Chapter 8  
Alkenes and Alkynes II:  
Addition Reactions

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

Additions to Alkenes

\[ \text{C} = \text{C} + \text{A} - \text{B} \xrightarrow{\text{addition}} \text{A} - \text{C} = \text{B} \]

Alkenes are electron rich

The \( \pi \) electrons of the double bond are loosely held and are a source of electron density

Alkenes are nucleophilic and react with electrophiles such as \( \text{H}^+ \) from a hydrogen halide to form a carbocation

\( \text{X-H} + \text{C}=\text{C} \rightarrow \text{X} + \text{C} = \text{C} \)

Addition of Hydrogen Halides to Alkenes: Markovnikov’s Rule

Addition of \( \text{HBr} \) to propene occurs to give 2-bromopropane

\[ \text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CHBrCH}_3 \]

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

Addition of Hydrogen Halides to Alkenes: Markovnikov’s Rule

- 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

Mechanism for hydrogen halide addition to an alkene

- The reaction has a highly endergonic first step (rate determining) and a highly exergonic 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

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**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.

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**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

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**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

Net result is Markovnikov addition of water to an alkene

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**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

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

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**Addition of HBr to butene yields only tert-butyl bromide**

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**Addition of HBr to butene yields only tert-butyl bromide**
Carbocation rearrangements are possible

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CH} \quad \xrightarrow{\text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{CH}_2\text{CH} \quad \xrightarrow{\text{H}^+} \text{CH}_3\text{CH} \\
3,3\text{-Dimethyl-1-butene} &\quad 2,3\text{-Dimethyl-2-butanol (major product)}
\end{align*}
\]

In this case not reversible. Why not?

Hydration of Alkenes Through Oxymercuration-Demercuration

An alternative to direct acid-catalyzed addition of water:
- Uses \(\text{Hg}^{2+}\) as the initial electrophile
- Removal of mercury with sodium borohydride (reducing agent)

Mechanism involves formation of a bridged mercurinium ion

Water attacks the bridged ion at the Markownikov carbon

After reduction with \(\text{NaBH}_4\), net effect is addition of water

- High yields
- No carbocation rearrangements
- Follows Markovnikov addition
Another way to make alcohols from Alkenes

Hydroboration-Oxidation

Important because addition of water ends up:
1. Anti-Markovnikov
2. Syn Hydration

\[ \text{CH}_2=\text{CH}_2 + \text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} \]

**Mechanism of Hydroboration**
- Boron hydride 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 + charge in the transition state to reside at the most substituted carbon
- The boron and hydride add with syn stereochemistry

**Step 1: Hydroboration**

Hydroboration: Synthesis of Alkylboranes
- The elements of hydrogen and boron are added across the double bond
- \( \text{BH}_3 \) is electron deficient (in equilibrium with its dimer \( \text{B}_2\text{H}_6 \))
- In practice, a borane complex with the solvent tetrahydrofuran (THF) is often used

\[ \text{Alkene} + \text{B} \rightarrow \text{Alkyloborane} \]

**Mechanism of hydroboration**
- 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

**Step 2: Oxidation and Hydrolysis of the Alkyloborane**

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

\[ \text{Trialkyl borane} + \text{H}_2\text{O} \rightarrow \text{Alcohol} \]
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: Markovnikov addition, no rearrangement
3. Hydroboration-Oxidation: anti-Markovnikov and syn addition, no rearrangements

Addition of Bromine and Chlorine to Alkenes

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

Alkenes readily accept Br₂ or Cl₂ to form vicinal dihalides

Note: anti addition

Mechanism of Halogen Addition

- Must account for exclusively anti addition
- Electron pair of alkene creates heterolytic cleavage of the weak and polarizable Br-Br bond
- A bromonium ion intermediate holds the geometry

Mechanism of Halogen Addition

- Must account for exclusively 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\textsubscript{N}2 attack on the bromonium ion intermediate.
- When cyclopentene reacts the product is a racemic mixture of trans 1,2-dibromocyclopentane enantiomers.

Halogenation of double bonds is stereospecific
- 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.

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 + charge density on the more substituted of the two carbons.
- The most substituted carbon can best accommodate the + charge.
- The water nucleophile will tend to react at the carbon with the most + charge.

Carbenes have a divalent, neutral carbon
Carbenes are highly reactive
Structure and Reaction of Methylene (CH\textsubscript{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:

\[
\text{CH}_2 \overset{\text{N}_2}{\rightarrow} \text{CH}_2 + \text{N}_2
\]

- Diazomethane
- Methylene
- Nitrogen

Methylene reacts with alkenes to form cyclopropanes:

\[
\text{CH}_2 + \text{Alkene} \rightarrow \text{Cyclopropane}
\]
Carbenes add to double bonds in a stereospecific manner.

Dihalocarbenes formed by α elimination of compounds such as chloroform.

Reactions of Other Carbenes: Dihalocarbenes

A carbone-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

**Carbenoids : the Simmon-Smith reaction**

**Oxidations of Alkenes**

1. Syn 1,2-Dihydroxylation
   - Either OsO₄ or KMnO₄ will give 1,2 diols (glycols)

   \[ \text{CH}_2\text{CH}_3 + \text{OsO}_4 \rightarrow \text{CH}_2\text{CH}(-\text{OH})_2 \]

   Propene

   \[ \text{CH}_2\text{CH}_3 + \text{KMnO}_4 \rightarrow \text{CH}_2\text{CH}(-\text{OH})_2 \]

   Ethene

   1,2-Ethandiol (ethylene glycol)

**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

**Oxidation 2 of Alkenes: Oxidative Cleavage**

- Reaction of an alkene with hot KMnO₄ results in cleavage of the double bond and formation of highly oxidized carbons
- Unsaturated carbons become CO₂, monosubstituted carbons become carboxylates and disubstituted carbons become ketones

\[ \text{CH}_2\text{CH} = \text{CH}_2 + \text{KMnO}_4 \rightarrow \text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \]

Ethene

1,2-Ethandiol (ethylene glycol)

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

**Useful to identify location of double bonds**

- An unknown alkene with formula C₇H₁₂ yields only the following product on oxidation with hot KMnO₄

\[ \text{C}_7\text{H}_12 + \text{KMnO}_4 \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \]

- Answer: Since no carbons are missing in the product, the alkene must be part of a ring in the original molecule
Oxidation 3 of Alkenes: Ozonolysis

Cleavage of alkenes with ozone and workup with zinc in acetic acid leads to less highly oxidized carbons than products from cleavage with hot KMnO₄.
- Unsubstituted carbons are oxidized to formaldehyde, monosubstituted carbons are oxidized to aldehydes and disubstituted carbons are oxidized to ketones.

Ozonides react with zinc and acetic acid to effect the cleavage.

Ozonolysis mechanism

- 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 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.

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

Oxidative Cleavage of Alkynes

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

What alkene would produce acetone, the only product on ozonolysis?

A. H₂C=C=CH₂
B. C₆H₅CH=CH₂
C. H₂C=CH₂
D. None of these
Example: Synthesis of 1-butene from compounds with two or fewer carbons

\[
\text{CH}_3\text{C} = \text{CH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2
\]

\[
\text{HC} = \text{C} = \text{H} + \text{Na}^+ \cdot \text{NH}_3 + \text{HgO} \rightarrow \text{HC} = \text{C}^+ \cdot \text{Na}^+
\]

\[
\text{CH}_3\text{C} = \text{CH} + \text{Na}^+ \cdot \text{BH}_3 + \text{HgO} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2
\]

Example: Synthesis of \((2R, 3R)\)-2,3-butandiol and its enantiomer from compounds of two carbon atoms or fewer

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CO}^+ \text{Cl}^- \rightarrow \text{CH}_3\text{CO}^+ \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CO}^+ \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{C} = \text{C} = \text{O} + \text{Na}^+ \cdot \text{NH}_3 + \text{HgO} \rightarrow \text{CH}_3\text{C} = \text{CH} + \text{Na}^+ \cdot \text{NH}_3
\]

\[
\text{H} + \text{C} = \text{C} + \text{H}_2 \rightarrow \text{H} = \text{C} = \text{C} = \text{H}
\]