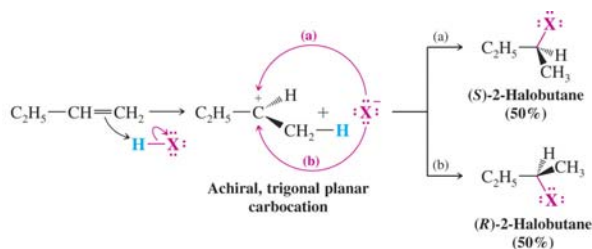
Addition of HBr to 2-methylpropene gives only *tert*-butyl bromide



- ♦ **Modern Statement of Markovnikov's Rule:** In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as an intermediate
- ♦ **Regioselective Reaction:** When a reaction that can potentially yield two or more constitutional isomers actually produces only one or a predominance of one isomer

Stereochemistry of the Ionic Addition to an Alkene

If the addition of HBr to butene yields a chiral molecule, a racemic mixture is produced because the intermediate carbocation is achiral.



Addition of Sulfuric Acid to Alkenes

Addition of concentrated sulfuric acid to an alkene leads to an alkyl hydrogen sulfate.

The addition follows Markovnikov's rule

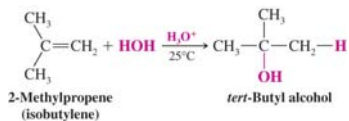


- ◆ The sulfate can be hydrolyzed by heating with water
 - The net result is **Markovnikov addition** of water to the alkene



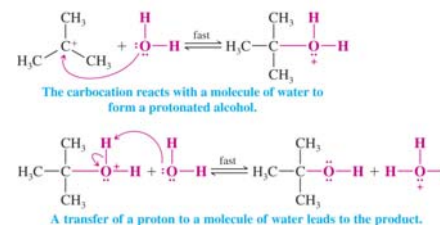
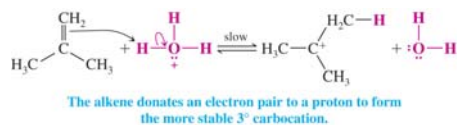
Addition of Water to Alkenes: Acid-Catalyzed Hydration

The reaction of alkenes with dilute aqueous acid leads to Markovnikov addition of water



The mechanism is the reverse of that for dehydration of an alcohol

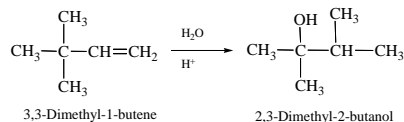
→ The first step in which a carbocation is formed is rate determining



- ◆ The hydration of alkenes and the dehydration of alcohols are simply reverse reactions of one other

- The reaction is governed by how you push the equilibria.
- **Hydration is favored** by addition a large amount of water and a low concentration of acid.
- **Dehydration is favored** by concentrated acid with the removal of water.

Carbocation rearrangements are possible

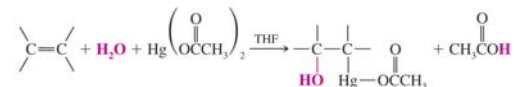


Hydration of Alkenes Through Oxymercuration-Demercuration

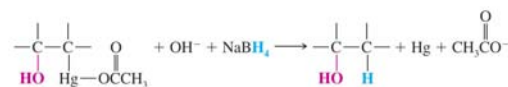
A third, alternative way to add water to an alkene:

- Uses Hg^{+2} as the initial electrophile
- Removal of mercury with sodium borohydride (a reducing agent)

Step 1: Oxymercuration

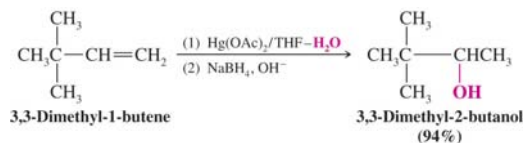
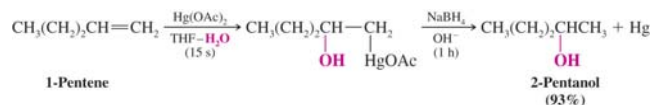


Step 2: Demercuration



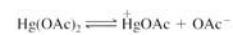
Hydration of Alkenes Through Oxymercuration-Demercuration

- High yields
- No carbocation rearrangements
- Follows Markovnikov addition



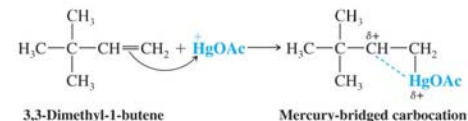
Mechanism involves formation of a bridged mercurinium ion

Step 1



Mercuric acetate dissociates to form a $\overset{\oplus}{\text{Hg}}\text{OAc}$ cation and an acetate anion.

Step 2



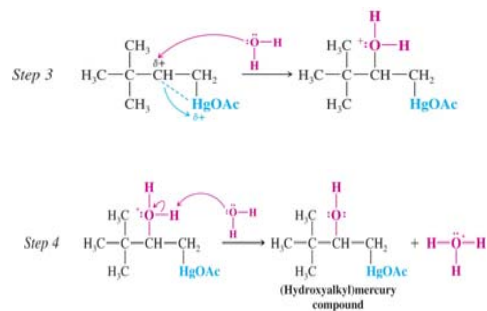
Why do we say it involves a bridged ion?

No rearrangements = **no free carbocation**

BUT Markovnikov addition means it must be a **partial carbocation**.

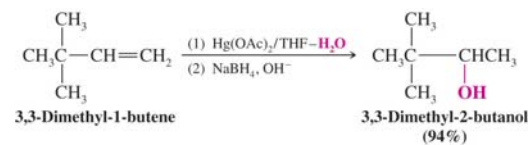
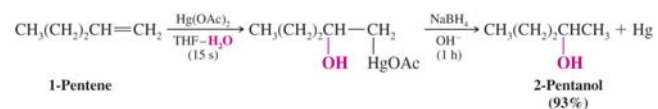
Mechanism involves formation of a bridged mercurinium ion

Water then attacks the bridged ion at the Markovnikov carbon



After reduction with NaBH₄, net result is the addition of water

- High yields
- No carbocation rearrangements
- Follows Markovnikov addition

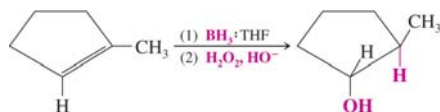


A Fourth Way to Make Alcohols from Alkenes

Hydroboration-Oxidation

An important method because it is:

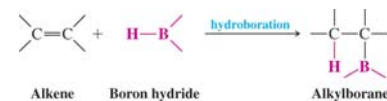
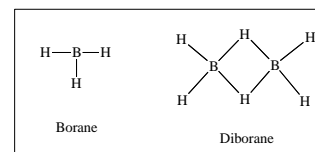
1. an anti-Markovnikov addition
2. a syn addition



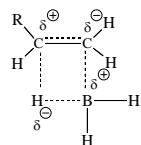
Step 1 : Hydroboration

Hydroboration: Synthesis of Alkylboranes

- In this addition reaction, one is adding boron (B) and hydrogen (H)
- BH₃ is an electrophile. It actually exists as its dimer B₂H₆.



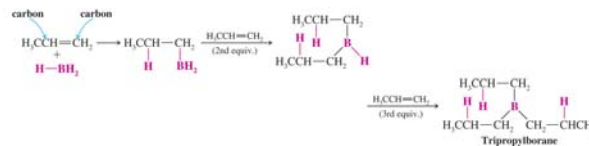
Mechanism of hydroboration



1. The B and the H add in a concerted fashion.
2. The B is δ^+ ; the H is δ^-

Mechanism of Hydroboration

- ◆ In reality, each borane molecule adds successively to three molecules of alkene.



Boron becomes attached to less substituted carbon of double bond

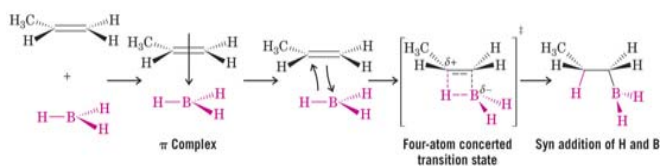
- Bulkier boron group approaches the less hindered carbon more easily
- This orientation also allows a δ^+ charge in the transition state to reside at the most substituted carbon

- ◆ The boron and hydride add with syn stereochemistry



Mechanism of hydroboration

Recall that boron compounds are Lewis acids, and in this case readily complexes with the electron pair of the alkene

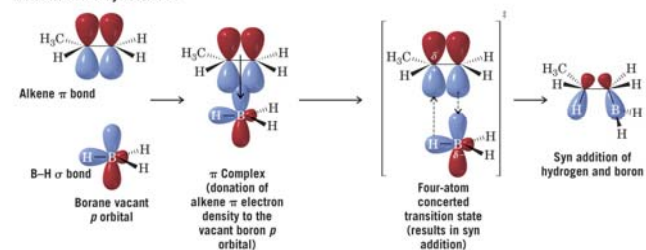


Transfer of B and H must be concerted to account for the syn addition

Process repeats to form a trialkyl borane

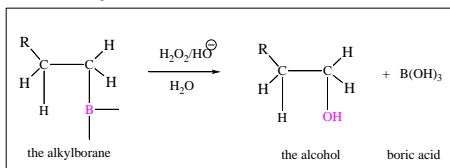
Mechanism of hydroboration

An orbital view of hydroboration

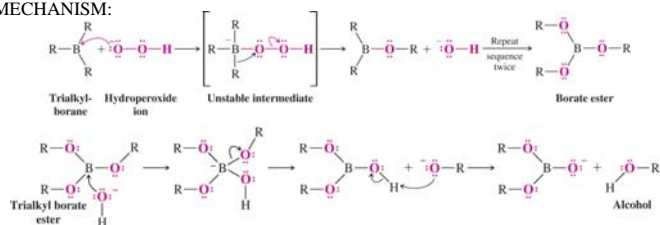


Step 2: Oxidation and Hydrolysis of the Alkylborane

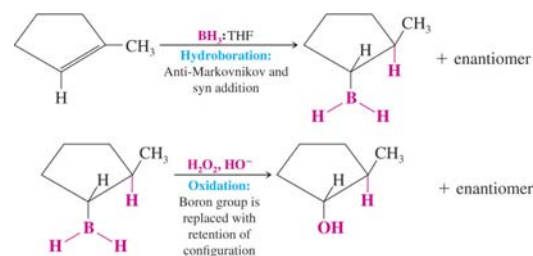
Once the alkylborane is formed by the addition reaction, oxidation to the alcohol takes place with retention of stereochemistry at the carbon bonded to boron.



MECHANISM:



Hydroboration: oxidation gives the anti-Markovnikov product with syn addition of the elements of water



Comparison of alkene Hydration Procedures

1. **Acid-catalyzed hydrolysis:** Markovnikov addition, reversible, possible rearrangements
2. **Oxymercuration/Demercuration:** Markovnikov addition, no rearrangement
3. **Hydroboration-Oxidation:** anti-Markovnikov and syn addition, no rearrangement

Addition of Bromine and Chlorine to Alkenes

- ◆ Alkenes readily accept Br₂ or Cl₂ to form **vicinal dihalides**



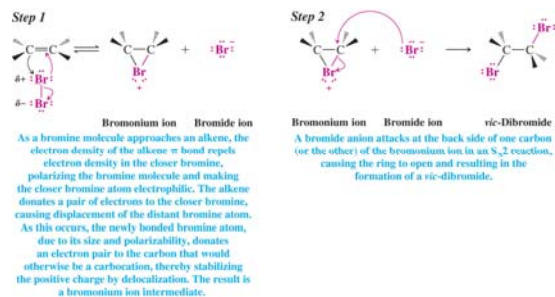
Note: *anti* addition

- ◆ Used as a test for alkenes because the red color of the bromine disappears when an alkene (or alkyne) is present.
 - Alkanes do not react with bromine in the dark



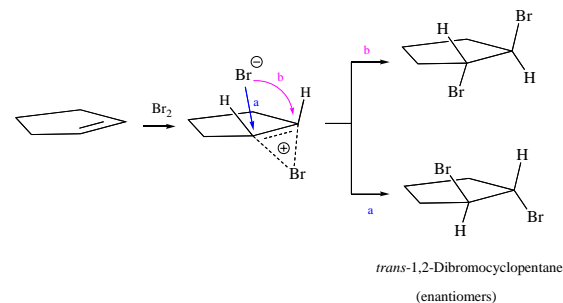
Mechanism of Halogen Addition

- ◆ Mechanism must explain the exclusive *anti*-addition
- ◆ A bromonium ion intermediate holds the geometry



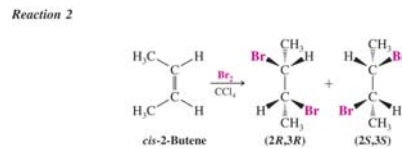
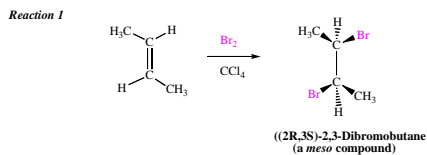
• Stereochemistry of the addition of Halogens to Alkenes

- The net result is *anti* addition because of S_N2 attack on the bromonium ion intermediate.
- For example, when cyclopentene reacts, the product is a racemic mixture of *trans*-1,2-dibromocyclopentane enantiomers.



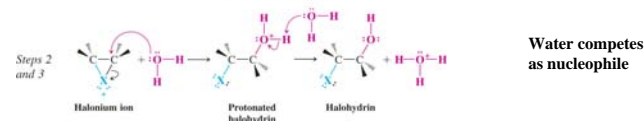
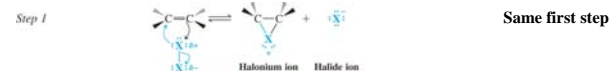
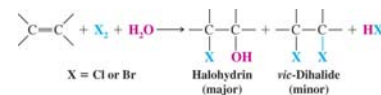
Halogenation of double bonds is stereospecific

- A reaction is said to be **stereospecific** if a particular stereoisomer of the starting material reacts in such a way that it gives a specific stereoisomer of the product
- Example: *cis*- and *trans*-2-butene give stereoisomeric products when halogenated



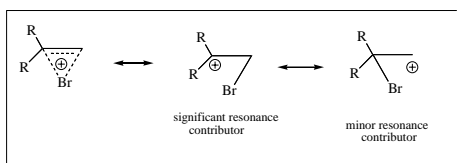
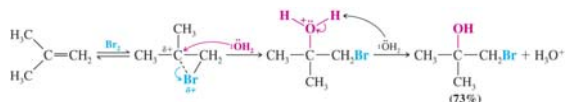
Halohydrin Formation

If halogenation is carried out in aqueous solvent, the water molecule can act as a nucleophile to open the halonium ion



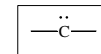
Reaction shows regioselectivity

- ◆ In unsymmetrical alkenes, the bromonium ion will have some of its $\delta+$ charge density on the more 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



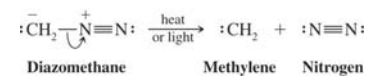
Divalent Carbon Compounds: Carbenes

- ◆ Carbenes have a divalent, neutral carbon
- ◆ Carbenes are highly reactive
- ◆ Structure and Reaction of Methylene (CH_2)

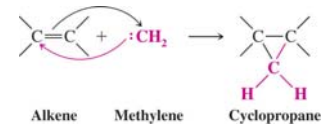


→ Methylene can be made by heat or light initiated decomposition of diazomethane

↳ Loss of a molecule of the stable gas nitrogen drives this reaction

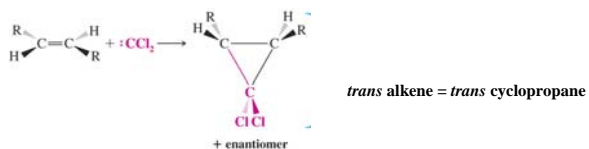


→ Methylene reacts with alkenes to form cyclopropanes

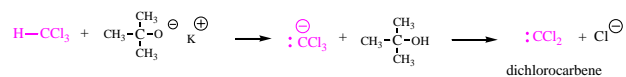


Reactions of Other Carbenes: Dihalocarbenes

Carbenes add to double bonds in a stereospecific manner

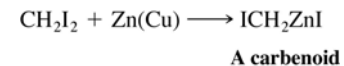


Dihalocarbenes formed by α elimination of compounds such as chloroform

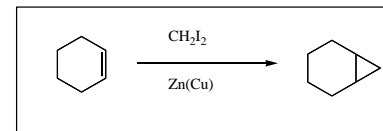


Carbenoids: the Simmon-Smith reaction

A carbene-like species is formed which then reacts with alkenes



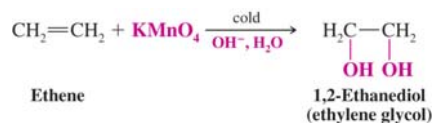
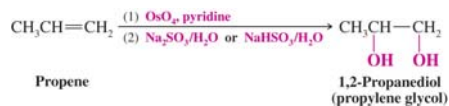
For example:



Oxidations of Alkenes

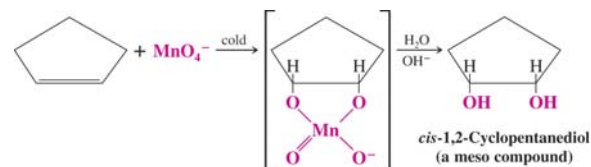
1. Syn 1,2-Dihydroxylation

- Either OsO_4 or KMnO_4 will give 1,2 diols (glycols)



Mechanism for Syn Hydroxylation of Alkenes

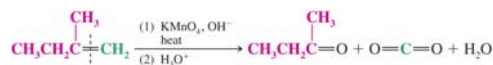
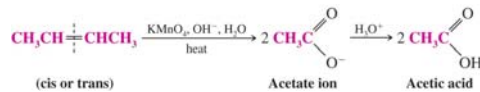
A cyclic intermediate results when an alkene reacts with MnO_4^- . A **syn addition** of the oxygens occurs resulting in a **cis-diol** after the oxygen-metal bonds are cleaved with the base.



Oxidation 2 of Alkenes: Oxidative Cleavage

- Reaction of an alkene with **hot KMnO_4** results in **cleavage of the double bond** and formation of highly oxidized carbons.

- Unsubstituted carbons become CO_2 , monosubstituted carbons become carboxylic acids, and disubstituted carbons become ketones.

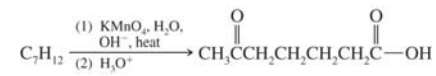


- This reaction can be used as a **chemical test for alkenes** in which the purple color of the KMnO_4 disappears and forms brown MnO_2 residue if an alkene (or alkyne) is present.

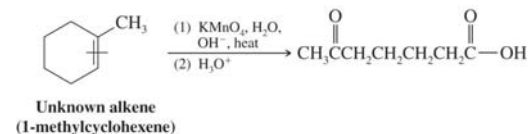
Useful to identify location of double bonds

- Example:**

→ An unknown alkene with formula C_7H_{12} yields only the following product on oxidation with hot KMnO_4 :



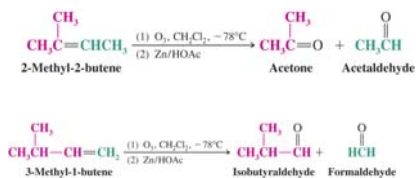
→ Answer: Since no carbons are missing and the product contains two carbonyl groups, the original alkene must be a ring.



Oxidation 3 of Alkenes: Ozonolysis

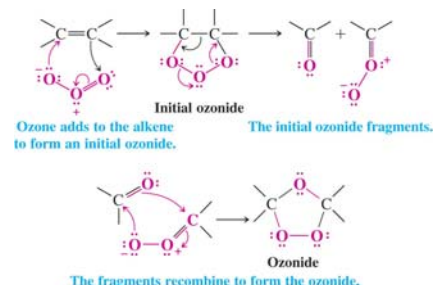
Cleavage of alkenes with ozone and workup with zinc in acetic acid also leads to highly oxidized carbons than products from cleavage with hot KMnO_4 .

- Unsubstituted carbons are oxidized to formaldehyde, monosubstituted carbons are oxidized to aldehydes and disubstituted carbons are oxidized to ketones.



Ozonolysis mechanism

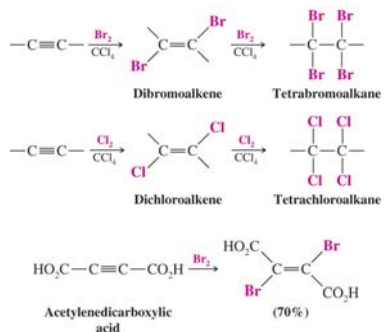
- ◆ Ozone adds across the double bond to form the initial ozonide which rearranges to a highly unstable ozonide



The ozonides then cleave with zinc and acetic acid to give the carbonyl products (aldehydes and ketones). □

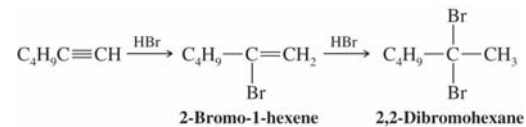
Addition of Bromine and Chlorine to Alkynes

- ◆ Addition of halogen to alkynes can occur once or twice depending on how many equivalents of the halogen are added
- ◆ Addition of one equivalent gives the trans dihalide



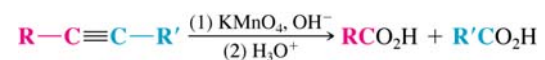
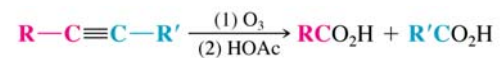
Addition of Hydrogen Halides to Alkynes

Addition of hydrogen halides occurs once or twice depending on how many molar equivalents of hydrogen halide are added. Both additions are Markovnikov and give *gem*-halides.



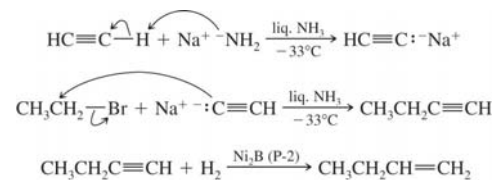
Oxidative Cleavage of Alkynes

Reaction of alkynes with ozone or basic potassium permanganate both lead to formation of carboxylic acids



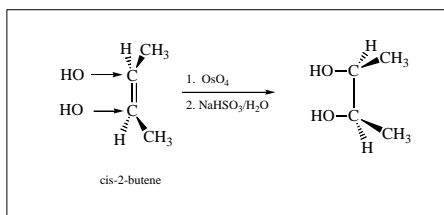
Synthetic Strategies Revisited

◆ EXAMPLE: How would you synthesize 1-butene starting from compounds with two or fewer carbons?



◆ Example: Synthesis of *meso*-2,3-butanediol from compounds of two carbon atoms or fewer

Working backwards, the last step would be:



Complete Synthesis

