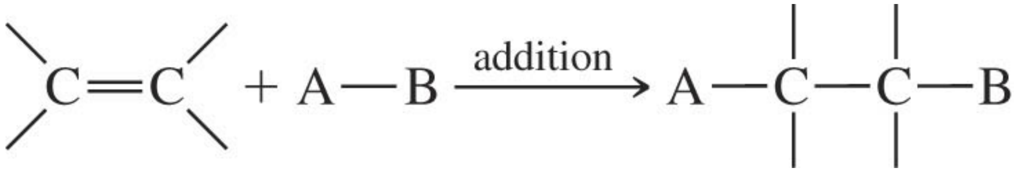
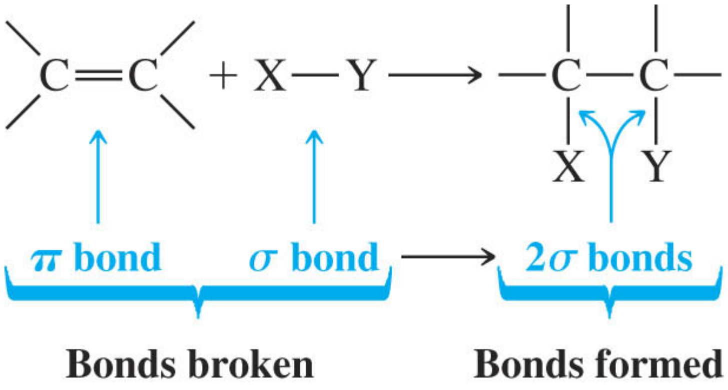
Chapter 8

Alkenes and Alkynes II: Addition Reactions

Additions to Alkenes



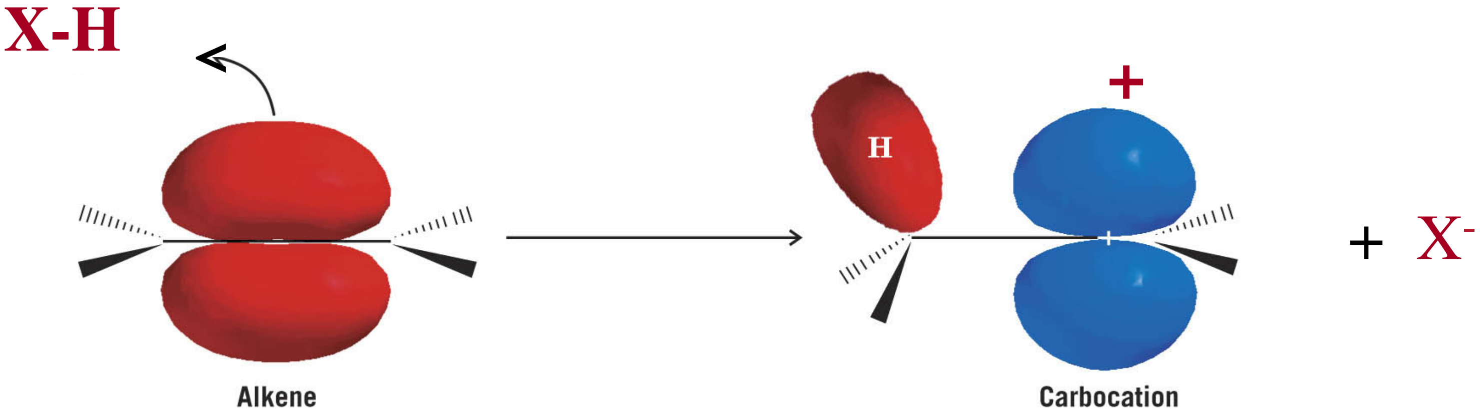
Generally the reaction is exothermic because one π and one σ bond are converted to two σ bonds



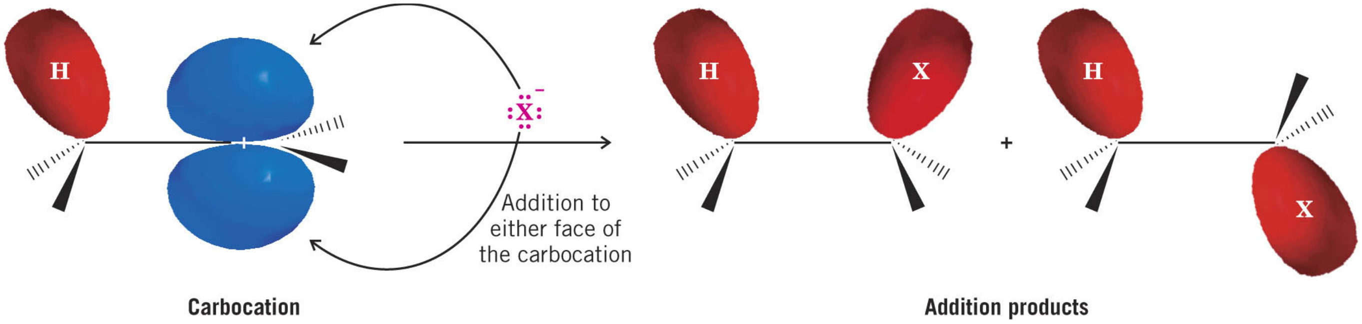
Alkenes are electron rich

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

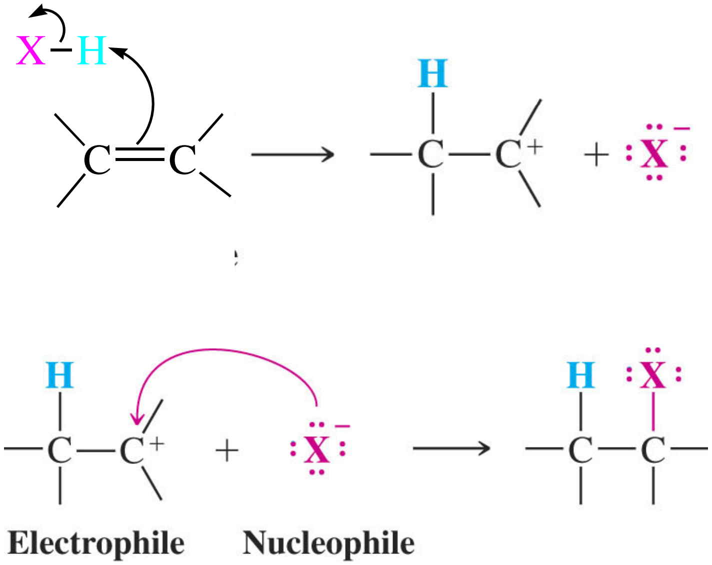
Alkenes are nucleophilic and react with electrophiles such as H^+ from a hydrogen halide to form a carbocation



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

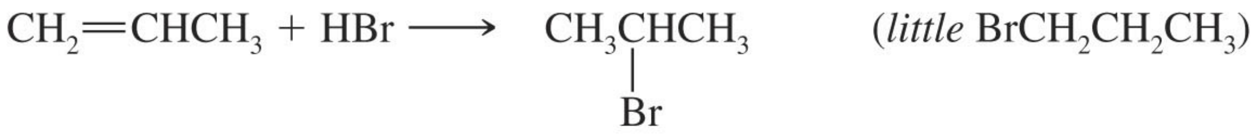


In addition reactions the alkene is a nucleophile in the first step and an electrophile in the second



Addition of Hydrogen Halides to Alkenes: Markovnikov’s Rule

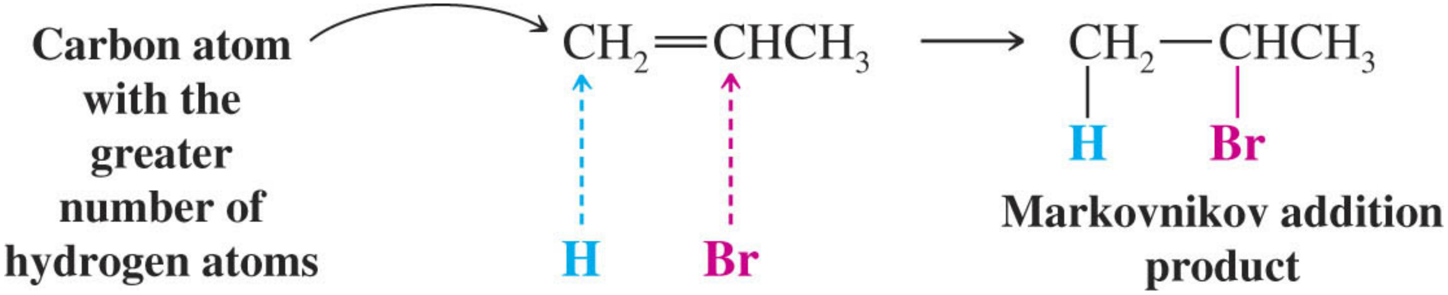
Addition of HBr to propene occurs to give 2-bromopropane



$$CH_2{=}CHCH_3 + HBr \longrightarrow \underset{\displaystyle Br}{CH_3\overset{}{C}HCH_3} \qquad (\textit{little}\ BrCH_2CH_2CH_3)$$

2-Bromopropane **1-Bromopropane**

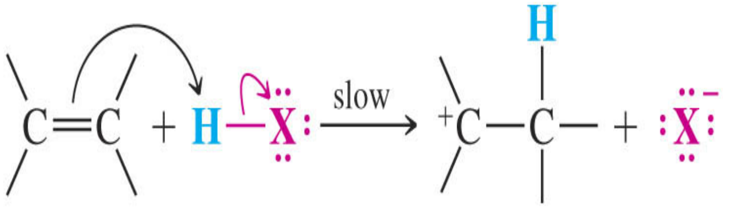
- **Markovnikov’s Rule (Original): addition of HX to an alkene proceeds so that the hydrogen atom adds to the carbon that already has the most hydrogen atoms**

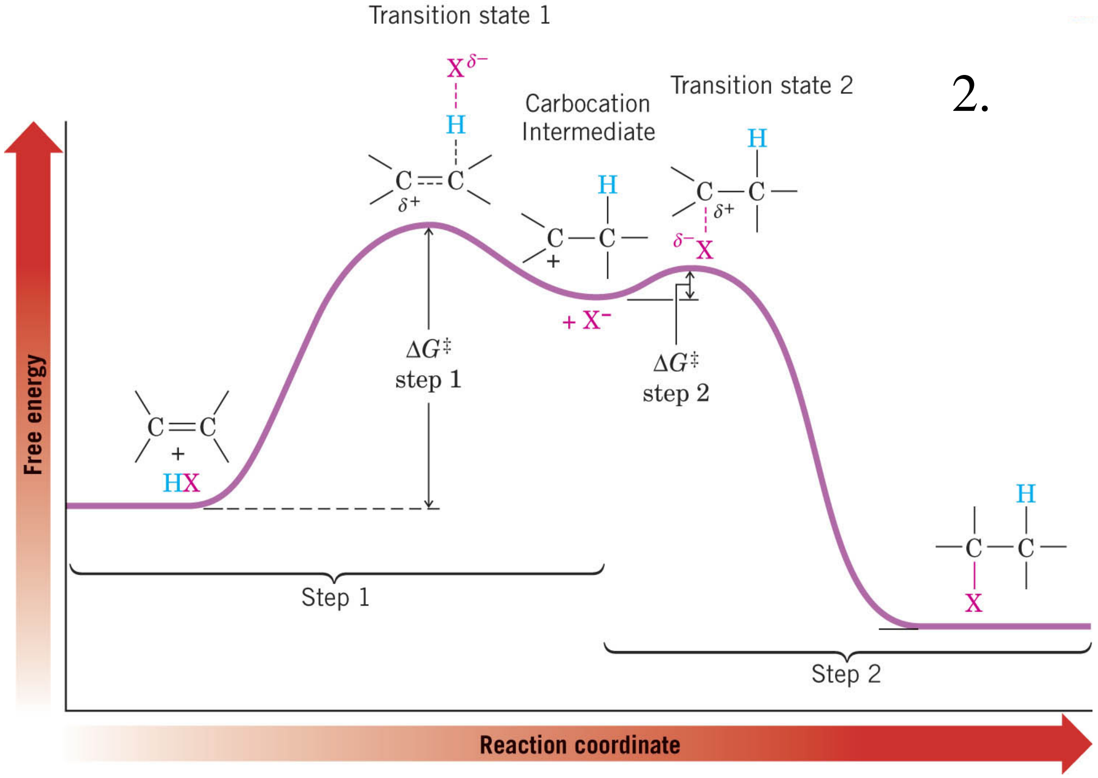


Mechanism for hydrogen halide addition to an alkene

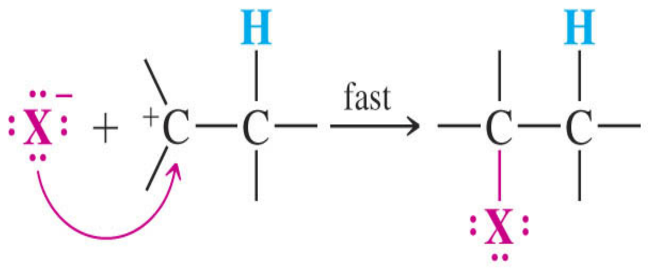
- The reaction has a highly endothermic first step (rate determining) and a highly exothermic second step

1.





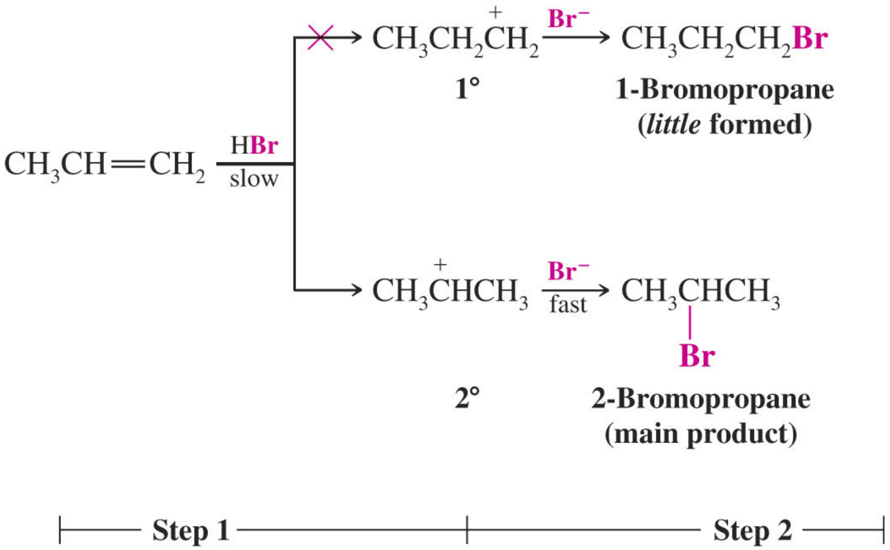
2.

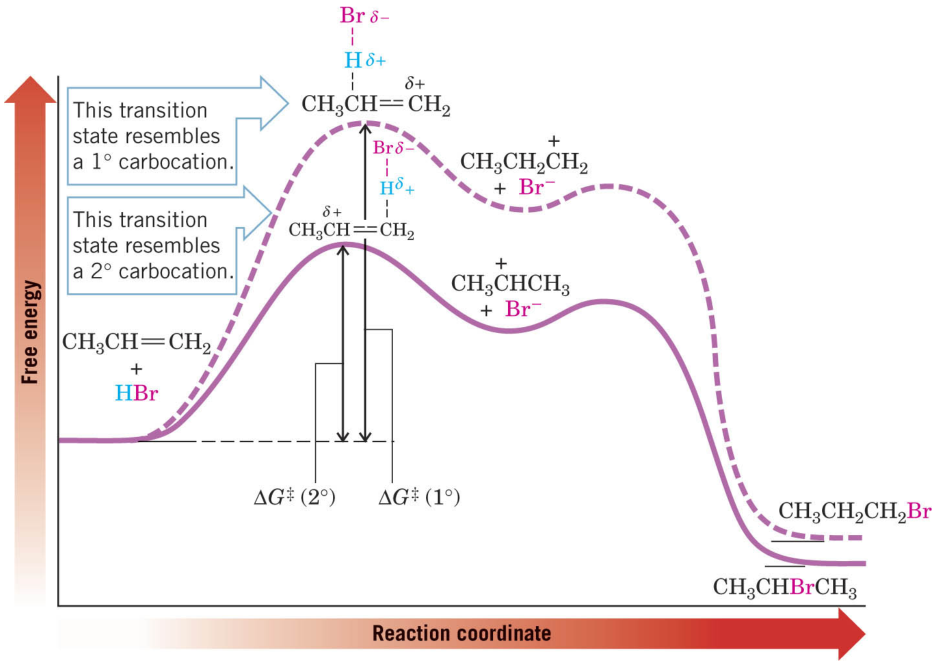


Theoretical Basis of Markovnikov's Rule

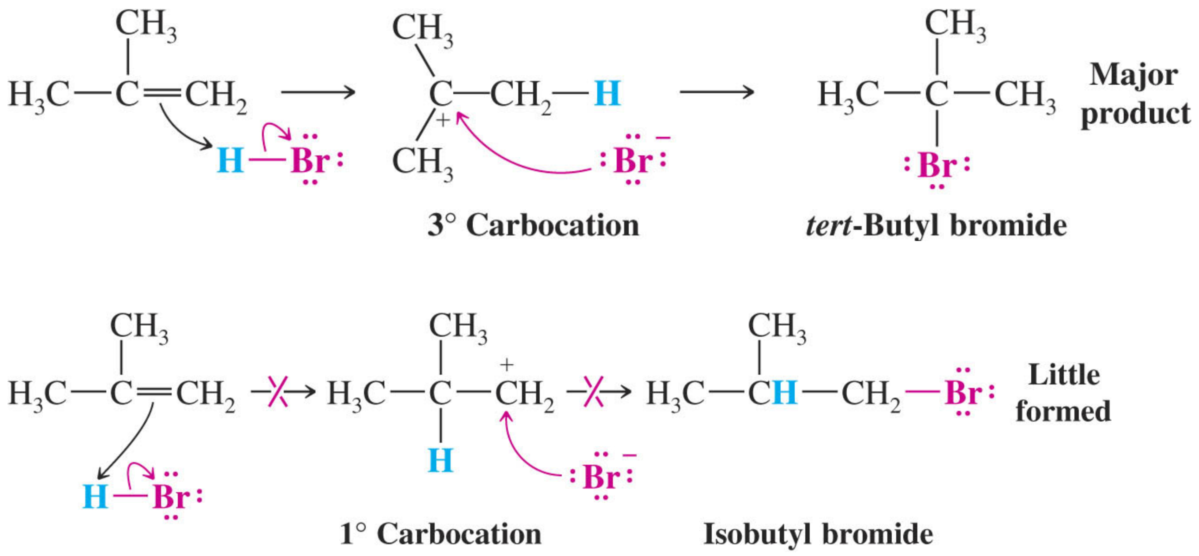
Product with the more stable carbocation intermediate predominates

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

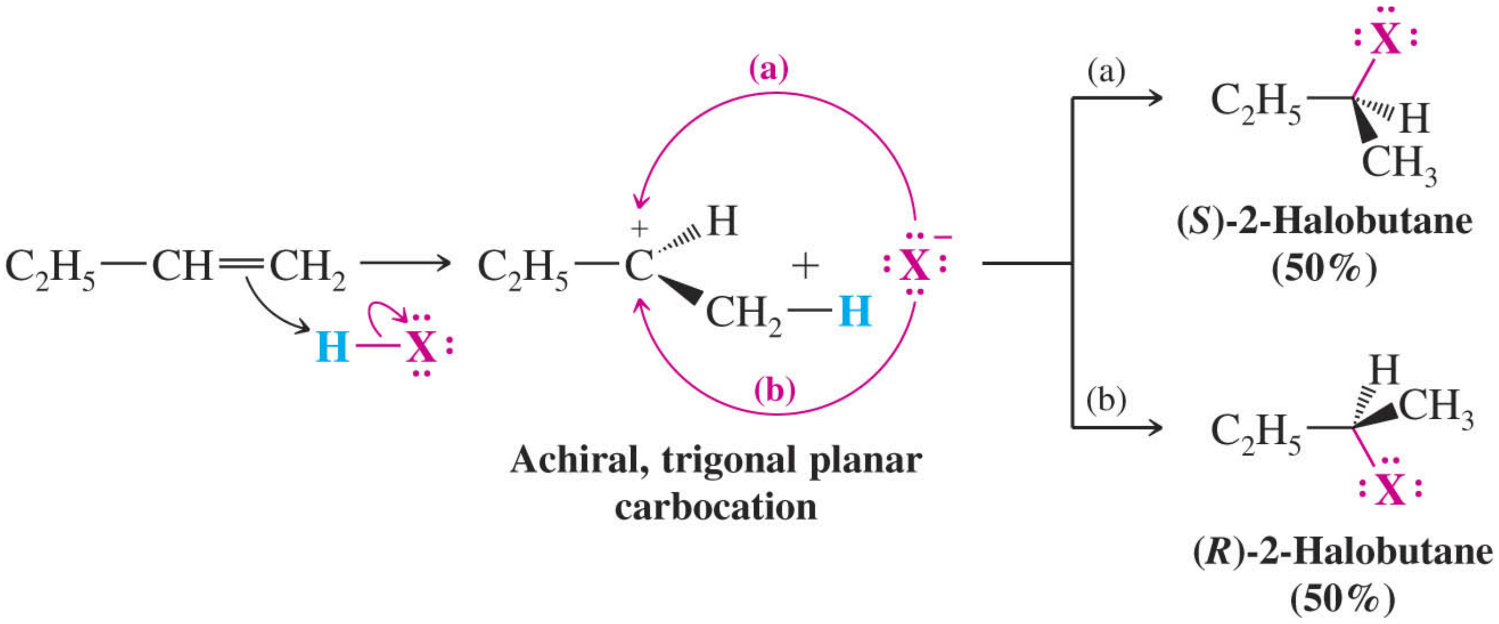


- **Modern Statement of Markovnikov’s Rule**: In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as an intermediate

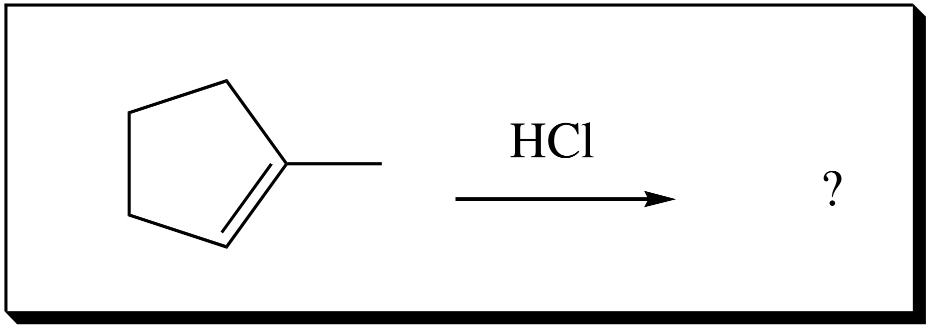
- **Regioselective Reaction**: When a reaction that can potentially yield two or more constitutional isomers actually produces only one or a predominance of one isomer

Stereochemistry of the Ionic Addition to an Alkene

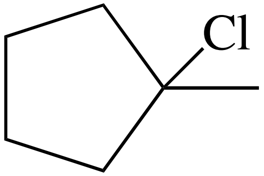
If the addition of HBr to butene yields a chiral molecule, a racemic mixture is produced because the intermediate carbocation is achiral.



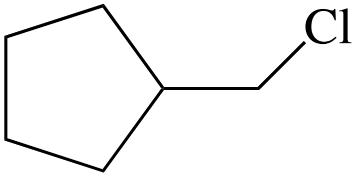
What is the major product?



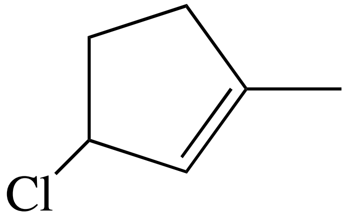
a.



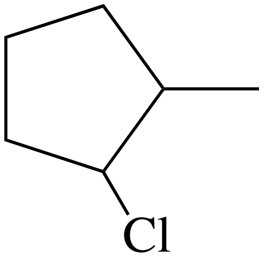
b.



c.



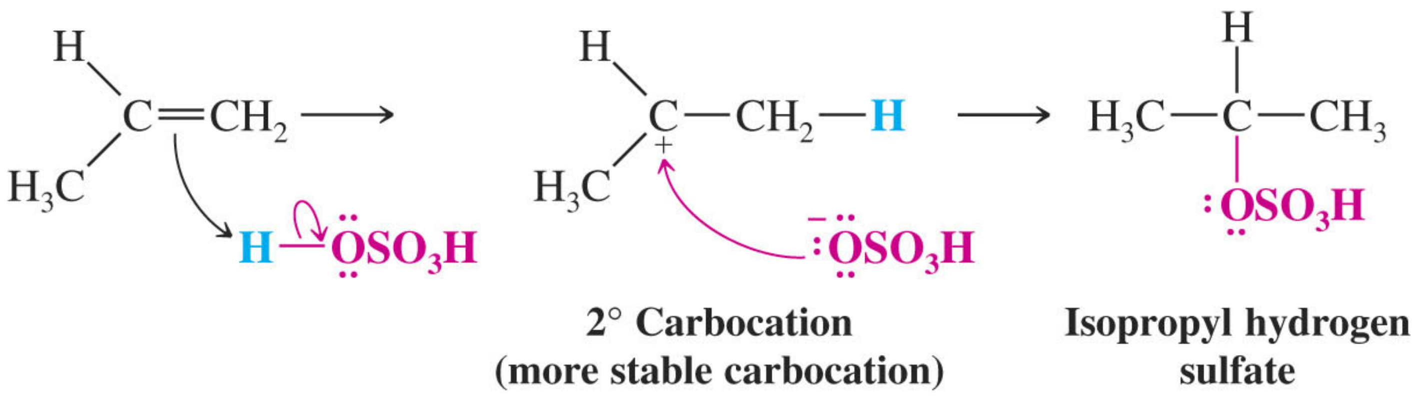
d.



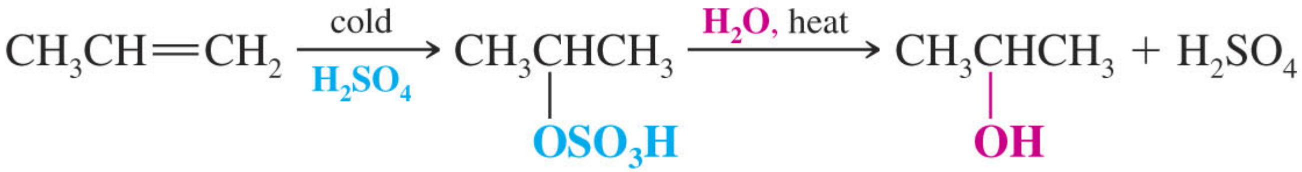
Addition of Sulfuric Acid to Alkenes

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

The addition follows Markovnikov' s rule



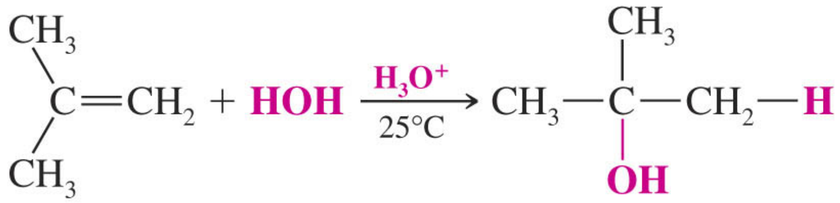
- **The sulfate can be hydrolyzed by heating with water**
  - **The net result is Markovnikov addition of water to the alkene**



$$CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{\text{cold}} \underset{\displaystyle OSO_3H}{CH_3\overset{}{C}HCH_3} \xrightarrow{H_2O,\ \text{heat}} \underset{\displaystyle OH}{CH_3CHCH_3} + H_2SO_4$$

Addition of Water to Alkenes: Acid-Catalyzed Hydration

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

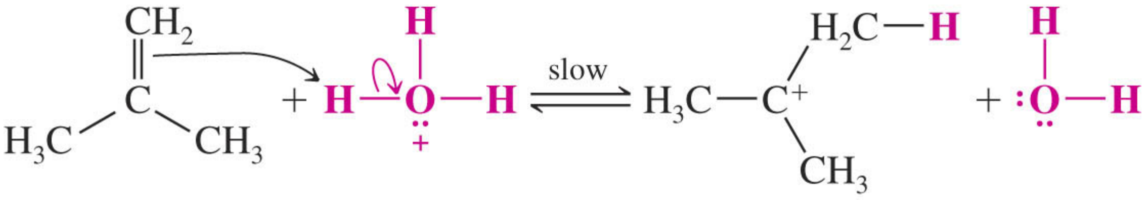


2-Methylpropene (isobutylene)

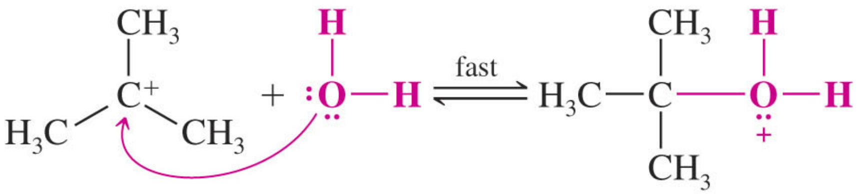
***tert*-Butyl alcohol**

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

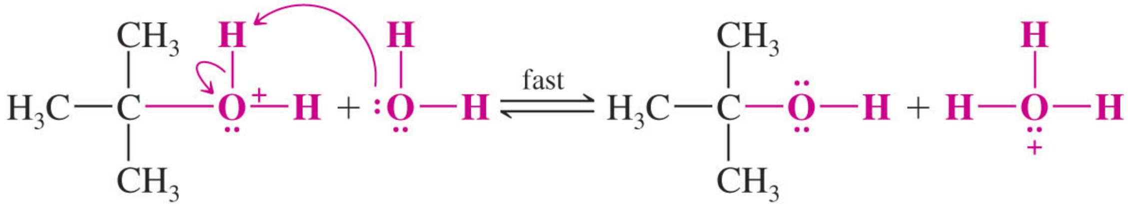
➡ **The first step in which a carbocation is formed is rate determining**



The alkene donates an electron pair to a proton to form the more stable 3° carbocation.



The carbocation reacts with a molecule of water to form a protonated alcohol.

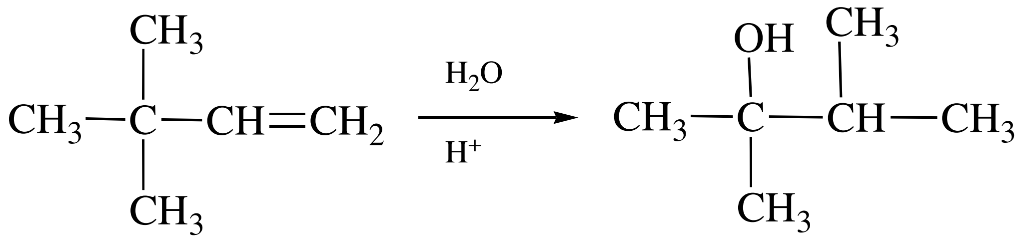


A transfer of a proton to a molecule of water leads to the product.

♦ **The hydration of alkenes and the dehydration of alcohols are simply reverse reactions of one other**

- **The reaction is governed by which direction 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



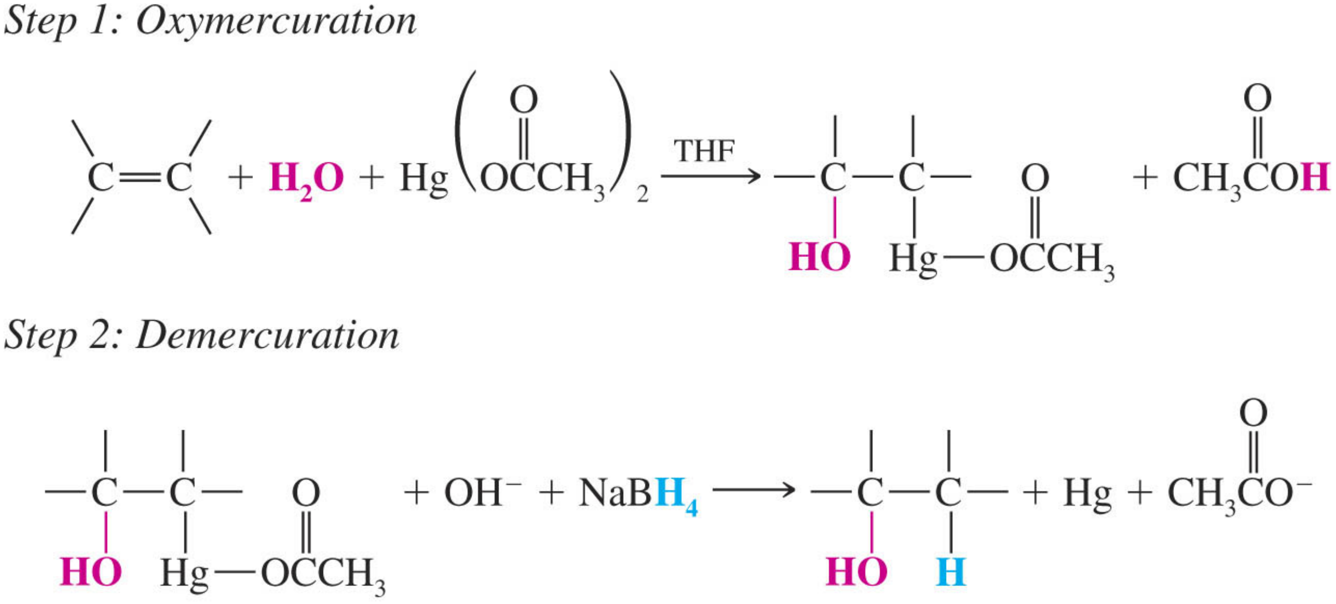
3,3-Dimethyl-1-butene

2,3-Dimethyl-2-butanol

Hydration of Alkenes Through Oxymercuration-Demercuration

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

- **Uses Hg^{+2} as the initial electrophile**
- **This is followed buy replacement of mercury by hydrogen using sodium borohydride [$NaBH_4$] (a reducing agent)**



Step 1: Oxymercuration

$$\mathrm{>C{=}C<} + H_2O + Hg\left(O\overset{O}{\overset{\|}{C}}CH_3\right)_2 \xrightarrow{THF} -\underset{HO}{\underset{|}{\overset{|}{C}}}-\underset{Hg-O\overset{O}{\overset{\|}{C}}CH_3}{\underset{|}{\overset{|}{C}}}- + CH_3\overset{O}{\overset{\|}{C}}OH$$

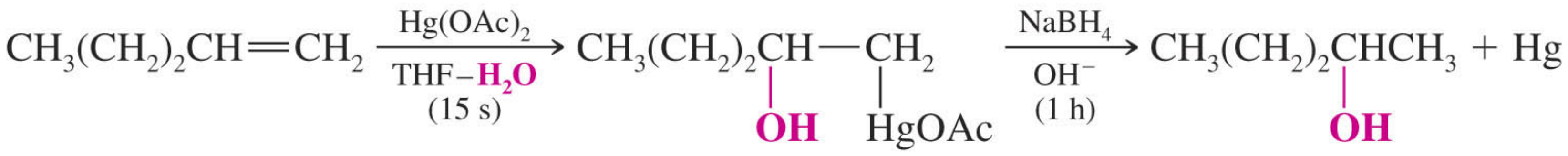
Step 2: Demercuration

$$-\underset{HO}{\underset{|}{\overset{|}{C}}}-\underset{Hg-O\overset{O}{\overset{\|}{C}}CH_3}{\underset{|}{\overset{|}{C}}}- + OH^- + NaBH_4 \longrightarrow -\underset{HO}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}- + Hg + CH_3\overset{O}{\overset{\|}{C}}O^-$$

Hydration of Alkenes Through Oxymercuration-Demercuration

ADVANTAGES:

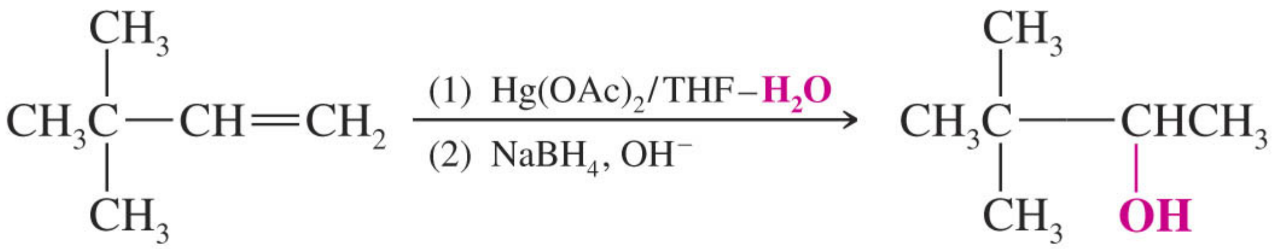
- **High yields**
- **No carbocation rearrangements**
- **Follows Markovnikov addition**



$$CH_3(CH_2)_2CH{=}CH_2 \xrightarrow[\text{THF}-H_2O\ (15\text{ s})]{Hg(OAc)_2} CH_3(CH_2)_2\underset{OH}{CH}-\underset{HgOAc}{CH_2} \xrightarrow[OH^-\ (1\text{ h})]{NaBH_4} CH_3(CH_2)_2\underset{OH}{CH}CH_3 + Hg$$

1-Pentene

2-Pentanol
(93%)



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2 \xrightarrow[(2)\ NaBH_4,\ OH^-]{(1)\ Hg(OAc)_2/\text{THF}-H_2O} CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}CH_3$$

3,3-Dimethyl-1-butene

3,3-Dimethyl-2-butanol
(94%)

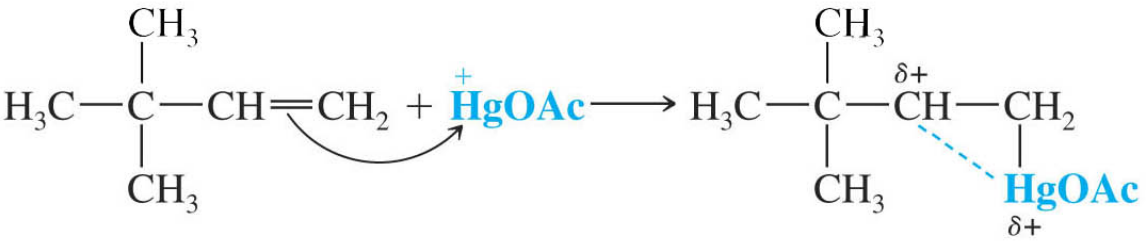
Mechanism involves formation of a bridged mercurinium ion

Step 1

$$\mathrm{Hg(OAc)_2} \rightleftharpoons \overset{+}{\mathrm{Hg}}\mathrm{OAc} + \mathrm{OAc^-}$$

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

Step 2



3,3-Dimethyl-1-butene

Mercury-bridged carbocation

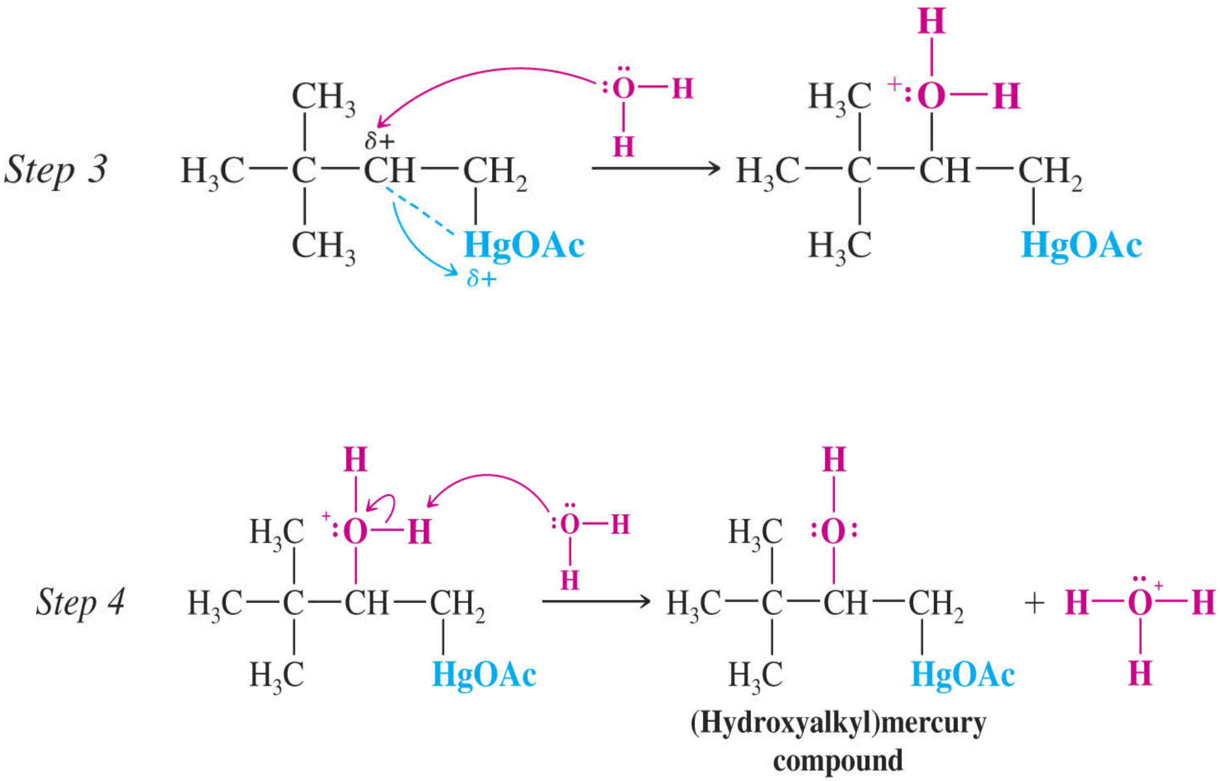
Why do we say it involves a bridged ion?

No rearrangements means no free carbocation

BUT Markovnikov addition indicates that it must be a partial carbocation.

Mechanism involves formation of a bridged mercurinium ion

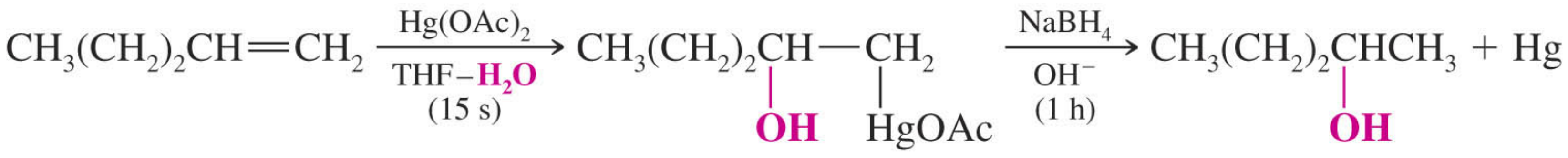
Water then attacks the bridged ion at the Markovnikov carbon:



After reduction with $NaBH_4$, net result is the addition of water

This leads to:

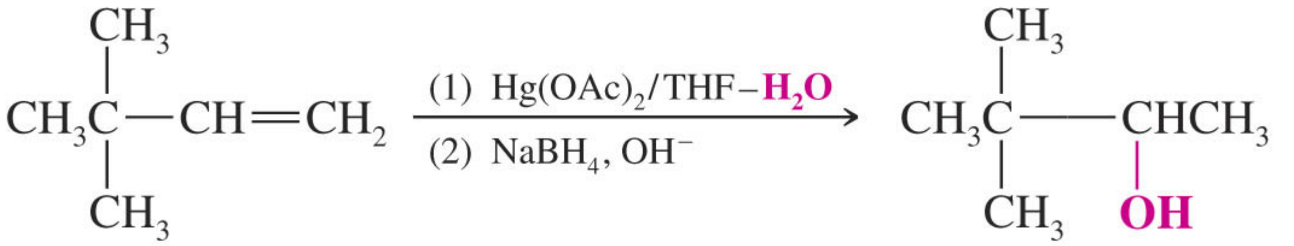
- **High yields**
- **No carbocation rearrangements**
- **Addition follows Markovnikov's Rule**



$$CH_3(CH_2)_2CH{=}CH_2 \xrightarrow[\substack{THF-H_2O \\ (15\ s)}]{Hg(OAc)_2} CH_3(CH_2)_2\underset{OH}{\underset{|}{C}H}-\underset{HgOAc}{\underset{|}{C}H_2} \xrightarrow[\substack{OH^- \\ (1\ h)}]{NaBH_4} CH_3(CH_2)_2\underset{OH}{\underset{|}{C}H}CH_3 + Hg$$

1-Pentene

2-Pentanol
(93%)



$$CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH{=}CH_2 \xrightarrow[(2)\ NaBH_4,\ OH^-]{(1)\ Hg(OAc)_2/THF-H_2O} CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\underset{OH}{\underset{|}{C}H}CH_3$$

3,3-Dimethyl-1-butene

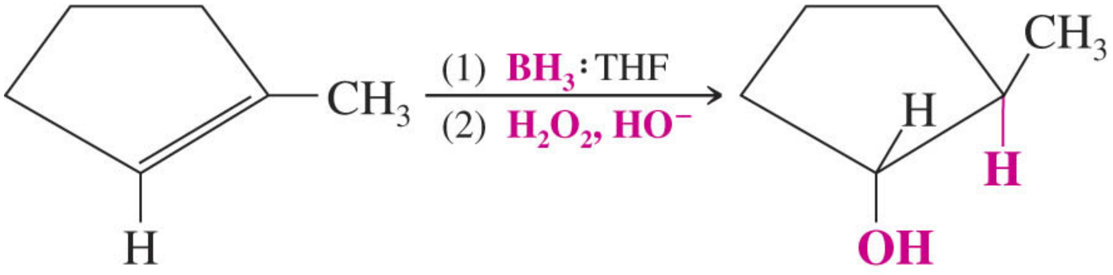
3,3-Dimethyl-2-butanol
(94%)

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**

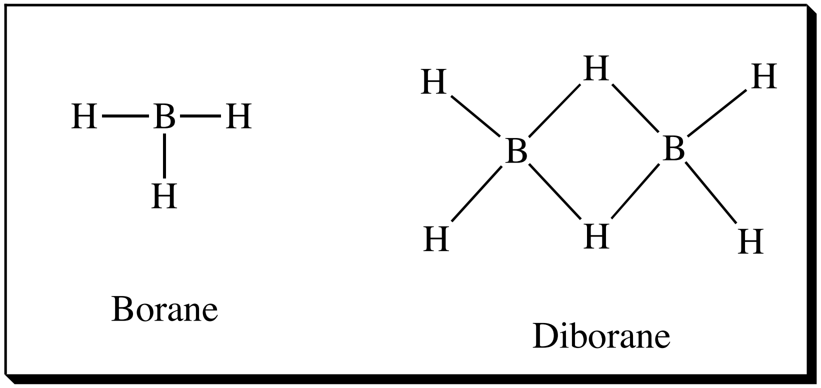


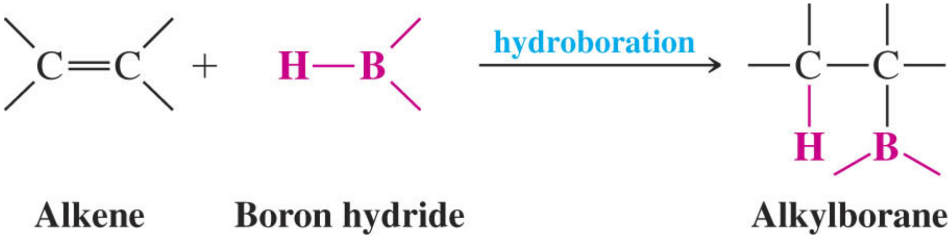
Step 1 : Hydroboration

Hydroboration: Synthesis of Alkylboranes

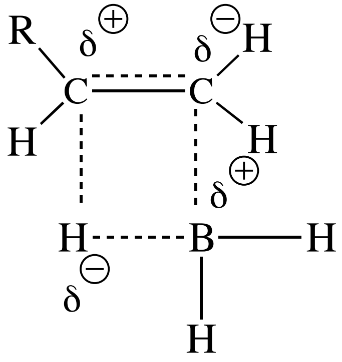
- In this addition reaction, one is adding boron (B) and hydrogen (H) to the alkene.

➡ BH_3 is an electrophile. It actually exists as its dimer B_2H_6.





Mechanism of Hydroboration

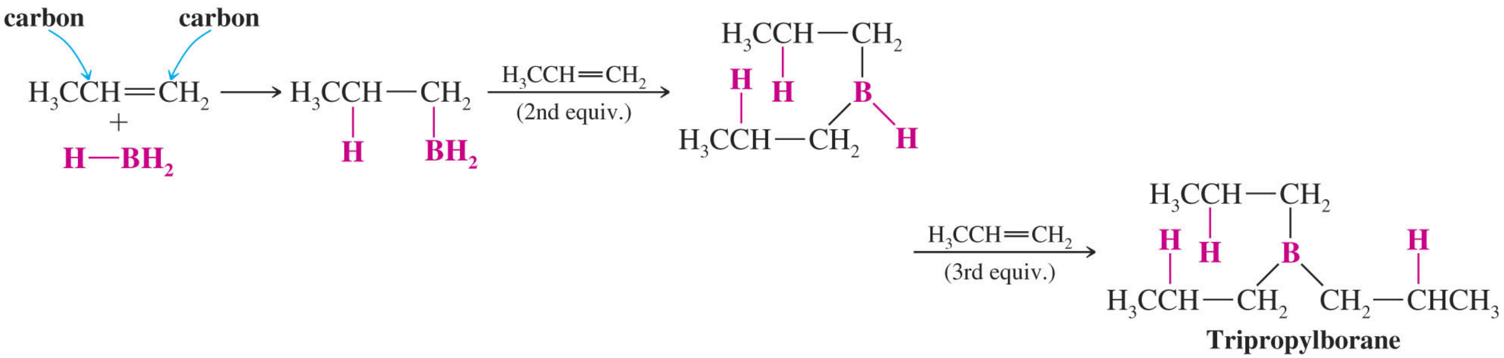


1. The B and the H add in a concerted fashion.

2. The B is δ^{+}; and the H is δ^{-}

Mechanism of Hydroboration

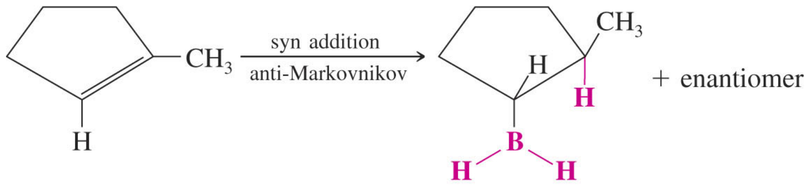
- In reality, each borane molecule adds successively to three molecules of alkene.



Boron becomes attached to the less substituted carbon of double bond

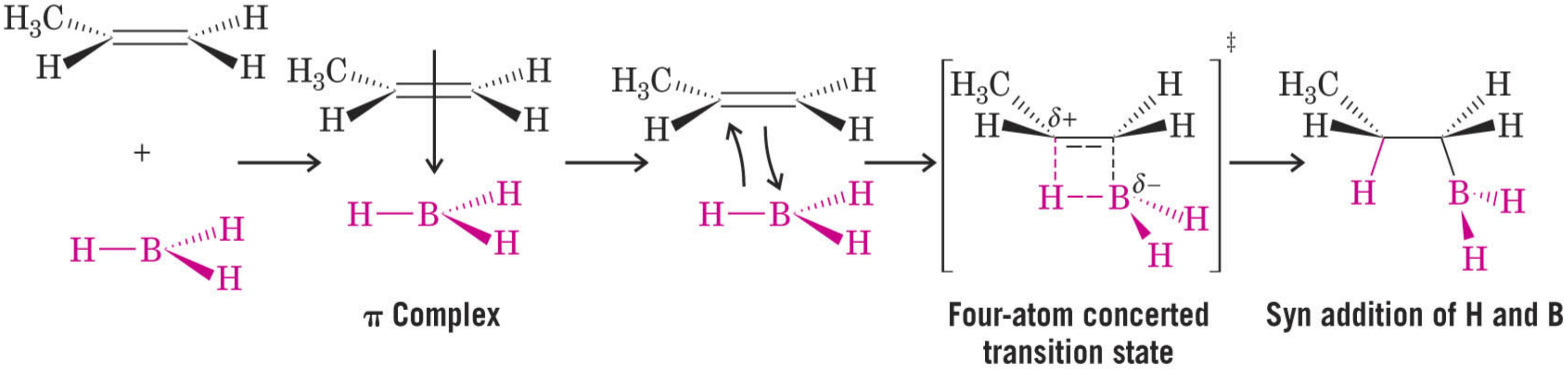
- The bulkier boron group approaches the less hindered carbon more easily.
- This orientation also allows a δ^+ charge in the transition state to reside at the more substituted carbon.

- The boron and hydride add with syn stereochemistry



Mechanism of hydroboration

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

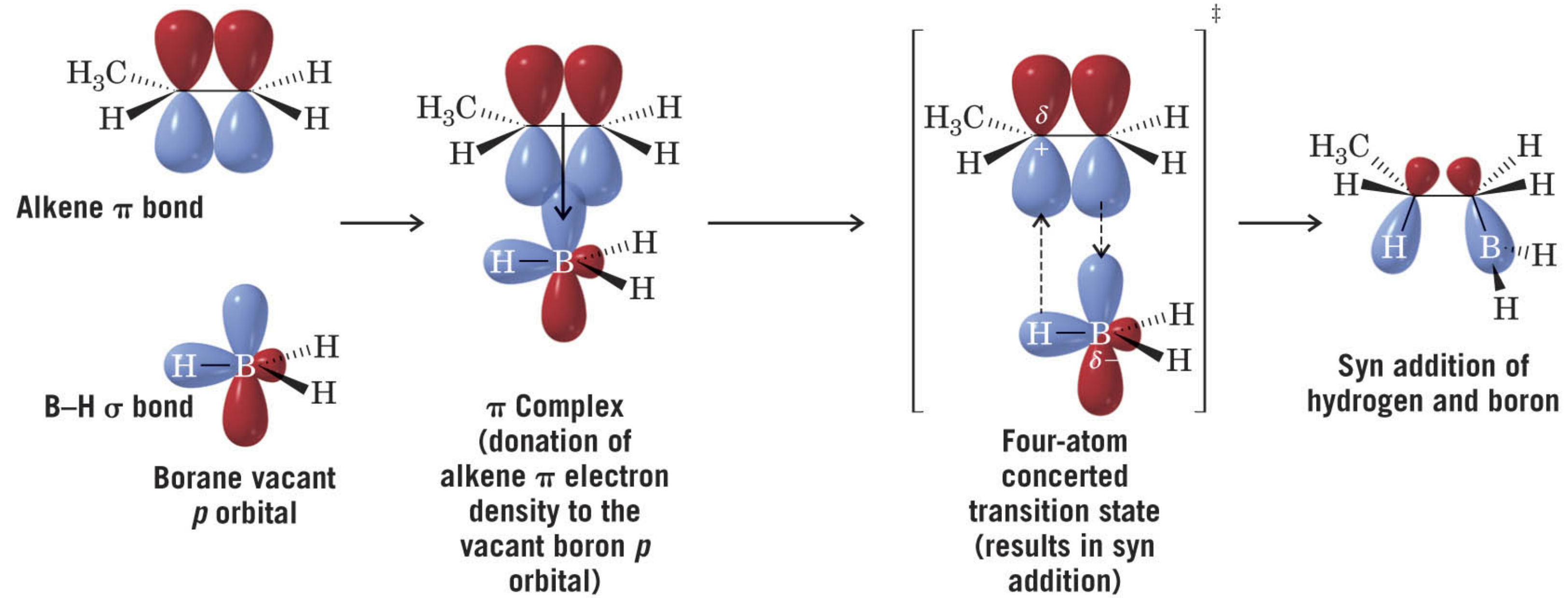


Transfer of B and H must be simultaneous (concerted) to account for the syn addition

Note that the process actually repeats to form a trialkyl borane

Mechanism of Hydroboration

An orbital view of hydroboration



Alkene π bond

B–H σ bond

Borane vacant *p* orbital

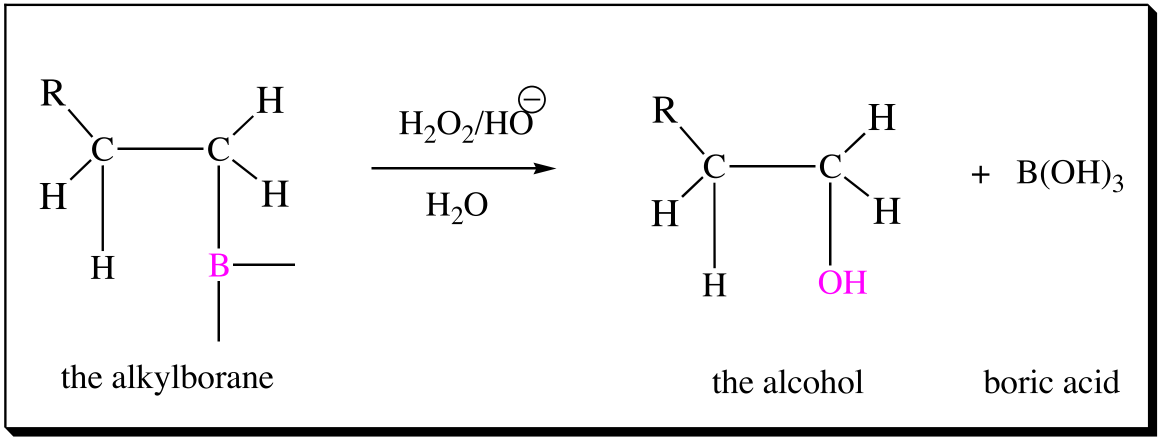
π Complex (donation of alkene π electron density to the vacant boron *p* orbital)

Four-atom concerted transition state (results in syn addition)

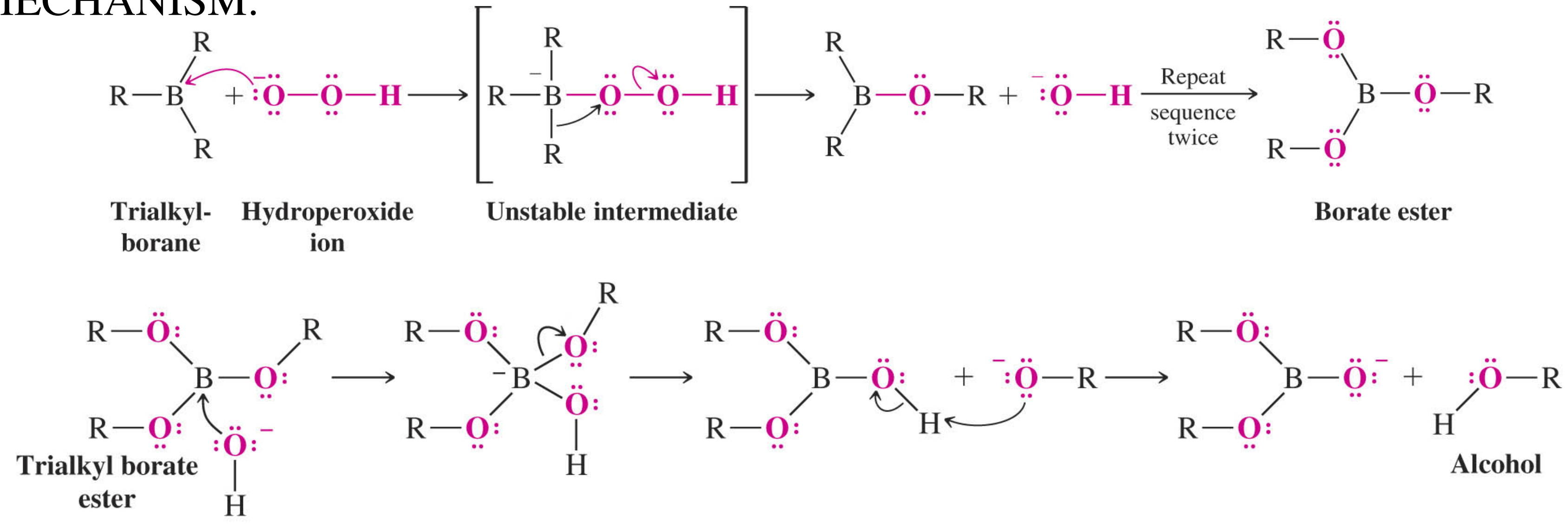
Syn addition of hydrogen and boron

Step 2: Oxidation and Hydrolysis of the Alkylborane

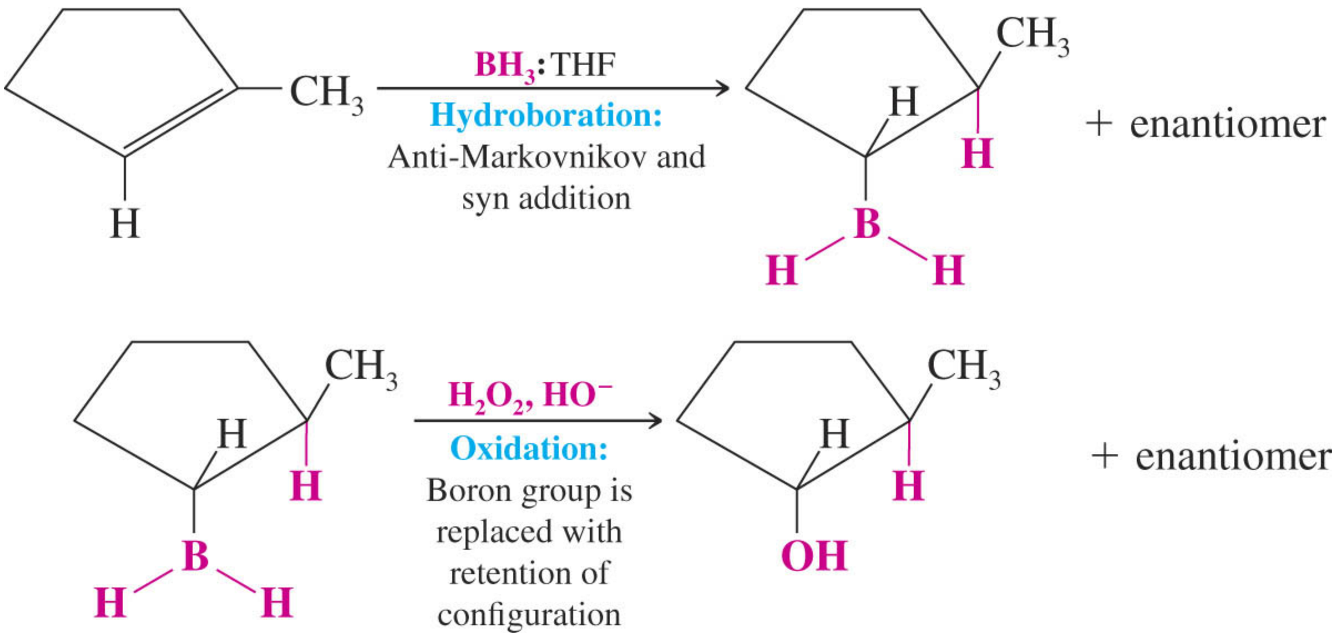
Once the alkylborane is formed by the addition reaction, oxidation by H_2O_2 to the alcohol takes place with retention of stereochemistry at the carbon bonded to boron.



MECHANISM:



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



Hydroboration: Anti-Markovnikov and syn addition

Oxidation: Boron group is replaced with retention of configuration

Comparison of Alkene Hydration Procedures

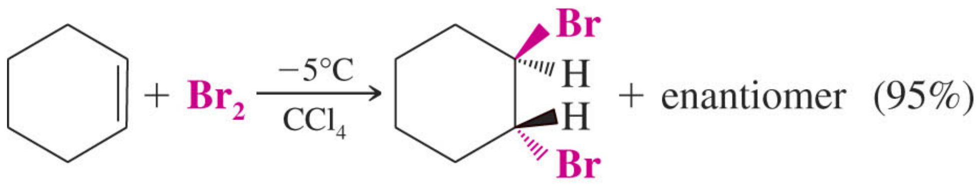
1. **Acid-catalyzed hydrolysis: Markovnikov addition, reversible, possible rearrangements**

2. **Oxymercuration/Demercuration: Markovnikov addition, no rearrangement**

3. **Hydroboration-Oxidation: anti-Markovnikov and *syn* addition, no rearrangement**

Addition of Bromine and Chlorine to Alkenes

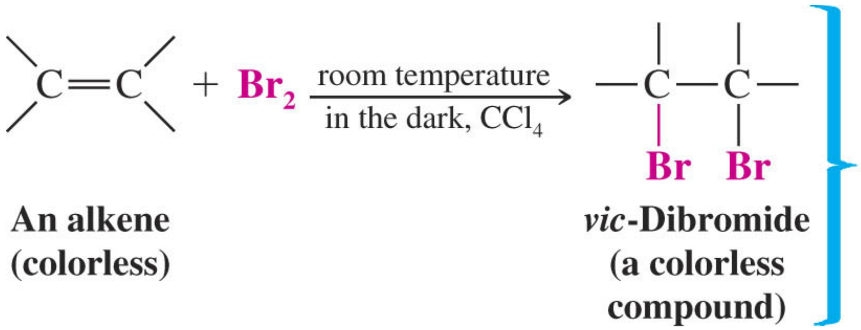
- Alkenes readily accept Br_2 or Cl_2 to form vicinal dihalides



trans-1,2-Dibromocyclohexane
(as a racemic form)

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



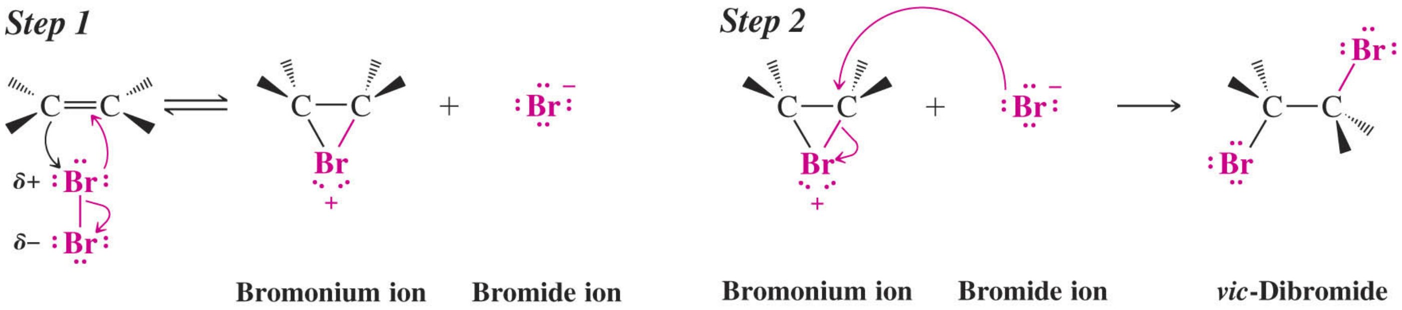
An alkene
(colorless)

vic-Dibromide
(a colorless
compound)

Rapid decolorization
of Br_2/CCl_4 is a
test for alkenes
and alkynes.

Mechanism of Halogen Addition

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



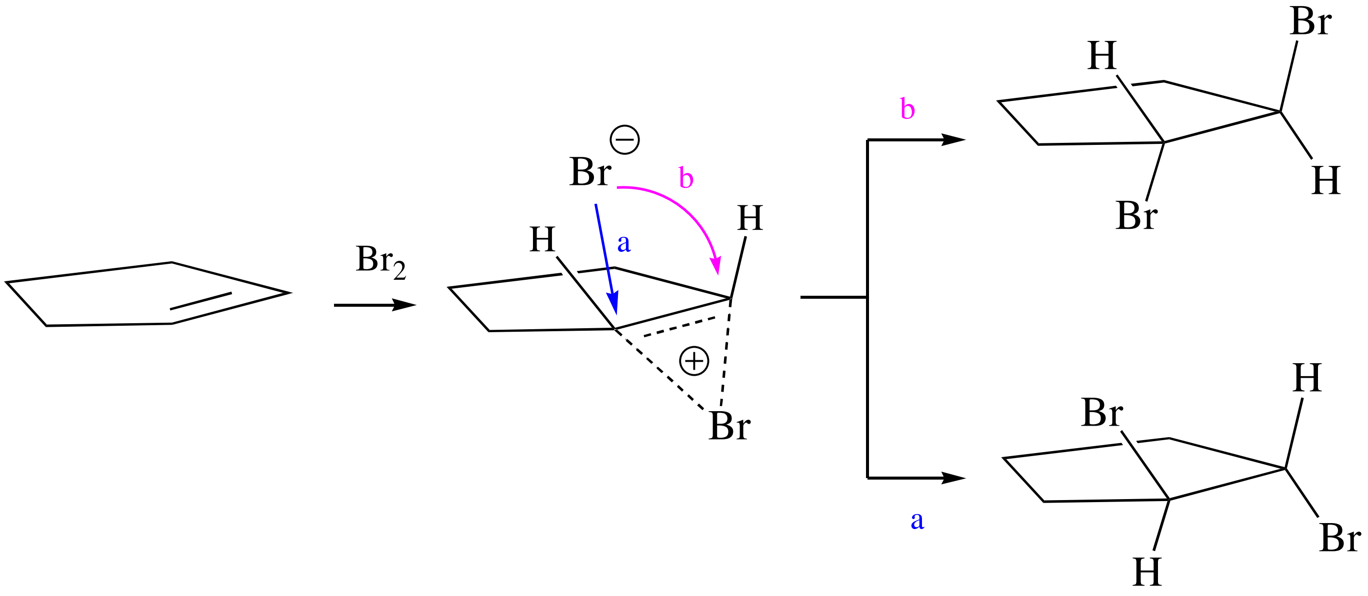
As a bromine molecule approaches an alkene, the electron density of the alkene π bond repels electron density in the closer bromine, polarizing the bromine molecule and making the closer bromine atom electrophilic. The alkene donates a pair of electrons to the closer bromine, causing displacement of the distant bromine atom. As this occurs, the newly bonded bromine atom, due to its size and polarizability, donates an electron pair to the carbon that would otherwise be a carbocation, thereby stabilizing the positive charge by delocalization. The result is a bromonium ion intermediate.

A bromide anion attacks at the back side of one carbon (or the other) of the bromonium ion in an S_N2 reaction, causing the ring to open and resulting in the formation of a *vic*-dibromide.

- **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.**



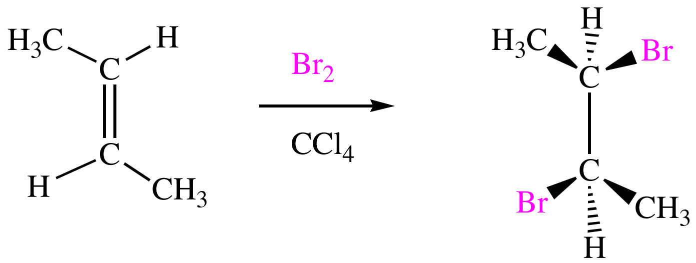
trans-1,2-Dibromocyclopentane

(enantiomers)

Halogenation of Double Bonds is Stereospecific

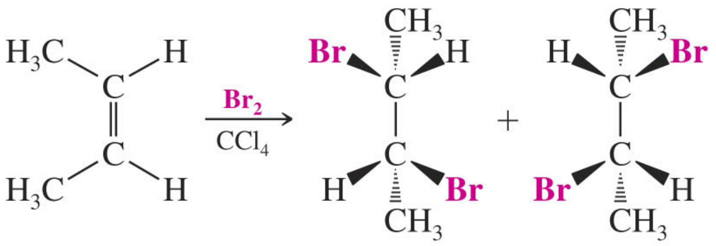
- A reaction is said to be **stereospecific** if a particular stereoisomer of the starting material reacts in such a way that it gives a specific stereoisomer of the product
- Example: *cis*- and *trans*-2-butene give different stereoisomeric products when halogenated

Reaction 1



((2R,3S)-2,3-Dibromobutane
(a *meso* compound)

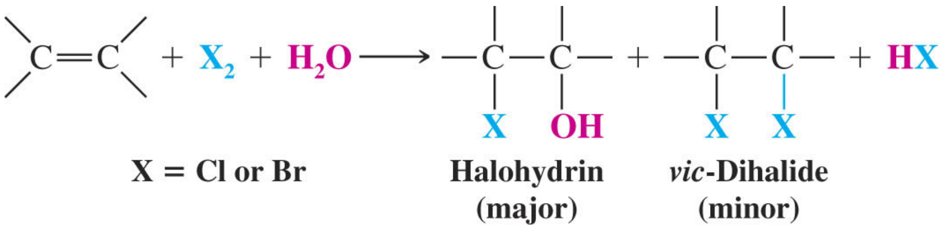
Reaction 2



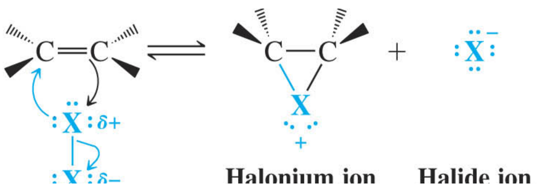
***cis*-2-Butene** **(2*R*,3*R*)** **(2*S*,3*S*)**

Halohydrin Formation

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

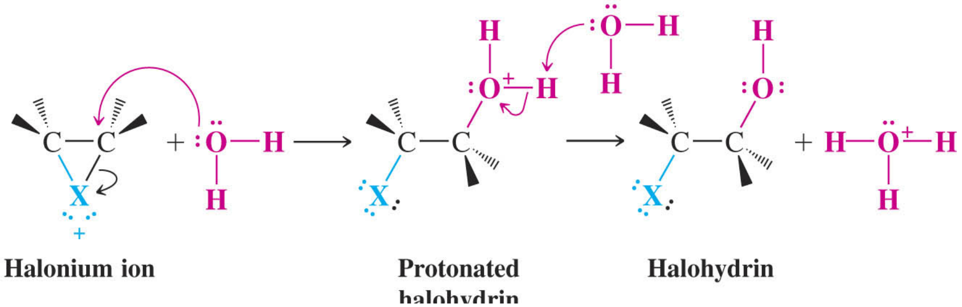


Step 1



Same first step

Steps 2 and 3

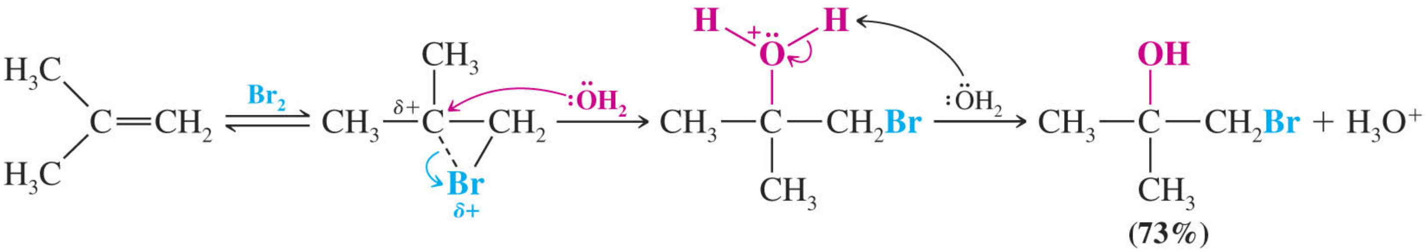


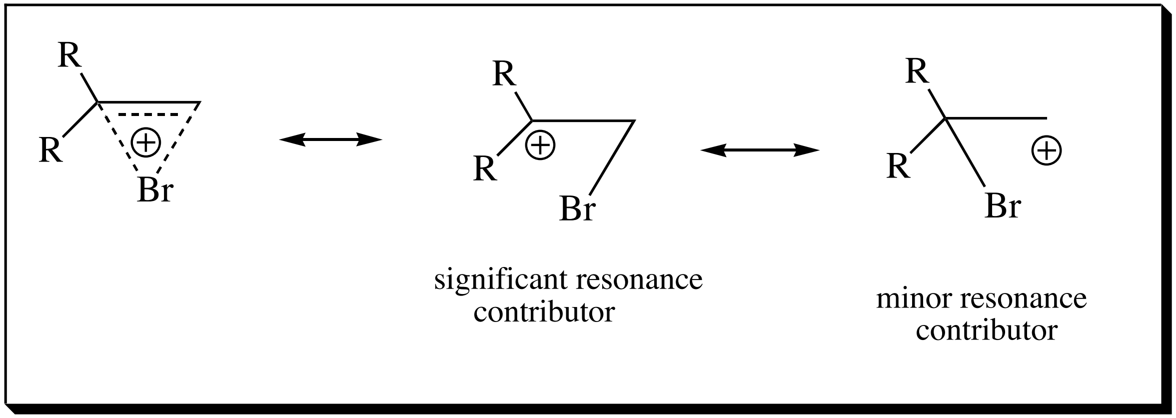
Water competes as nucleophile

Reaction Shows Regioselectivity

- **In unsymmetrical alkenes, the bromonium ion will have some of its δ^+ charge density on the more substituted of the two carbons**
  - **The most substituted carbon can best accommodate δ^+ charge**

- **The water nucleophile will tend to react at the carbon with the more δ^+ charge**

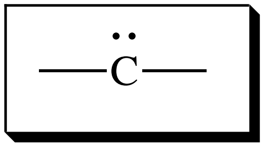




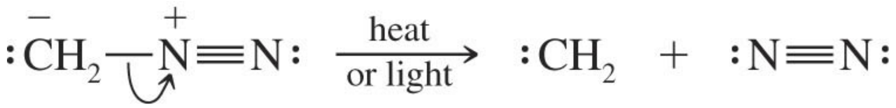
significant resonance contributor

minor resonance contributor

Divalent Carbon Compounds: Carbenes

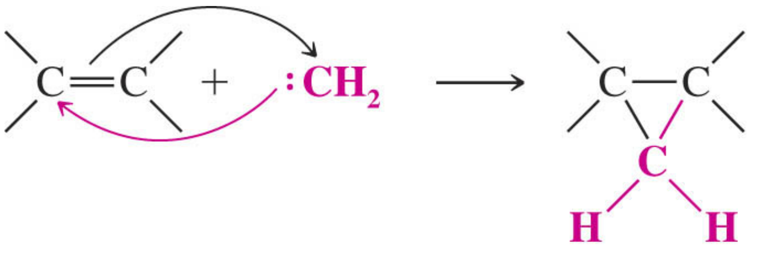


- Carbenes have a divalent, neutral carbon
- Carbenes are highly reactive
- Structure and Reaction of Methylene (CH_2)
  - Methylene can be made by heat- or light-initiated decomposition of diazomethane (CH_2N_2)
    - Loss of a molecule of the stable gas, nitrogen, drives this reaction



Diazomethane Methylene Nitrogen

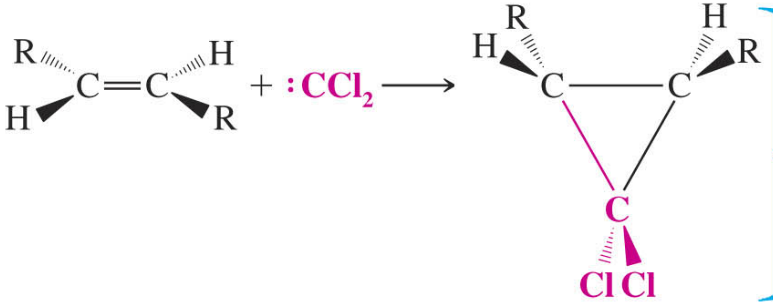
  - Methylene reacts with alkenes to form cyclopropanes



Alkene Methylene Cyclopropane

Reactions of Other Carbenes: Dihalocarbenes

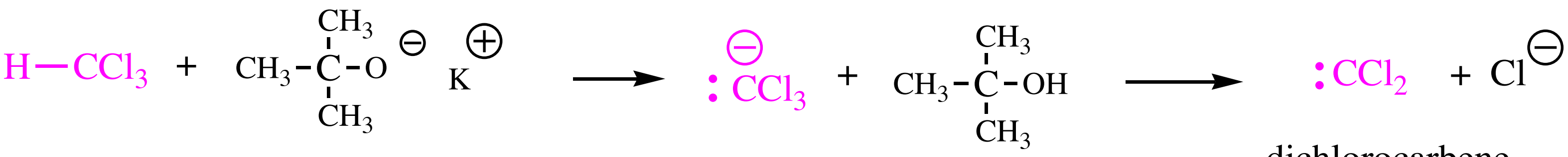
Carbenes add to double bonds in a stereospecific manner



+ enantiomer

trans alkene → *trans* cyclopropane

Dihalocarbenes (:CX_2) are formed by the α-elimination of compounds such as chloroform:



$$H{-}CCl_3 + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}O^{\ominus}\ K^{\oplus} \longrightarrow :\overset{\ominus}{C}Cl_3 + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH \longrightarrow :CCl_2 + Cl^{\ominus}$$

dichlorocarbene

Carbenoids: the Simmon-Smith Reaction

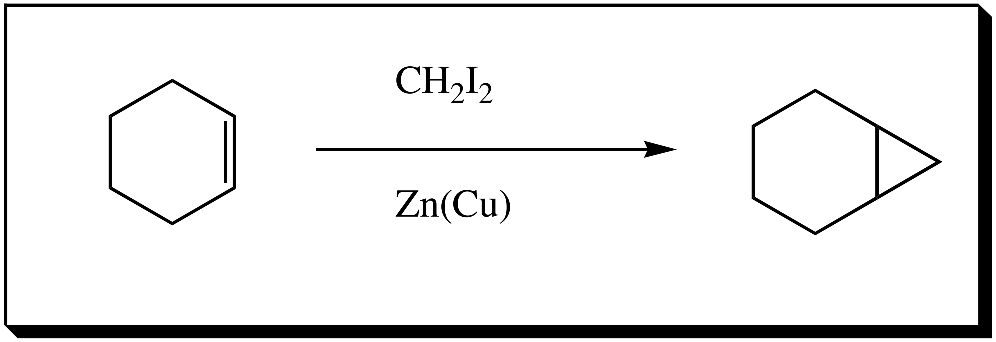
A carbene-like species is formed which then reacts with alkenes

$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$

A carbenoid

Behaves like $:CH_2$

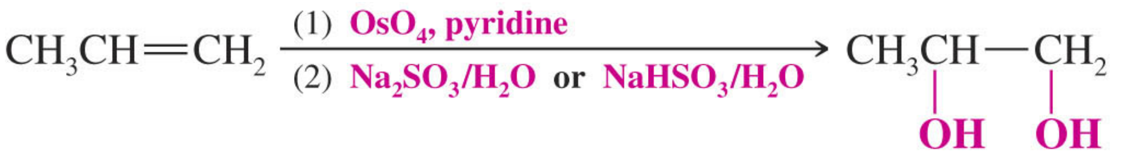
For example:



Oxidations of Alkenes

1. *syn* 1,2-Dihydroxylation

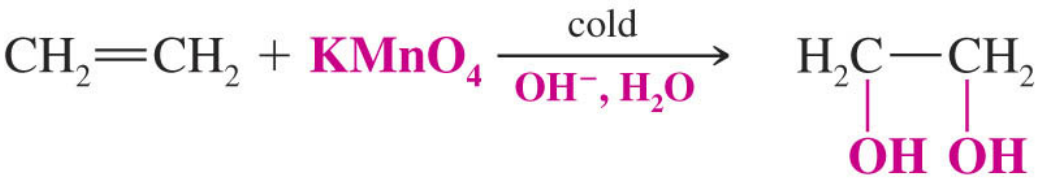
- **Either OsO_4 or $KMnO_4$ will give 1,2-diols (glycols)**



$$CH_3CH{=}CH_2 \xrightarrow[\text{(2) } Na_2SO_3/H_2O \text{ or } NaHSO_3/H_2O]{\text{(1) } OsO_4\text{, pyridine}} CH_3\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$$

Propene

1,2-Propanediol (propylene glycol)



$$CH_2{=}CH_2 + KMnO_4 \xrightarrow[OH^-,\ H_2O]{\text{cold}} \underset{OH}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}}$$

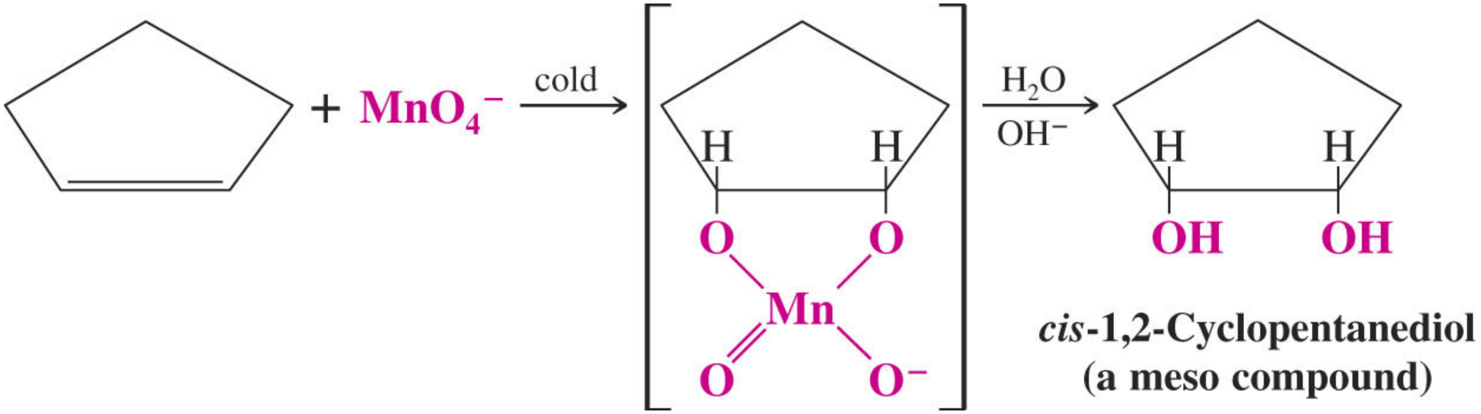
Ethene

1,2-Ethanediol (ethylene glycol)

Mechanism for Syn Hydroxylation of Alkenes

A cyclic intermediate results when an alkene reacts with MnO_4^-

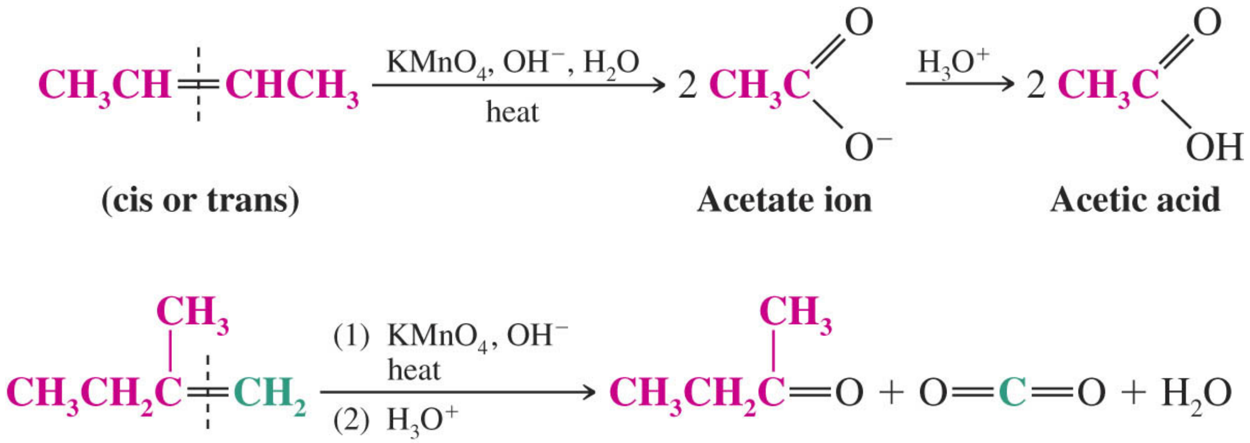
syn-Addition of the oxygens occurs resulting in a *cis*-diol after the oxygen-metal bonds are cleaved by the base.



cis-1,2-Cyclopentanediol
(a meso compound)

Another Oxidation of Alkenes: Oxidative Cleavage

- Reaction of an alkene with hot $KMnO_4$ results in the cleavage of the double bond and the formation of highly oxidized carbons.
    - Unsubstituted carbons become CO_2, monosubstituted carbons become carboxylic acids, and disubstituted carbons become ketones.



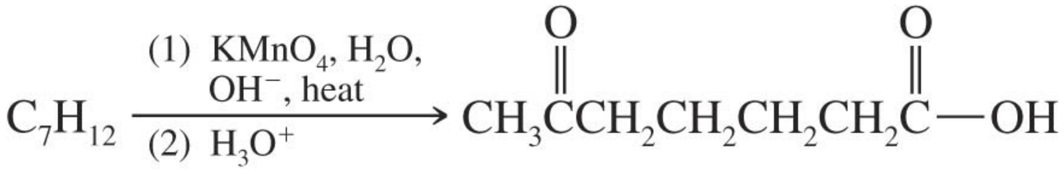
$$CH_3CH=CHCH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-,\ H_2O} 2\ CH_3CO_2^- \xrightarrow{H_3O^+} 2\ CH_3CO_2H$$

$$CH_3CH_2C(CH_3)=CH_2 \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ \text{heat}} CH_3CH_2C(CH_3)=O + O=C=O + H_2O$$

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

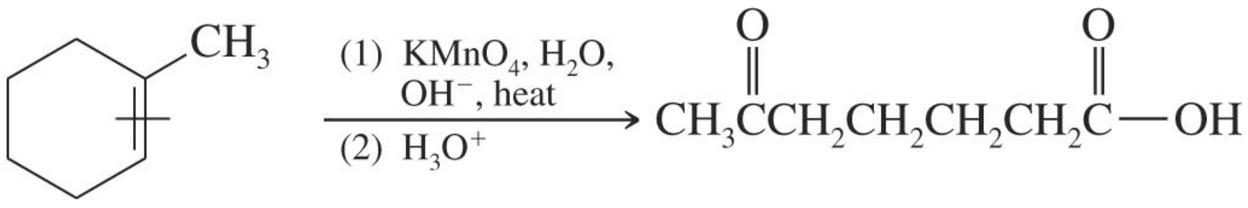
Useful to Identify Location of Double Bonds

- **Example:**
  - ➡ **An unknown alkene with formula C_7H_{12} yields only the following product upon oxidation with hot $KMnO_4$. What is the structure of the alkene?**



$$C_7H_{12} \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ H_2O,\ OH^-,\ \text{heat}} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$

  - ➡ **Answer: Since no carbons are missing and the product contains two carbonyl groups, the alkene double bond must be in a ring.**

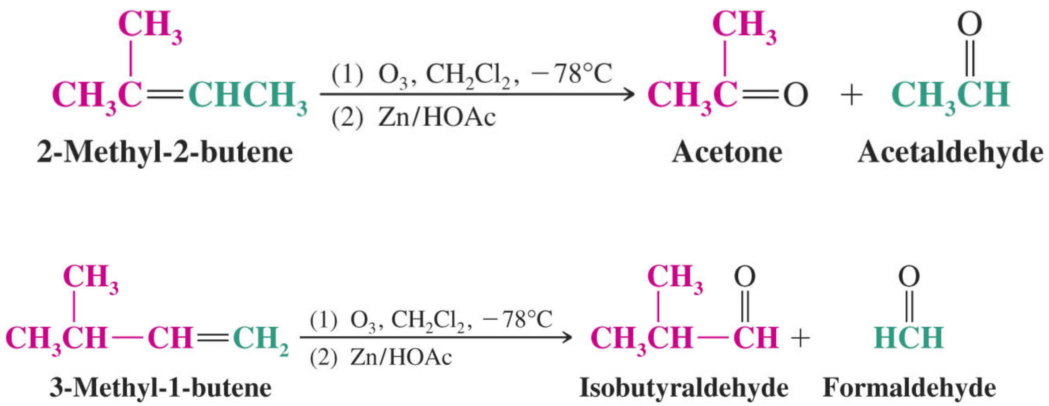


Unknown alkene
(1-methylcyclohexene)

A Third Oxidation of Alkenes: Ozonolysis

Cleavage of alkenes with ozone (O_3) followed by treatment with zinc in acetic acid also leads to highly-oxidized carbons; the products are similar to those formed by the cleavage of alkenes with hot $KMnO_4$.

- **Unsubstituted carbons are oxidized to formaldehyde, Monosubstituted carbons are oxidized to aldehydes and Disubstituted carbons are oxidized to ketones.**



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow[(2)\ Zn/HOAc]{(1)\ O_3,\ CH_2Cl_2,\ -78^\circ C} CH_3\overset{CH_3}{\overset{|}{C}}{=}O + CH_3\overset{O}{\overset{\|}{C}}H$$

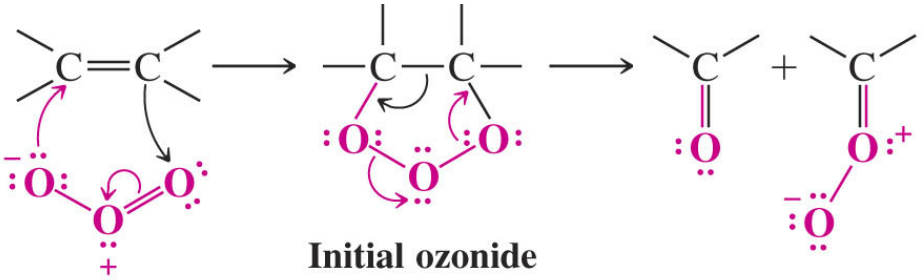
2-Methyl-2-butene Acetone Acetaldehyde

$$CH_3\overset{CH_3}{\overset{|}{C}}H{-}CH{=}CH_2 \xrightarrow[(2)\ Zn/HOAc]{(1)\ O_3,\ CH_2Cl_2,\ -78^\circ C} CH_3\overset{CH_3}{\overset{|}{C}}H{-}\overset{O}{\overset{\|}{C}}H + H\overset{O}{\overset{\|}{C}}H$$

3-Methyl-1-butene Isobutyraldehyde Formaldehyde

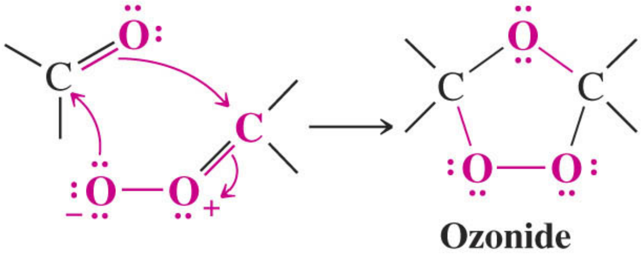
Ozonolysis Mechanism

Ozone adds across the double bond to form an “initial ozonide” which immediately rearranges to a highly-unstable ozonide



Ozone adds to the alkene
to form an initial ozonide.

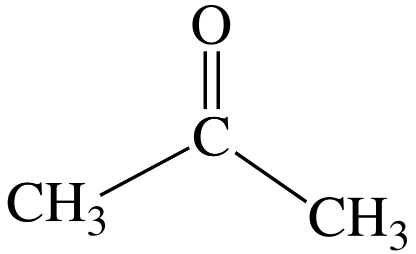
The initial ozonide fragments.



The fragments recombine to form the ozonide.

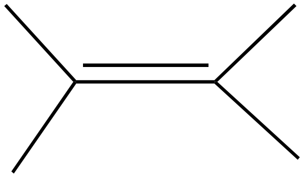
The ozonides then cleave with zinc and acetic acid to give the final carbonyl products (aldehydes and ketones).

What alkene would produce acetone as the only product upon ozonolysis?

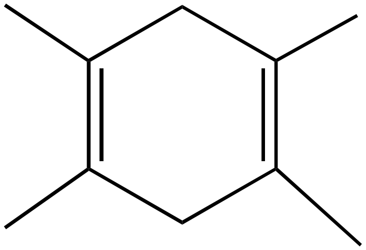


$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

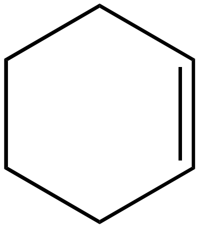
a.



c.



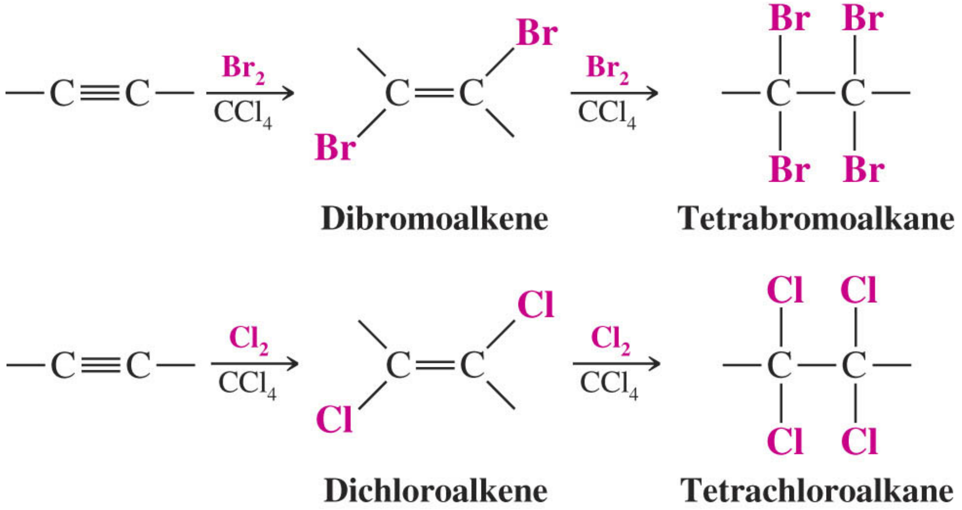
a.



d. none of these

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 used.**
- ♦ **Addition of one equivalent gives the *trans*-dihalide**

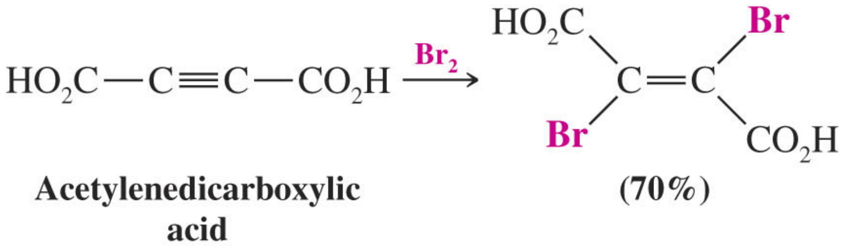


Dibromoalkene

Tetrabromoalkane

Dichloroalkene

Tetrachloroalkane



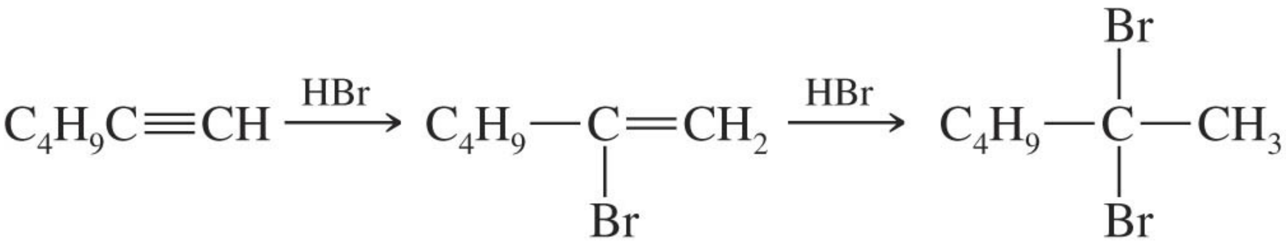
Acetylenedicarboxylic acid

(70%)

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*-dihalides.



$$C_4H_9C\equiv CH \xrightarrow{HBr} C_4H_9-\underset{\underset{\displaystyle Br}{|}}{C}=CH_2 \xrightarrow{HBr} C_4H_9-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$$

2-Bromo-1-hexene

2,2-Dibromohexane

Oxidative Cleavage of Alkynes

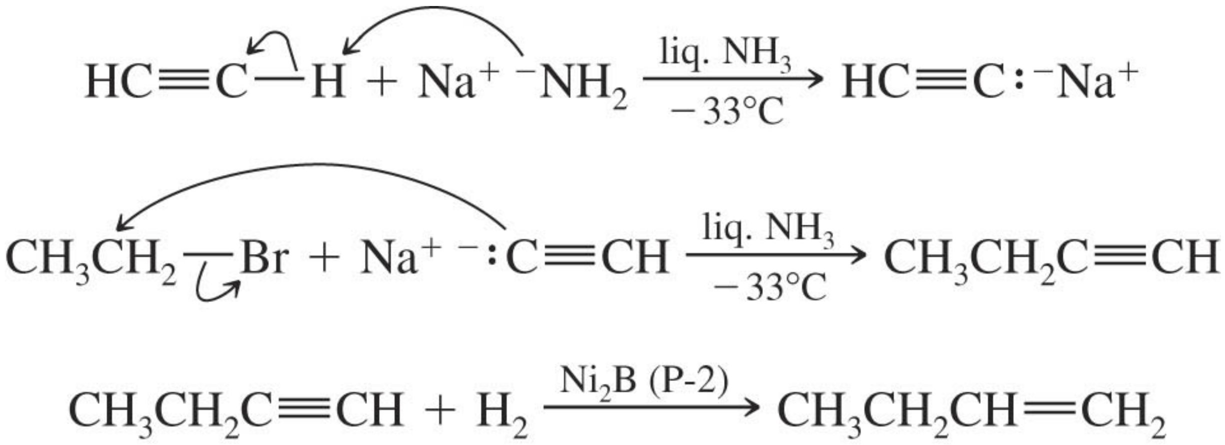
Reaction of alkynes with ozone or basic potassium permanganate both lead to formation of carboxylic acids

$$\mathrm{R{-}C{\equiv}C{-}R'} \xrightarrow[\text{(2) HOAc}]{\text{(1) }\mathrm{O_3}} \mathrm{RCO_2H} + \mathrm{R'CO_2H}$$

$$\mathrm{R{-}C{\equiv}C{-}R'} \xrightarrow[\text{(2) }\mathrm{H_3O^+}]{\text{(1) }\mathrm{KMnO_4,\ OH^-}} \mathrm{RCO_2H} + \mathrm{R'CO_2H}$$

More Practice with Synthesis

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



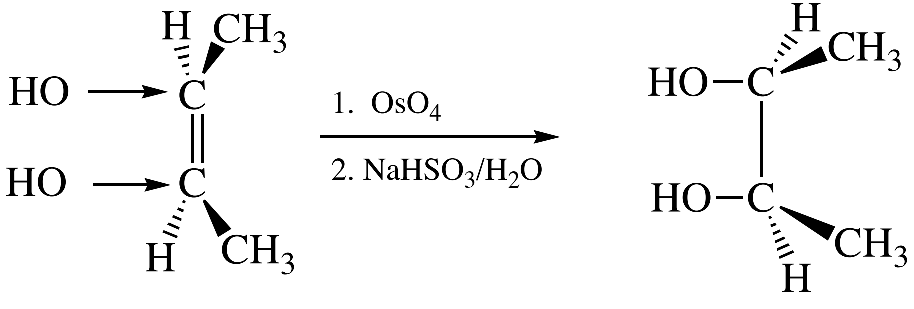
$$\mathrm{HC{\equiv}C{-}H + Na^{+}\ {}^{-}NH_2 \xrightarrow[-33^{\circ}C]{liq.\ NH_3} HC{\equiv}C{:}^{-}Na^{+}}$$

$$\mathrm{CH_3CH_2{-}Br + Na^{+}\ {}^{-}{:}C{\equiv}CH \xrightarrow[-33^{\circ}C]{liq.\ NH_3} CH_3CH_2C{\equiv}CH}$$

$$\mathrm{CH_3CH_2C{\equiv}CH + H_2 \xrightarrow{Ni_2B\ (P\text{-}2)} CH_3CH_2CH{=}CH_2}$$

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

Working backwards, the last step would be:



cis-2-butene

The Complete Synthesis would therefore be:

$$H-C\equiv C-H \xrightarrow[\text{(2) } \mathbf{CH_3I}]{\text{(1) } NaNH_2/\text{liq. } NH_3} \mathbf{CH_3}-C\equiv C-H$$

$$CH_3-C\equiv C-H \xrightarrow[\text{(2) } \mathbf{CH_3I}]{\text{(1) } NaNH_2/\text{liq. } NH_3} CH_3-C\equiv C-\mathbf{CH_3}$$