

Alkenes and Alkynes II

Addition Reactions

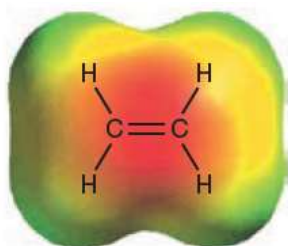
Addition Reactions of Alkenes

- Using **E** for an electrophilic portion of a reagent and **Nu** for a nucleophilic portion.
- **E–Nu** added across the double bond.

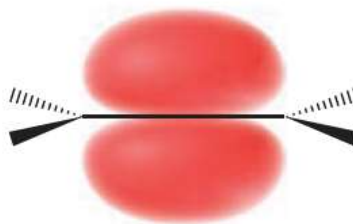


Why Do Addition Reactions Occur?

1. π electrons present an exposed region of electron density in a molecule that is above and below the σ bonding framework.
 - π electrons are therefore more available for reaction than σ electrons.
2. Electrophiles are attracted to the exposed electron density of π bonds.

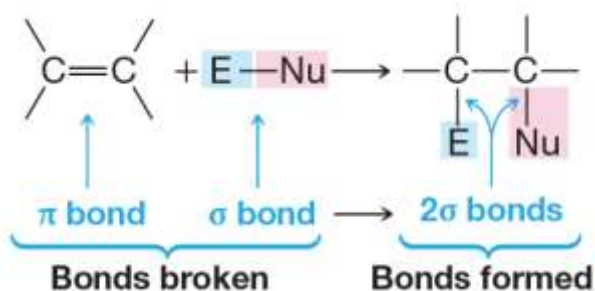


An electrostatic potential map for ethene shows the higher density of negative charge in the region of the π bond.

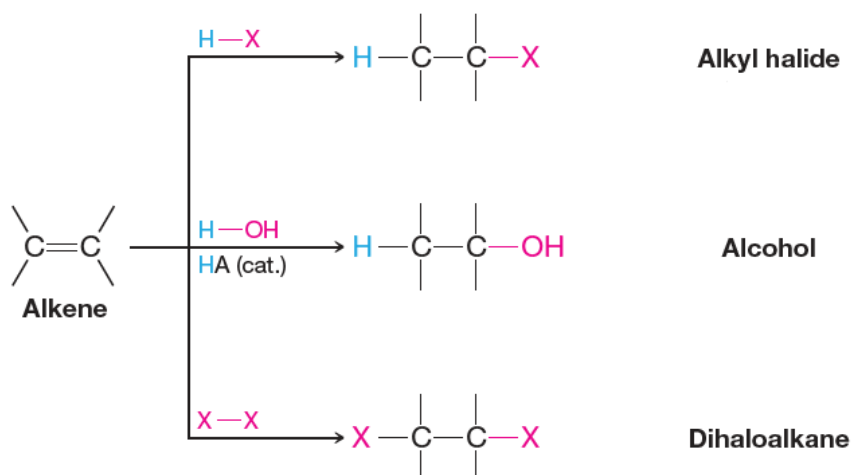


The electron pair of the π bond is distributed throughout both lobes of the π molecular orbital.

3. π electrons are in higher energy orbitals than σ electrons, and π bonds are weaker than σ bonds. Thus, reactions that convert π bonds to σ bonds are usually energetically favorable.
 - In an alkene addition reaction, one π bond and one σ bond are converted to two σ bonds, lowering the energy of the system.



- Some specialized reagents that also undergo addition reactions with alkenes.



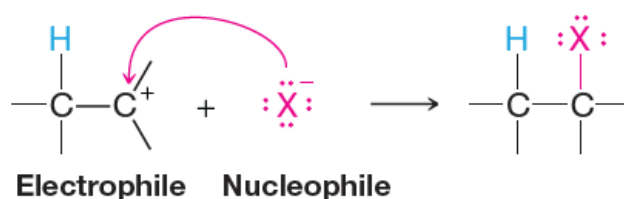
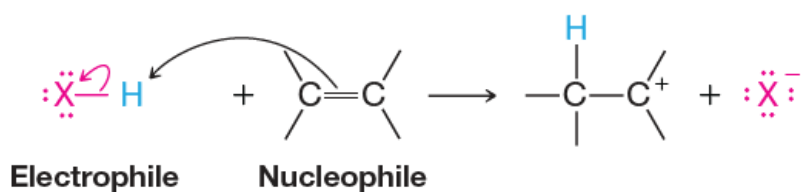
Electrophilic Addition to an Alkene

Electrophiles

- Seek electrons.
- They are attracted to sites of negative charge.
- Electrophiles include
 - Proton donors: Brønsted–Lowry acids
 - Neutral reagents: bromine (because it can be polarized so that one end is positive)
 - Lewis acids: BH_3 , BF_3 , and AlCl_3 .
 - Metal ions that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+})

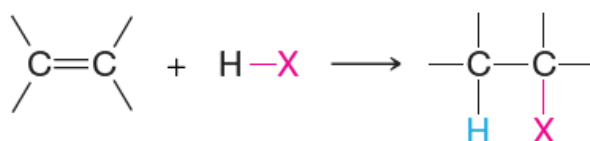
Nucleophiles

- Electron donors.
- They are attracted to sites of positive charge.
- Nucleophiles include halide ions and water molecules.

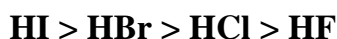


Electrophilic Addition of Hydrogen Halides to Alkenes

- Hydrogen halides (HI, HBr, HCl, and HF) added to the double bond of alkenes.

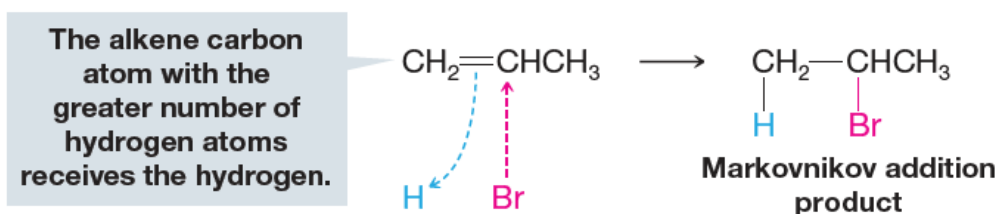


- The order of reactivity of the hydrogen halides in alkene addition is

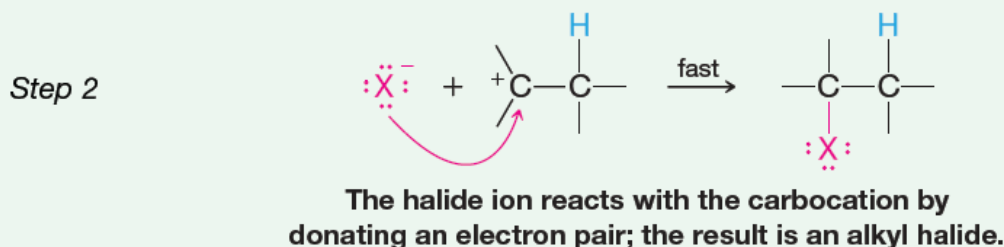
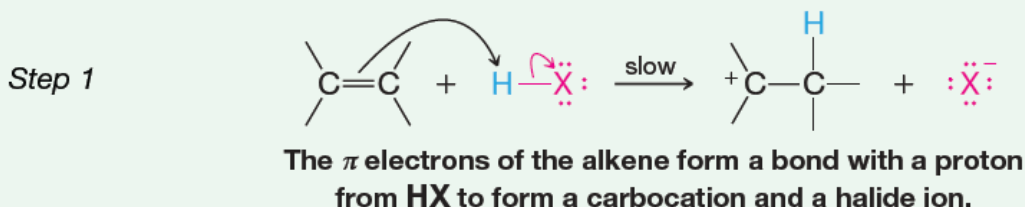


Markovnikov's Rule

- **Markovnikov's rule:** is to say that *in the addition of HX to an alkene, the hydrogen atom adds to the carbon atom of the double bond that already has the greater number of hydrogen atoms.*

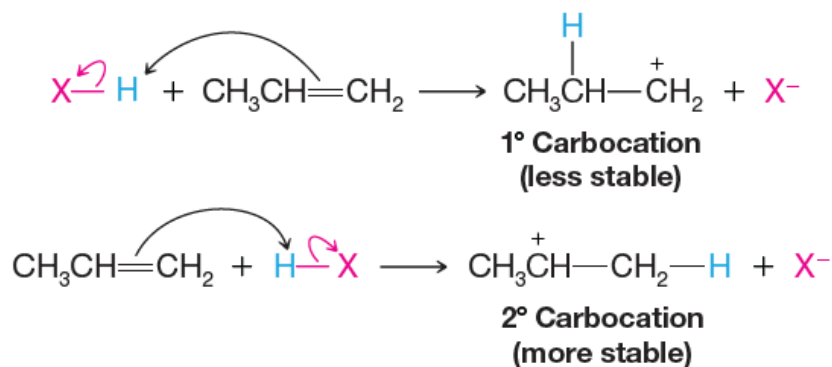


A Mechanism for the Reaction

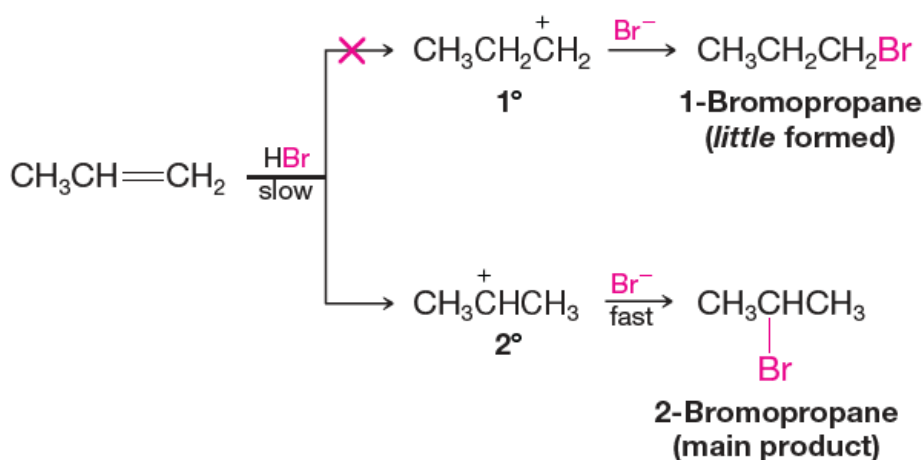


Theoretical Explanation of Markovnikov's Rule

- If the alkene that undergoes addition of a hydrogen halide is an unsymmetrical alkene such as propene, then step 1 could conceivably lead to two different carbocations:



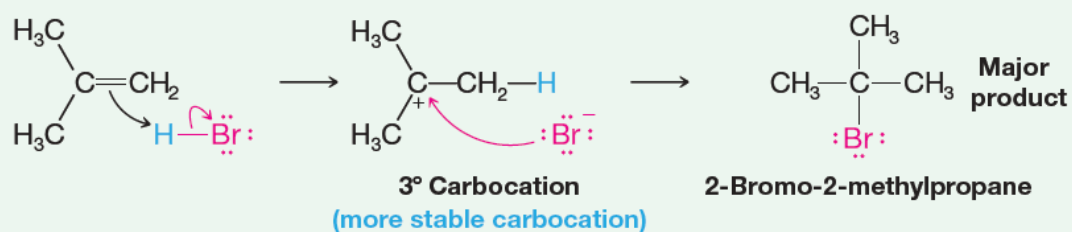
- The secondary carbocation is *more stable*, and it is the greater stability of the secondary carbocation that accounts for the correct prediction of the overall addition by Markovnikov's rule.



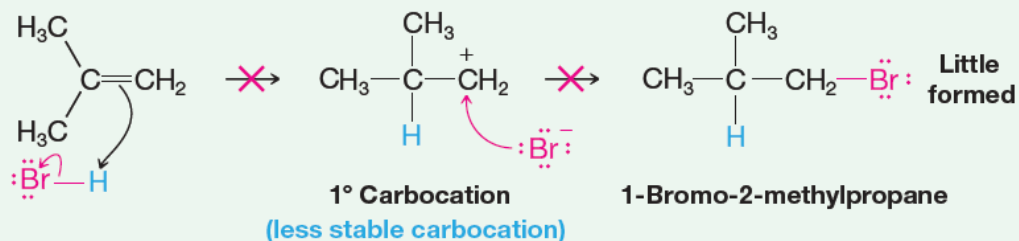
- The more stable carbocation predominates **because** it is formed faster.

A Mechanism for the Reaction: Addition of HBr to 2-Methylpropene

This reaction takes place:

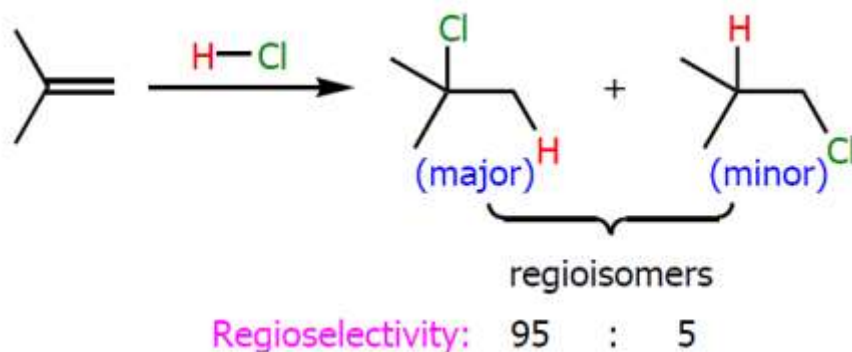


This reaction does *not occur* to any appreciable extent:



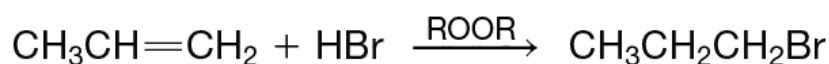
Regioselective Reactions

- A **regioselective reaction**: is one that can potentially yield two or more constitutional isomers but that actually produces only one (or a predominance of one).



Anti-Markovnikov Addition of HBr in the Presence of Peroxides

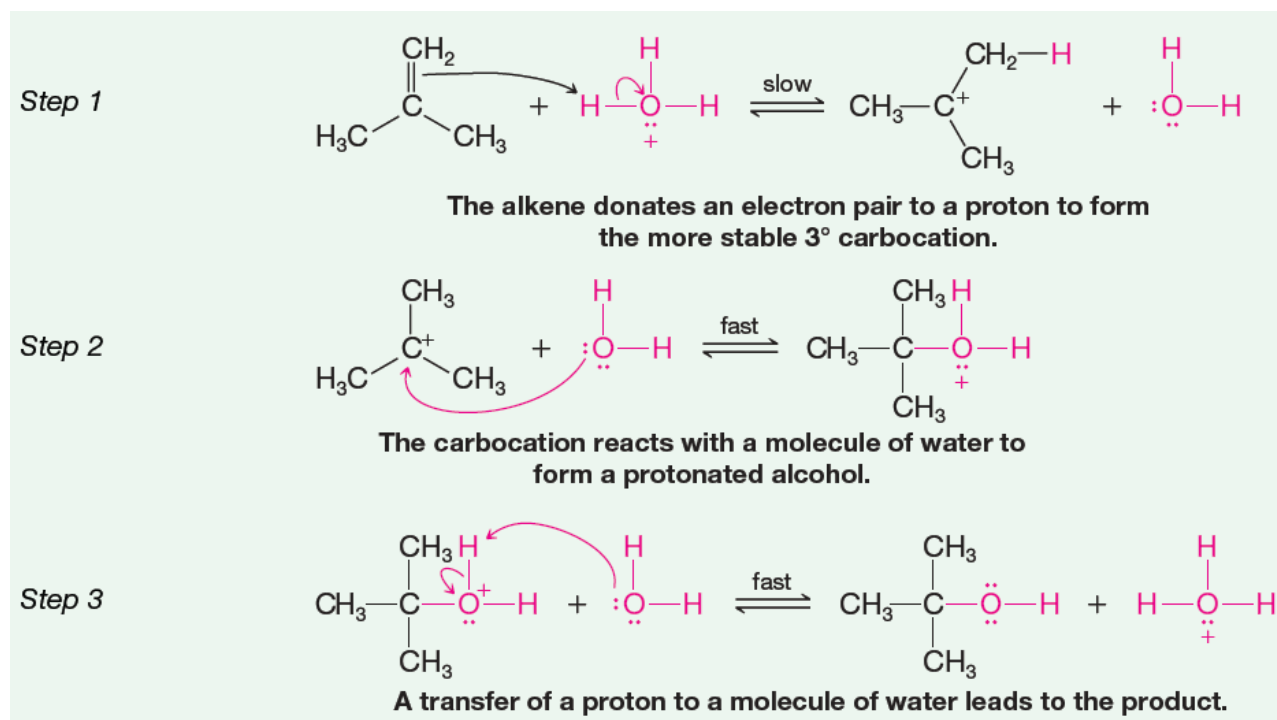
- **Anti-Markovnikov addition**: stated that when alkenes are treated with HBr in the presence of peroxides, the hydrogen atom becomes attached to the carbon atom with the fewer hydrogen atoms.
- This anti-Markovnikov addition occurs *only when HBr is used in the presence of peroxides* and does not occur significantly with HF, HCl, and HI even when peroxides are present.



Stereochemistry of the Ionic Addition to an Alkene

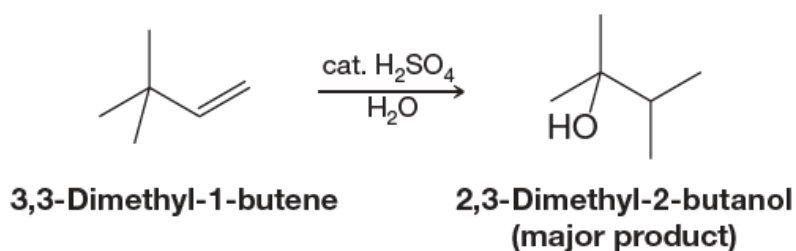
- The product can exist as a pair of enantiomers.
- The carbocation that is formed in the first step of the addition is trigonal planar and is *achiral*.
- When the halide ion reacts with this achiral carbocation in the second step, *reaction is equally likely at either face*.
- The reactions leading to the two enantiomers occur at the same rate, and produced in equal amounts *as a racemic mixture*.

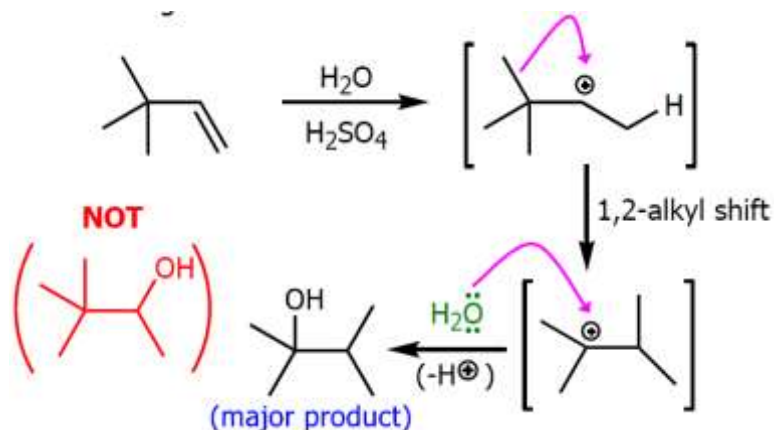
A Mechanism for the Reaction



Rearrangements

- Rearrangement can occur with certain carbocations.
- Because the reaction involves the formation of a carbocation in the first step, the carbocation formed initially invariably rearranges to a more stable one.
- **For example:** the formation of 2,3-dimethyl-2-butanol as the major product when 3,3-dimethyl-1-butene is hydrated.

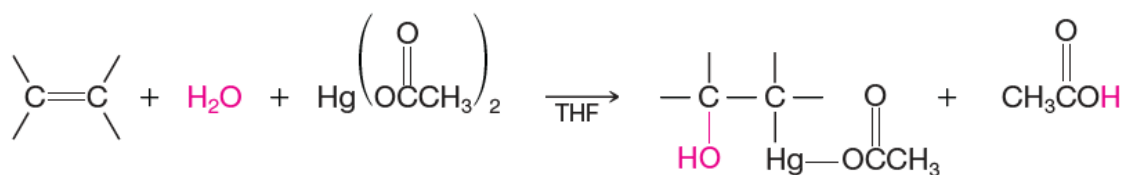




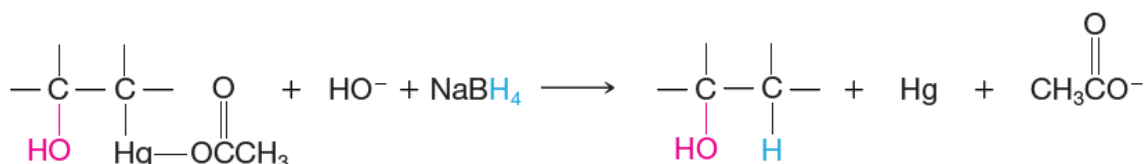
Alcohols from Alkenes through Oxymercuration-Demercuration: Markovnikov Addition

- **Oxymercuration–demercuration:** is a two-step method for synthesizing alcohols from alkenes that avoids rearrangement.
- Alkenes react with mercuric acetate in a mixture of tetrahydrofuran (THF) and water to produce (hydroxyalkyl)mercury compounds.
 - These (hydroxyalkyl)mercury compounds can be reduced to alcohols with sodium borohydride.
 - In the first step, **oxymercuration:** water and mercuric acetate add to the double bond.
 - In the second step, **demercuration:** sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen.

Step 1: Oxymercuration

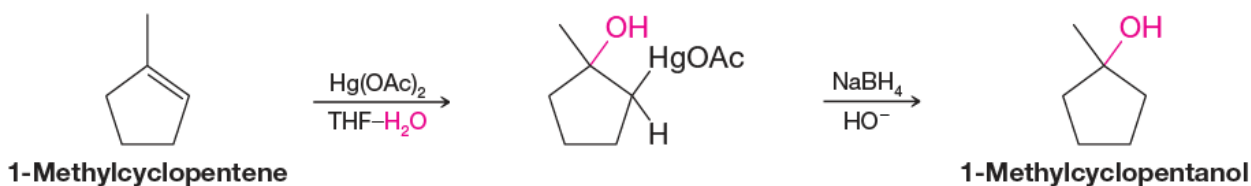
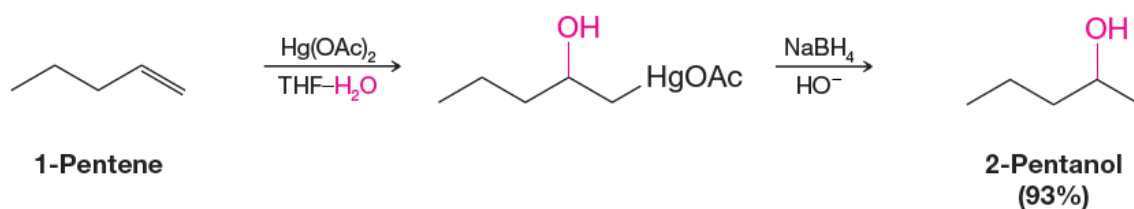
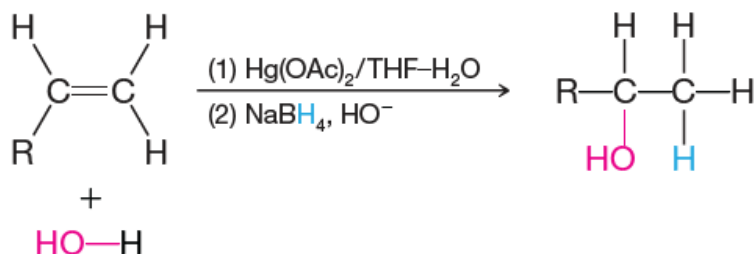


Step 2: Demercuration



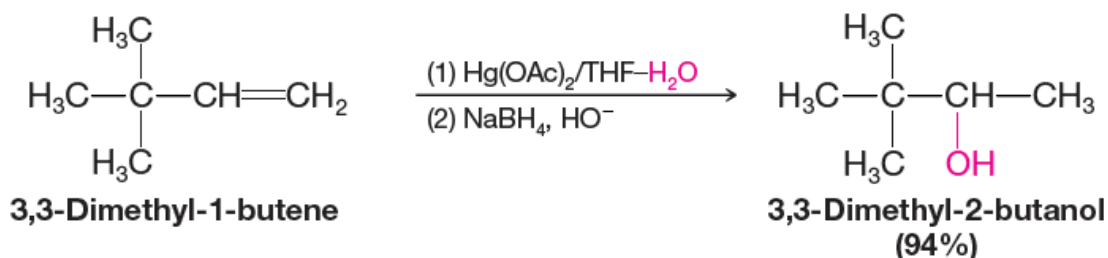
Regioselectivity of Oxymercuration-Demercuration

- Oxymercuration–demercuration is highly regioselective.
- The reactions follow **Markovnikov's rule**.



Rearrangements Seldom Occur in Oxymercuration-Demercuration

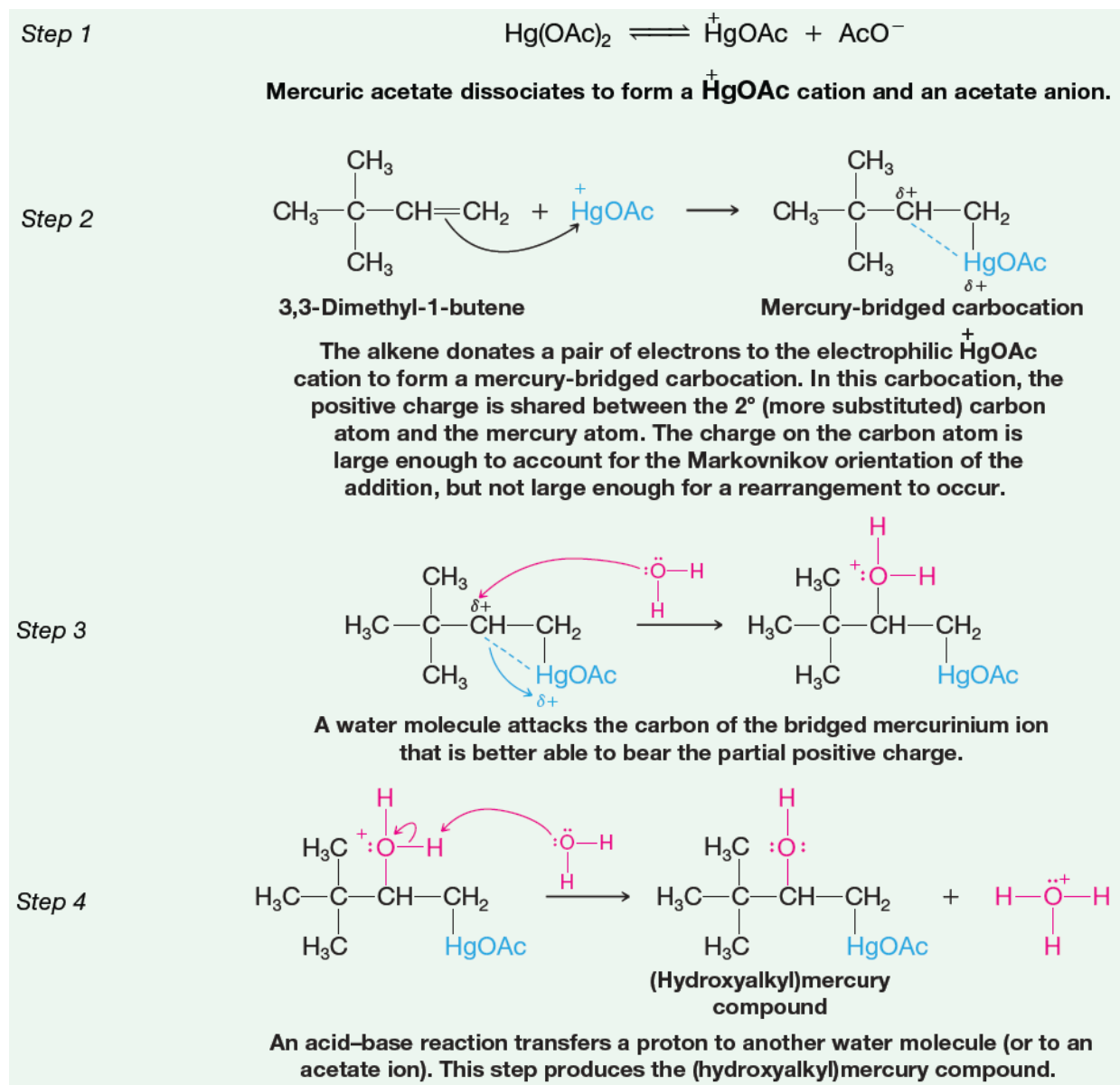
- Rearrangements of the carbon skeleton seldom occur in oxymercuration-demercuration.



Mechanism of Oxymercuration

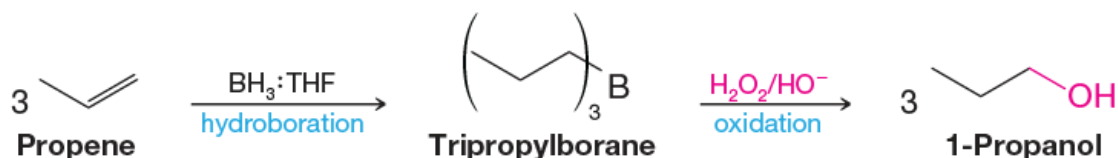
A Mechanism for the Reaction

3,3-dimethyl-1-butene



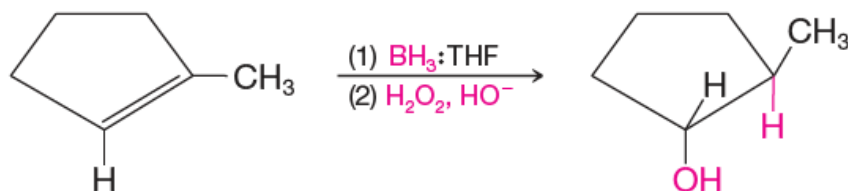
Alcohols from Alkenes through Hydroboration-Oxidation: Anti-Markovnikov Syn Hydration

- **Anti-Markovnikov hydration** of a double bond can be achieved through the use of diborane (B_2H_6) or a solution of borane in tetrahydrofuran ($\text{BH}_3:\text{THF}$).
 - **For example:** the hydroboration-oxidation of propene



➤ Hydroboration-oxidation takes place with **syn** stereochemistry, as well as anti-Markovnikov regiochemistry.

- **For example:** the hydroboration–oxidation of 1-methylcyclopentene



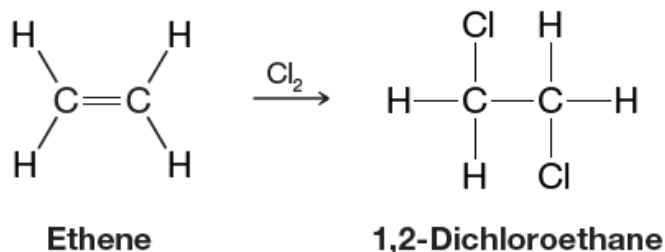
Summary of Methods for Converting an Alkene to an Alcohol

| Reaction | Conditions | Regiochemistry | Stereochemistry | Occurrence of Rearrangements |
|------------------------------|--|---------------------------|--|------------------------------|
| Acid-catalyzed hydration | cat. HA, H ₂ O | Markovnikov addition | Not controlled | Frequent |
| Oxymercuration–demercuration | (1) Hg(OAc) ₂ , THF–H ₂ O (2) NaBH ₄ , HO [−] | Markovnikov addition | Not controlled | Seldom |
| Hydroboration–oxidation | (1) BH ₃ :THF (2) H ₂ O ₂ , HO [−] | Anti-Markovnikov addition | Stereospecific: syn addition of –h and –oh | Seldom |

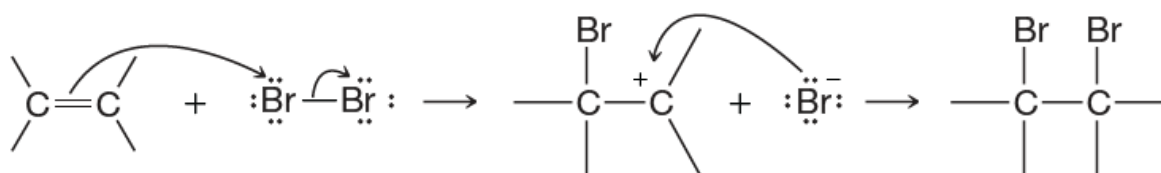
Electrophilic Addition of Bromine and Chlorine to Alkenes

➤ Alkenes react rapidly with bromine and chlorine in nonnucleophilic solvents to form **vicinal dihalides**.

- **For example:** the addition of chlorine to ethene.

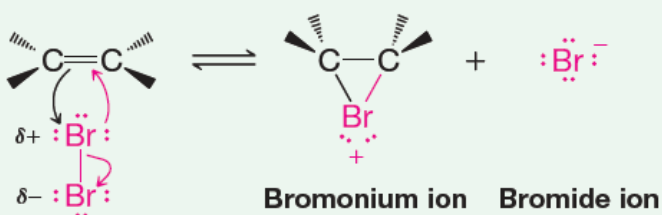


Mechanism of Halogen Addition



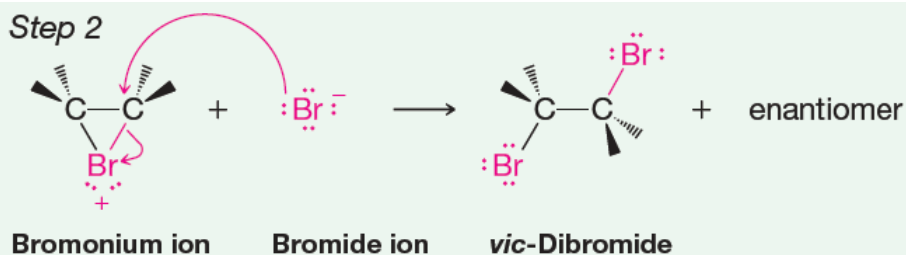
A Mechanism for the Reaction

Step 1



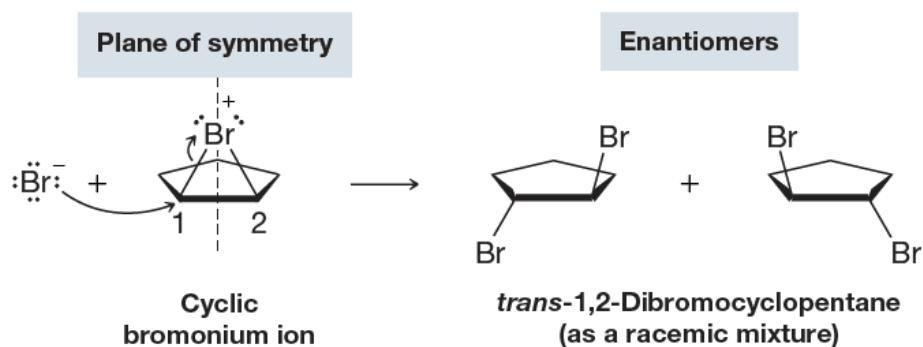
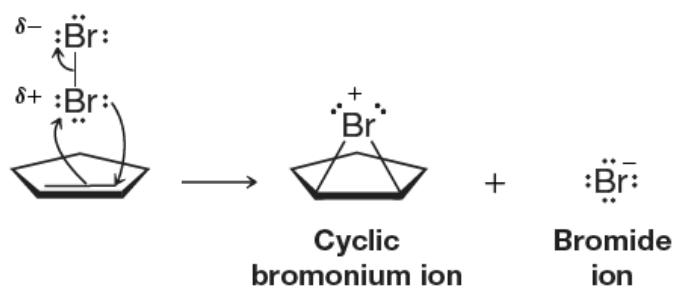
As a bromine molecule approaches an alkene, the electron density of the alkene π bond repels electron density in the closer bromine, polarizing the bromine molecule and making the closer bromine atom electrophilic. The alkene donates a pair of electrons to the closer bromine, causing displacement of 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 bridged bromonium ion intermediate.

Step 2



A bromide anion attacks at the back side of one carbon (or the other) of the bromonium ion in an $\text{S}_{\text{N}}2$ reaction, causing the ring to open and resulting in the formation of a vic-dibromide.

➤ **Example:** the addition of bromine to cyclopentene



- Attack at either carbon of the cyclopentene bromonium ion is equally likely **because** the cyclic bromonium ion is symmetric.

