Chapter 8
Alkenes and Alkynes II: Addition Reactions
Introduction: Additions to Alkenes

Generally the reaction is exothermic because one $\pi$ and one $\sigma$ bond are converted to two $\sigma$ bonds

$\pi$ bond \quad \sigma$ bond \quad $2\sigma$ bonds

Bonds broken \quad \text{Bonds formed}

The $\pi$ electrons of the double bond are loosely held and are a source of electron density, i.e. they are nucleophilic

Alkenes 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 changes from a nucleophile in the first step to an electrophile in the second.
Addition of Hydrogen Halides to Alkenes: Markovnikov’s Rule

- Addition of HBr to propene occurs to give 2-bromopropane as the major product

\[
\text{CH}_2\text{=CHCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CHCH}_3 \quad \text{(little BrCH}_2\text{CH}_2\text{CH}_3) \\
\text{Br} \\
2\text{-Bromopropane} \quad 1\text{-Bromopropane}
\]

- 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

**Step 1**

\[ \text{C} = \text{C} + \text{H} + \text{HX} \rightarrow \text{C} = \text{C} + \text{HX}^- \]

The π electrons of the alkene form a bond with a proton from HX to form a carbocation and a halide ion.

**Step 2**

\[ \text{HX}^- + \text{C} = \text{C} \rightarrow \text{C} = \text{C} + \text{HX}^- \]

The halide ion reacts with the carbocation by donating an electron pair; the result is an alkyl halide.

The reaction has a highly endergonic first step (rate determining) and a highly exergonic second step.
- **Theoretical Explanation of Markovnikov’s Rule**
  - The product with the more stable carbocation intermediate predominates
  - The most stable carbocation is formed fastest because it has a lower $\Delta G^+$
    - The 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

 Addition of HBr to butene yields a chiral molecule
 A racemic mixture is produced because the intermediate carbocation is achiral

1-Butene donates a pair of electrons to the proton of HX to form an achiral carbocation.

The carbocation reacts with the halide ion at equal rates by path (a) or (b) to form the enantiomers as a racemate.
Addition of Sulfuric Acid to Alkenes

Addition of concentrated sulfuric acid to alkenes leads to alkyl hydrogen sulfates which are soluble in the acid. The addition follows Markovnikov’s rule.

The sulfate can be hydrolyzed by heating with water. The net result is Markovnikov addition of water to an alkene.

\[
\text{CH}_3\text{CH}═\text{CH}_2 \xrightarrow{\text{cold} \ H_2\text{SO}_4} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{H}_2\text{O}, \text{heat}} \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{SO}_4
\]
Addition of Water to Alkenes: Acid-Catalyzed Hydration

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

\[
\text{CH}_3\text{CH}=\text{CH}_2 + \text{HOH} \xrightleftharpoons{\text{H}_2\text{O}^+ \atop 25^\circ\text{C}} \text{CH}_3\text{CH}({\text{CH}_3})\text{CH}_2\text{OH}
\]

2-Methylpropene (isobutylene) 

\textit{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 hydration of alkenes and the dehydration of alcohols are simply reverse reactions of one other.

- The reaction is governed by the position of all the equilibria.
- Hydration is favored by addition of a small amount of acid and a large amount of water.
- Dehydration is favored by concentrated acid with very little water present (removal of water produced also helps favor dehydration).

Carbocation rearrangements can occur.

Chapter 8
Alcohols from Alkenes Through Oxymercuration-Demercuration: Markovnikov Addition

The procedure gives high yields of alcohols and avoids rearrangements

**Step 1: Oxymercuration**

\[
\text{C} = \text{C} + \text{H}_2\text{O} + \text{Hg}(\text{OCCH}_3)_2 \xrightarrow{\text{THF}} \text{C} - \text{C} - \text{O} + \text{CH}_3\text{COH}
\]

**Step 2: Demercuration**

\[
\text{C} - \text{C} - \text{O} + \text{OH}^- + \text{NaBH}_4 \xrightarrow{} \text{C} - \text{C} - \text{H} + \text{Hg} + \text{CH}_3\text{CO}^-
\]

The reaction shows Markovnikov selectivity

\[
\text{CH}_3(\text{CH}_2)_2\text{CH} = \text{CH}_2 \xrightarrow{\text{Hg(OAc)}_2, \text{THF-H}_2\text{O}} \text{CH}_3(\text{CH}_2)_2\text{CH} - \text{CH}_2 \xrightarrow{\text{NaBH}_4, \text{OH}^- (1\text{ h})} \text{CH}_3(\text{CH}_2)_2\text{CHCH}_3 + \text{Hg}
\]

1-Pentene

\[
\text{CH}_3\text{C} - \text{CH} = \text{CH}_2 \xrightarrow{(1) \text{Hg(OAc)}_2/\text{THF-H}_2\text{O}, (2) \text{NaBH}_4, \text{OH}^-} \text{CH}_3\text{C} - \text{CHCH}_3
\]

3,3-Dimethyl-1-butene

2-Pentanol (93%)

3,3-Dimethyl-2-butanol (94%)
The mechanism involves formation of a bridged mercurinium ion

**Step 1**

\[ \text{Hg(OAc)}_2 \rightarrow \text{HgOAc} + \text{OAc}^- \]

Mercuric acetate dissociates to form a \( \text{HgOAc} \) cation and an acetate anion.

**Step 2**

3,3-Dimethyl-1-butene  
Mercury-bridged carbocation

The alkene donates a pair of electrons to the electrophilic \( \text{HgOAc}^+ \) cation to form a mercury-bridged carbocation. In this carboxication, the positive charge is shared between the 2° (more substituted) carbon atom and the mercury atom. The charge on the carbon atom is large enough to account for the Markovnikov orientation of the addition, but not large enough for a rearrangement to occur.

**Step 3**

A water molecule attacks the carbon of the bridged mercurinium ion that is better able to bear the partial positive charge.

**Step 4**

An acid–base reaction transfers a proton to another water molecule (or to an acetate ion). This step produces the (hydroxyalkyl)mercury compound.
Alcohols from Alkenes through Hydroboration-Oxidation: Anti-Markovnikov Syn Hydration

- The reaction leads to syn and anti-Markovnikov addition of water to alkenes

\[
\text{(1) BH}_3 \cdot \text{THF} \\
\text{(2) H}_2\text{O}_2, \text{HO}^-
\]

Hydroboration: Synthesis of Alkylboranes

- The elements of hydrogen and boron are added across the double bond

In practice, a borane complex with the solvent tetrahydrofuran (THF) is often used

\[
\text{C} = \text{C} + \text{H}\text{B} \xrightarrow{\text{hydroboration}} \text{C} - \text{C} \\
\text{Alkene} \quad \text{Boron hydride} \quad \text{Alkylborane}
\]

\[
\text{B}_2\text{H}_6 + 2 \text{O} \xrightarrow{\text{THF}} 2 \text{H} - \text{B} - \text{O}^+ \\
\text{Diborane} \quad \text{THF (tetrahydrofuran)} \quad \text{BH}_3 \cdot \text{THF}
\]
- **Mechanism of Hydroboration**

  ➔ Boron hydride adds successively to three molecules of alkene

  ![Mechanism of Hydroboration Diagram]

  ➔ Boron becomes attached to the least substituted carbon of the double bond

  - The bulky boron group can approach the least sterically hindered carbon more easily
  - This orientation also allows a $\delta^+$ charge in the transition state to reside at the most substituted carbon
  - This orientation leads to anti-Markovnikov product

  ➔ The boron and hydride add with syn stereochemistry

  ![Addition of Boron and Hydride Diagram]
Addition takes place through the initial formation of a π complex, which changes into a cyclic four-atom transition state with the boron adding to the less hindered carbon atom. The dashed bonds in the transition state represent bonds that are partially formed or partially broken. The transition state results in syn addition of the hydrogen and boron group, leading to an alkylborane. The other B–H bonds of the alkylborane can undergo similar additions, leading finally to a trialkylborane.

An orbital view of hydroboration
**Oxidation and Hydrolysis of Alkylboranes**

- Oxidation and hydrolysis to the alcohol takes place with retention of stereochemistry at the carbon bonded to boron.

![Chemical reaction diagram]

- The boron atom accepts an electron pair from the hydroperoxide ion to form an unstable intermediate.
- An alkyl group migrates from boron to the adjacent oxygen atom as a hydroxide ion departs.
- The configuration at the migrating carbon remains unchanged.

- Hydroxide anion attacks the boron atom of the borate ester.
- An alkoxide anion departs from the borate anion, reducing the formal charge on boron to zero.
- Proton transfer completes the formation of one alcohol molecule. The sequence repeats until all three alkoxy groups are released as alcohols and inorganic borate remains.
Hydroboration of methylcyclopentene gives the anti-Markovnikov product with syn addition of the elements of water.

- **Summary of Alkene Hydration Methods**
  - Acid-catalyzed hydrolysis: Markovnikov addition
  - Oxymercuration: Markovnikov addition
  - Hydroboration-Oxidation: anti-Markovnikov and syn addition
Addition of Bromine and Chlorine to Alkenes

Addition produces vicinal dihalides

\[ \text{trans-1,2-Dibromocyclohexane} \]
(as a racemic form)

This reaction is used as a test for alkenes because the red color of the bromine reagent disappears when an alkene (or alkyne) is present.

Alkanes do not react with bromine in the dark.

An alkene (colorless)

\[ \text{Rapid decolorization of Br}_2/\text{CCl}_4 \text{ is a test for alkenes and alkynes.} \]
Mechanism of Halogen Addition

A bromonium ion intermediate results instead of the carbocation seen in other addition reactions.

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 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 S₅₂ 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
  - When cyclopentene reacts the product is a racemic mixture of *trans*-1,2-dibromocyclopentane enantiomers
Stereospecific Reactions

A reaction is stereospecific if a particular stereoisomeric form of the starting material reacts in such a way that it gives a specific stereoisomeric form of the product.

Example: cis- and trans-2-butene give stereoisomeric products when halogenated.

Halogenation of double bonds is stereospecific.

Reaction 1

\[
\text{trans-2-Butene} \xrightarrow{\text{Br}_2, \text{CCl}_4} \text{(2R,3S)-2,3-Dibromobutane (a meso compound)}
\]

Reaction 2

\[
\text{cis-2-Butene} \xrightarrow{\text{Br}_2, \text{CCl}_4} \text{(2R,3R)} + \text{(2S,3S)}
\]
Halohydrin Formation

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

\[ \text{Halohydrin (major)} \quad \text{and} \quad \text{Halide ion} \]

This step is the same as for halogen addition to an alkene (see Section 8.12A).

Steps 2 and 3

Here, however, a water molecule acts as the nucleophile and attacks a carbon of the ring, causing the formation of a protonated halohydrin. The protonated halohydrin loses a proton (it is transferred to a molecule of water). This step produces the halohydrin and hydronium ion.
In unsymmetrical alkenes, the bromonium ion will have some of its $\delta^+$ charge density on the most 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 divalent but neutral carbons with a lone pair of electrons
- Carbenes are highly reactive

**Structure and Reaction of Methylene**

- Methylene can be made by heat or light initiated decomposition of diazomethane
- Loss of a molecule of the stable gas nitrogen drives this reaction

\[
\text{CH}_2\text{N}\equiv\text{N} \xrightarrow{\text{heat or light}} \text{CH}_2 + \text{N}\equiv\text{N} \\
\text{Diazomethane} \quad \text{Methylene} \quad \text{Nitrogen}
\]

- Methylene reacts with alkenes to form cyclopropanes

\[
\text{C}\equiv\text{C} + \text{CH}_2 \rightarrow \text{C} - \text{C} \\
\text{Alkene} \quad \text{Methylene} \quad \text{Cyclopropane}
\]
• Reactions of Other Carbenes: Dihalocarbenes
  ➔ Carbenes add to double bonds in a stereospecific manner

  ![Chemical structure](image)

  The addition of :CX₂ is stereospecific. If the R groups of the alkene are trans, they will be trans in the product. (If the R groups were initially cis, they would be cis in the product.)

  ➔ Dihalocarbenes are formed by α elimination of compounds such as chloroform

  \[
  R\overset{=}{{\vdash}} K^+ + H:CCl_3 \rightleftharpoons R\overset{=}{{\vdash}} H + \overset{=}{{\vdash}} CCl_3 + K^+ \overset{\text{slow}}{\rightarrow} :CCl_2 + \overset{=}{{\vdash}} Cl^- \]

  Dichlorocarbene

• Carbenoids: The Simmons-Smith Cyclopropane Synthesis
  ➔ A carbene-like species is formed which then reacts with alkenes

  \[
  \text{CH}_2\text{I}_2 + \text{Zn(Cu)} \rightarrow \text{ICH}_2\text{ZnI} \]

  A carbenoid
**Oxidations of Alkenes: Syn 1,2-Dihydroxylation**

→ Either OsO₄ or KMnO₄ will give 1,2 diols (glycols)

![Chemical reaction diagram](image)

- **Mechanism for Syn Hydroxylation of Alkenes**
  → Cyclic intermediates result from reaction of the oxidized metals
  → The initial syn addition of the oxygens is preserved when the oxygen-metal bonds are cleaved and the products are syn diols

![Mechanism diagram](image)

Chapter 8
Oxidative Cleavage of Alkenes

- Reaction of an alkene with hot KMnO₄ results in cleavage of the double bond and formation of highly oxidized carbons.

  - Unsubstituted carbons become CO₂, monosubstituted carbons become carboxylates and disubstituted carbons become ketones.

\[
\text{CH}_3\text{CH} \rightleftharpoons \text{CHCH}_3 \xrightarrow{\text{KMnO}_4, \text{OH}^-, \text{H}_2\text{O}, \text{heat}} 2 \text{CH}_3\text{C} \rightleftharpoons \text{O} \xrightarrow{\text{H}_3\text{O}^+} 2 \text{CH}_3\text{C} \rightleftharpoons \text{OH}
\]

(cis or trans) \hspace{1cm} \text{Acetate ion} \hspace{1cm} \text{Acetic acid}

- This be used as a chemical test for alkenes in which the purple color of the KMnO₄ disappears and forms brown MnO₂ residue if alkene (or alkyne) is present.
Solved Problem

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

$$C_7H_{12} \xrightarrow{(1) \text{ KMnO}_4, \text{H}_2\text{O}, \text{OH}^-, \text{heat}} \xrightarrow{(2) \text{H}_3\text{O}^+} \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}--\text{OH}$$

Answer: Since no carbons are missing in the product, the alkene must be part of a ring in the original molecule

Unknown alkene
(1-methylcyclohexene)
Ozonolysis of Alkenes

Cleavage of alkenes with ozone and workup with zinc in acetic acid leads to less 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.

2-Methyl-2-butene

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{C} &= \text{C} \equiv \text{CHCH}_3 & \text{(1) O}_3, \text{CH}_2\text{Cl}_2, \text{−78°C} & \text{(2) Zn/} \text{HOAc} & \text{CH}_3\text{C} &= \text{O} & \text{CH}_3\text{CH} \\
\end{align*}
\]

Acetone + Acetaldehyde

3-Methyl-1-butene

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CH} &= \text{C} \equiv \text{CH}_2 & \text{(1) O}_3, \text{CH}_2\text{Cl}_2, \text{−78°C} & \text{(2) Zn/} \text{HOAc} & \text{CH}_3\text{CH} &= \text{CH} + \text{HCH} \\
\end{align*}
\]

Isobutyraldehyde + Formaldehyde
Ozone adds across the double bond to form the initial ozonide which rearranges to a highly unstable ozonide.

The ozonides react with zinc and acetic acid to effect the cleavage.
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 usually proceeds to give the trans dihalide.

![Chemical structures showing the addition of bromine and chlorine to alkynes.](image)
Addition of Hydrogen Halides to Alkynes

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

\[
\begin{align*}
\text{C}_4\text{H}_9\text{C}≡\text{CH} & \xrightarrow{\text{HBr}} \text{C}_4\text{H}_9\text{C}=\text{CH}_2 \xrightarrow{\text{HBr}} \text{C}_4\text{H}_9\text{C}-\text{CH}_3 \\
\text{2-Bromo-1-hexene} & \quad \text{2,2-Dibromohexane}
\end{align*}
\]

- HBr can be generated by reaction of acetyl bromide and alumina.

\[
\begin{align*}
\text{C}_5\text{H}_{11}\text{C}≡\text{CH} & \xrightarrow{\text{CH}_3\text{COBr}/\text{alumina}} \text{C}_5\text{H}_{11}\text{C}=\text{CH}_2 \\
\text{(82%)}
\end{align*}
\]

- Anti-Markovnikov addition of HBr occurs in the presence of peroxide (See Chapter 10).

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} & \xrightarrow{\text{HBr/ peroxides}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C≡CHBr} \\
\text{(74%)}
\end{align*}
\]
Oxidative Cleavage of Alkynes

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

\[
R\ce{\equiv}C\ce{\equiv}C\ce{\equiv}R' \xrightarrow{(1) \text{O}_3, (2) \text{HOAc}} \mathrm{RCO}_2\text{H} + \mathrm{R'CO}_2\text{H}
\]

\[
R\ce{\equiv}C\ce{\equiv}C\ce{\equiv}R' \xrightarrow{(1) \text{KMnO}_4, \text{OH}^-; (2) \text{H}_3\text{O}^+} \mathrm{RCO}_2\text{H} + \mathrm{R'CO}_2\text{H}
\]
Synthetic Strategies Revisited

Example: Synthesis of 1-butene from compounds with two or fewer carbons

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}≡\text{CH}_2 & \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{C}≡\text{CH} + \text{H}_2 \\
\text{CH}_3\text{CH}_2\text{C}≡\text{CH} & \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{Br} + \text{NaC}≡\text{CH} \\
\text{NaC}≡\text{CH} & \quad \rightarrow \quad \text{HC}≡\text{CH} + \text{NaNH}_2 \\
\text{HC}≡\text{C} & \quad \text{H} + \text{Na}^+\text{-NH}_2 \quad \text{(liq. NH}_3\text{)}_{-33ºC} \quad \rightarrow \quad \text{HC}≡\text{C}^:\text{-Na}^+ \\
\text{CH}_3\text{CH}_2\text{Br} & \quad \text{Na}^+\text{-C}≡\text{CH} \quad \text{(liq. NH}_3\text{)}_{-33ºC} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \\
\text{CH}_3\text{CH}_2\text{C}≡\text{CH} + \text{H}_2 & \quad \text{Ni}_2\text{B (P-2)} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{CH}≡\text{CH}_2
\end{align*}
\]
Example: Synthesis of (2R, 3R)-2,3-butandiol and its enantiomer from compounds of two carbon atoms or fewer

\[
\begin{align*}
\text{(R, R)} & \quad \text{Enantiomeric 2,3-butanediols} \\
\text{(S, S)} & \quad \text{trans-2-Butene}
\end{align*}
\]

\[
\text{trans-2-Butene} \xrightarrow{(1) \text{ OsO}_4} \xrightarrow{(2) \text{ NaHSO}_3, \text{H}_2\text{O}} \text{Enantiomeric 2,3-butanediols}
\]
trans-2-Butene

\[
\text{CH}_3\text{C}≡\text{C}H \xrightarrow{\text{anti addition}} \text{CH}_3\text{C}≡\text{C}H + \text{H}_2
\]

2-Butyne

\[
\text{CH}_3\text{C}≡\text{C}H \xrightarrow{\text{(1) Li, EtNH}_2, (2) NH}_3\text{Cl}} \text{anti addition of H}_2
\]

\[
\text{H}_3\text{C\text{H}}\]

trans-2-Butene

\[
\text{CH}_3\text{H} \rightarrow \text{CH}_3\text{C}≡\text{C}^-\text{Na}^+ + \text{CH}_3\text{I}
\]

\[
\text{CH}_3\text{C}≡\text{C}^-\text{Na}^+ \rightarrow \text{CH}_3\text{C}≡\text{C}^-\text{H} + \text{NaNH}_2
\]

\[
\text{CH}_3\text{C}≡\text{C}^-\text{H} \xrightarrow{\text{(1) NaNH}_2/\text{liq. NH}_3, (2) CH}_3\text{I}} \text{CH}_3\text{C}≡\text{C}^-\text{CH}_3
\]

\[
\text{H}^-\text{C}≡\text{C}^-\text{H} \xrightarrow{\text{(1) NaNH}_2/\text{liq. NH}_3, (2) CH}_3\text{I}} \text{CH}_3\text{C}≡\text{C}^-\text{H}
\]

Chapter 8