Chapter 6
Reactions of Alkenes

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The most characteristic reaction of alkenes is addition to the carbon-carbon double bond.

- The pi bond is broken.
- In its place, sigma bonds form to two new atoms or groups of atoms.
## Characteristic Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Descriptive Name(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}=\text{C} + \text{HCl (HX)} \rightarrow \text{C}=\text{C} \text{Cl}(X) )</td>
<td>Hydrochlorination (hydrohalogenation)</td>
</tr>
<tr>
<td>( \text{C}=\text{C} + \text{H}_2\text{O} \rightarrow \text{C}=\text{C} \text{OH} )</td>
<td>Hydration</td>
</tr>
<tr>
<td>( \text{C}=\text{C} + \text{Br}_2 (X_2) \rightarrow \text{C}=\text{C} \text{Br}(X) )</td>
<td>Bromination (halogenation)</td>
</tr>
<tr>
<td>( \text{C}=\text{C} + \text{Br}_2 (X_2) + \text{H}_2\text{O} \rightarrow \text{C}=\text{C} \text{Br}(X) )</td>
<td>Halohydrin formation (Bromohydrin formation) 6-3</td>
</tr>
</tbody>
</table>
Characteristic Reactions

\[
\text{C} = \text{C} + \text{Hg(OAc)}_2 \xrightarrow{\text{H}_2\text{O}} \text{C} = \text{C} + \text{HgOAc}
\]

Oxymercuration

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

Hydroboration

\[
\text{C} = \text{C} + \text{OsO}_4 \rightarrow \text{C} = \text{C}
\]

Diol formation (oxidation)

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

Hydrogenation (reduction)
A reaction mechanism describes how a reaction occurs and explains the following.

- Which bonds are broken and which new ones are formed.
- The order and relative rates of the various bond-breaking and bond-forming steps.
- If in solution, the role of the solvent.
- If there is a catalyst, the role of a catalyst.
- The position of all atoms and energy of the entire system during the reaction.
Gibbs Free Energy

- **Gibbs free energy change, $\Delta G^0$:**
  - A thermodynamic function relating enthalpy, entropy, and temperature.
    \[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]
  - **Exergonic reaction:** A reaction in which the Gibbs free energy of the products is lower than that of the reactants; the position of equilibrium for an exergonic reaction favors products.
  - **Endergonic reaction:** A reaction in which the Gibbs free energy of the products is higher than that of the reactants; the position of equilibrium for an endergonic reaction favors starting materials.
Gibbs Free Energy

• A change in Gibbs free energy is directly related to chemical equilibrium

\[ \Delta G^0 = -RT \ln \textit{Keq} \]

• Summary of the relationships between \( \Delta G^0 \), \( \Delta H^0 \), \( \Delta S^0 \), and the position of chemical equilibrium

<table>
<thead>
<tr>
<th>( \Delta H^0 )</th>
<th>( \Delta S^0 &lt; 0 )</th>
<th>( \Delta S^0 &gt; 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H^0 &gt; 0 )</td>
<td>( \Delta G^0 &gt; 0 ); the position of equilibrium favors reactants</td>
<td>At higher temperatures when ( T\Delta S^0 &gt; \Delta H^0 ) and ( \Delta G^0 &lt; 0 ), the position of equilibrium favors products</td>
</tr>
<tr>
<td>( \Delta H^0 &lt; 0 )</td>
<td>At lower temperatures when ( T\Delta S^0 &lt; \Delta H^0 ) and ( \Delta G^0 &lt; 0 ), the position of equilibrium favors products</td>
<td>( \Delta G^0 &lt; 0 ); the position of equilibrium favors products</td>
</tr>
</tbody>
</table>
Energy Diagrams

- **Enthalpy change, $\Delta H^0$:** The difference in total bond energy between reactants and products.
  - a measure of bond making (exothermic) and bond breaking (endothermic).

- **Heat of reaction, $\Delta H^0$:** The difference in enthalpy between reactants and products.
  - **Exothermic reaction:** A reaction in which the enthalpy of the products is lower than that of the reactants; a reaction in which heat is released.
  - **Endothermic reaction:** A reaction in which the enthalpy of the products is higher than that of the reactants; a reaction in which heat is absorbed.
**Energy Diagrams**

- **Energy diagram**: A graph showing the changes in energy that occur during a chemical reaction.

- **Reaction coordinate**: A measure in the change in positions of atoms during a reaction.
Activation Energy

**Transition state:**
- An unstable species of maximum energy formed during the course of a reaction.
- A maximum on an energy diagram.

**Activation Energy, \( \Delta G^\ddagger \):** The difference in Gibbs free energy between reactants and a transition state.
- If \( \Delta G^\ddagger \) is large, few collisions occur with sufficient energy to reach the transition state; reaction is slow.
- If \( \Delta G^\ddagger \) is small, many collisions occur with sufficient energy to reach the transition state; reaction is fast.
Energy Diagram

- An energy diagram for a one-step reaction with no intermediate.
An energy diagram for a two-step reaction with one intermediate.
Developing a Reaction Mechanism

How it is done:

- Design experiments to reveal the details of a particular chemical reaction.
- Propose a set or sets of steps that might account for the overall transformation.
- A mechanism becomes established when it is shown to be consistent with every test that can be devised.
- This does mean that the mechanism is correct, only that it is the best explanation we are able to devise.
Why Mechanisms?

- They are the framework within which to organize descriptive chemistry.
- They provide an intellectual satisfaction derived from constructing models that accurately reflect the behavior of chemical systems.
- They are tools with which to search for new information and new understanding.
Electrophilic Additions

- Hydrohalogenation using HCl, HBr, HI
- Hydration using H₂O in the presence of H₂SO₄
- Halogenation using Cl₂, Br₂
- Halohydrination using HOCl, HOBr
- Oxymercuration using Hg(OAc)₂, H₂O followed by reduction
Chem Activity 17: Electrophilic Addition

- Split quickly in groups of 4
- Read hand-out (Chem Activity 17)
- Work on the critical thinking questions (Part A)
- You have 15 min for Part A
- We will discuss the questions in 5-10 min
1. Addition of HX

- Carried out with pure reagents or in a polar solvent such as acetic acid.

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

- Addition is regioselective
  - **Regioselective reaction:** An addition or substitution reaction in which one product is formed in preference to all others that might be formed.
  - **Markovnikov’s rule:** In the addition of HX or H\textsubscript{2}O to an alkene, H adds to the carbon of the double bond having the greater number of hydrogens.
HBr + 2-Butene

◆ A two-step mechanism

Step 1: Proton transfer from HBr to the alkene gives a carbocation intermediate.

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{H}^-\text{Br}^+ \quad \text{slow, rate determining} \quad \text{CH}_3\text{CH}^+\text{CHCH}_3^- + \text{Br}^-
\]

sec-Butyl cation
a 2° carbocation

Step 2: Reaction of the sec-butyl cation (an electrophile) with bromide ion (a nucleophile) completes the reaction.

\[
\text{Br}^- + \text{CH}_3\text{CHCH}_2\text{CH}_3^+ \quad \text{fast} \quad \text{CH}_3\text{CHCH}_2\text{CH}_3^- + \text{Br}^-
\]

Bromide ion
(a nucleophile)
sec-Butyl cation
(an electrophile)
2-Bromobutane
**Carbocations**

- **Carbocation**: A species in which a carbon atom has only six electrons in its valence shell and bears a positive charge.

- Carbocations:
  - Are classified as 1°, 2°, or 3° depending on the number of carbons bonded to the carbon bearing the + charge.
  - Are **electrophiles**; that is, they are electron-loving.
  - Are **Lewis acids**.
  - Have bond angles of approximately 120° about the positively charged carbon.
  - Use $sp^2$ hybrid orbitals to form sigma bonds from carbon to the three attached groups.
  - The unhybridized $2p$ orbital lies perpendicular to the sigma bond framework and contains no electrons.
**Carbocations**

- The structure of the *tert-butyl cation*.
Carbocation Stability

- relative stability

\[
\text{H--C}^+\quad \text{CH}_3\text{--C}^+\quad \text{CH}_3\text{--C}^+\quad \text{CH}_3\text{--C}^+ \\
\text{Methyl cation (methyl)}\quad \text{Ethyl cation (1°)}\quad \text{Isopropyl cation (2°)}\quad \text{t-Butyl cation (3°)}
\]

**Increasing carbocation stability**

- Methyl and primary carbocations are so unstable that they are never observed in solution.
Carbocation Stability

• We can account for the relative stability of carbocations if we assume that alkyl groups bonded to a positively charged carbon are electron releasing and thereby delocalize the positive charge of the cation.

• We account for this electron-releasing ability of alkyl groups by (1) the inductive effect, and (2) hyperconjugation.
The Inductive Effect

- The positively charged carbon polarizes electrons of adjacent sigma bonds toward it.
- The positive charge on the cation is thus delocalized over nearby atoms.
- The larger the volume over which the positive charge is delocalized, the greater the stability of the cation.
Hyperconjugation

- Involves partial overlap of the $\sigma$-bonding orbital of an adjacent C-H or C-C bond with the vacant $2p$ orbital of the cationic carbon.

- The result is delocalization of the positive charge.
HBr + 2-Butene

An energy diagram for the two-step addition of HBr to 2-butene.

- The reaction is exergonic.
2. Addition of H₂O

- Addition of water is called hydration.
- Acid-catalyzed hydration of an alkene is regioselective; hydrogen adds preferentially to the less substituted carbon of the double bond (to the carbon bearing the greater number of hydrogens).
- HOH adds in accordance with Markovnikov’s rule.

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CH}_2 & \quad + \quad \text{H}_2\text{O} & \quad \xrightarrow{\text{H}_2\text{SO}_4} & \quad \text{CH}_3\quad \text{CH}-\text{CH}_2 \\
\text{Propene} & \quad & \quad & \quad \text{2-Propanol} \\
\text{CH}_3 & \quad \text{CH}_3\text{C}=\text{CH}_2 & \quad + \quad \text{H}_2\text{O} & \quad \xrightarrow{\text{H}_2\text{SO}_4} & \quad \text{CH}_3\quad \text{C}-\text{CH}_2 \\
\text{2-Methylpropene} & \quad & \quad & \quad \text{2-Methyl-2-propanol}
\end{align*}
\]
Addition of $\text{H}_2\text{O}$

- **Step 1:** Proton transfer from $\text{H}_3\text{O}^+$ to the alkene.
  \[
  \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{O}^+ \]
  A $2^\circ$ carbocation intermediate

- **Step 2:** Reaction of the carbocation (an electrophile) with water (a nucleophile) gives an **oxonium ion**.
  \[
  \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{O}^+ \rightarrow \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{O}^+ \]
  An oxonium ion

- **Step 3:** Proton transfer to water gives the alcohol.
  \[
  \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{O}^+ \rightarrow \text{CH}_3\text{CHCH}_3 + \text{H}_2\text{O}^+ \]
Carbocation Rearrangements

In electrophilic addition to alkenes, there is the possibility for rearrangement if a carbocation is involved.

Rearrangement: A change in connectivity of the atoms in a product compared with the connectivity of the same atoms in the starting material.
Chem Activity 17: Electrophilic Addition

- Split quickly in groups of 4
- Read hand-out (Chem Activity 17)
- Work on the critical thinking questions (Part B)
- You have 12 min for Part B
- We will discuss the questions in 5 min
Carbocation Rearrangements

- In addition of HCl to an alkene.

\[ \text{3,3-Dimethyl-1-butene} + \text{HCl} \rightarrow \text{2-Chloro-3,3-dimethylbutane} + \text{2-Chloro-2,3-dimethylbutane} \]

3,3-Dimethyl-1-butene (the expected product; 17%) 2-Chloro-3,3-dimethylbutane (the major product; 83%)

- In acid-catalyzed hydration of an alkene.

\[ \text{3-Methyl-1-butene} + \text{H}_2 \text{O} \xrightarrow{\text{H}_2 \text{SO}_4} \text{2-Methyl-2-butanol} \]
Carbocation Rearrangements

• The driving force is rearrangement of a less stable carbocation to a more stable one.

\[
\begin{align*}
\text{CH}_3 \text{CCH} &= \text{CH}_2 + \overset{\text{slow, rate determining}}{H-\text{Cl}} & \rightarrow & & \text{CH}_3 \overset{\text{H}}{\text{C}-\text{CHCH}_3} + \overset{\text{A 2° carbocation intermediate}}{\text{Cl}^-} \\
\text{3-Methyl-1-butene} & & & & \\
\text{CH}_3 \overset{\text{H}}{\text{C}-\text{CHCH}_3} + \overset{\text{fast}}{\text{H}} & \rightarrow & \text{CH}_3 \overset{\text{H}}{\text{C}-\text{CHCH}_3} & \overset{\text{A 3° carbocation}}{+} \\
\end{align*}
\]

• The less stable 2° carbocation rearranges to a more stable 3° carbocation by 1,2-shift of a hydride ion.
Carbocation Rearrangements

- Reaction of the more stable carbocation (an electrophile) with chloride ion (a nucleophile) completes the reaction.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C-CH}_2 \text{CH}_3 & + & \text{Cl}^- & \quad \text{fast} & \quad \text{CH}_3 & \quad \text{C-CH}_2 \text{CH}_3 \\
\text{CH}_3 & \quad \text{C-CH}_2 \text{CH}_3 & + & \text{Cl}^- & \quad \text{2-Chloro-2-methylbutane}
\end{align*}
\]
3. Addition of Cl₂ and Br₂

- Carried out with either the pure reagents or in an inert solvent such as CH₂Cl₂.

\[
\begin{align*}
\text{CH}_3\text{CH}=&\text{CHCH}_3 + \text{Br}_2 & \text{CH}_2\text{Cl}_2 & \text{Br} & \text{Br} \\
2\text{-Butene} & & & & \text{CH}_3\text{CH-CHCH}_3 \\
& & \text{2,3-Dibromobutane}
\end{align*}
\]

- Addition of bromine or chlorine to a cycloalkene gives a *trans*-dihalocycloalkane as a racemic mixture.

\[
\begin{align*}
\text{\textbullet} & \quad \text{Cyclohexene} + \text{Br}_2 & \text{CH}_2\text{Cl}_2 & \text{Br} & \text{Br} \\
& & & \text{trans- 1,2-Dibromocyclohexane} \\
& & & \text{(a racemic mixture)}
\end{align*}
\]

- Addition occurs with **anti stereoselectivity**; halogen atoms add from the opposite face of the double bond.

- We will discuss this selectivity in detail in Section 6.7.
Addition of Cl$_2$ and Br$_2$

- Step 1: Formation of a bridged bromonium ion intermediate.

These carbocations are major contributing structures

The bridged bromonium ion retains the geometry
Addition of $\text{Cl}_2$ and $\text{Br}_2$

- Step 2: Attack of halide ion (a nucleophile) from the opposite side of the bromonium ion (an electrophile) opens the three-membered ring to give the product.

![Chemical reaction diagram]
Addition of Cl₂ and Br₂

- For a cyclohexene, anti coplanar addition corresponds to *trans* diaxial addition.
- The initial *trans* diaxial conformation is in equilibrium with the more stable *trans* diequatorial conformation.
- Because the bromonium ion can form on either face of the alkene with equal probability, the *trans* enantiomers are formed as a racemic mixture.
4. Addition of HOCl and HOBr

- Treatment of an alkene with Br$_2$ or Cl$_2$ in water forms a halohydrin.

- **Halohydrin:** A compound containing -OH and -X on adjacent carbons.

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

Propene \hspace{1cm} 1-Chloro-2-propanol (a chlorohydrin)
Addition of HOCl and HOBr

• Reaction is both regioselective (OH adds to the more substituted carbon) and anti stereoselective.
• Both selectivities are illustrated by the addition of HOBr to 1-methylcyclopentene.

\[
\text{Br}_2 / \text{H}_2 \text{O} \quad \xrightarrow{\text{1-Methylcyclopentene}} \quad \text{2-Bromo-1-methylcyclopentanol} + \text{HBr}
\]

( a racemic mixture )

• To account for the regioselectivity and the anti stereoselectivity, chemists propose a three-step mechanism (next two slides).
Addition of HOCl and HOBr

Step 1: Formation of a bridged halonium ion intermediate.

\[
\text{bridged bromonium ion}
\]

Step 2: Attack of H\(_2\)O on the more substituted carbon opens the three-membered ring.
Addition of HOCl and HOBr

- Step 3: Proton transfer to $\text{H}_2\text{O}$ completes the reaction

As the elpot map on the next slide shows:
- The C-X bond to the more substituted carbon is longer than the one to the less substituted carbon.
- Because of this difference in bond lengths, the transition state for ring opening can be reached more easily by attack of the nucleophile at the more substituted carbon.
Addition of HOCl and HOBr

- Bridged bromonium ion from propene.
5. Oxymercuration/Reduction

- Oxymercuration followed by reduction results in hydration of a carbon-carbon double bond.
  - **oxymercuration**
    \[
    \text{1-Pentene} + \text{Hg(OAc)}_2 + \text{H}_2\text{O} \rightarrow \text{2-Pentanol} + \text{HgOAc} + \text{CH}_3\text{COH}
    \]
  - **reduction**
    \[
    \text{2-Pentanol} \xrightarrow{\text{NaBH}_4} \text{2-Pentanol} + \text{Hg} + \text{CH}_3\text{COH}
    \]
Oxymercuration/Reduction

- An important feature of oxymercuration/reduction is that it occurs without rearrangement.

\[
\begin{align*}
\text{3,3-Dimethyl-1-butene} & \xrightarrow{1. \text{Hg(OAc)}_2, \text{H}_2\text{O}} \text{3,3-Dimethyl-2-butanol} \\
& \xrightarrow{2. \text{NaBH}_4}
\end{align*}
\]

- Oxymercuration occurs with anti stereoselectivity.

\[
\begin{align*}
\text{Cyclopentene} & \xrightarrow{\text{Hg(OAc)}_2, \text{H}_2\text{O}} \text{Hg OAc} \\
& \xrightarrow{\text{NaBH}_4} \text{Cyclopentanol}
\end{align*}
\]

(Anti addition of OH and HgOAc)
Oxymercuration/Reduction

- **Step 1:** Dissociation of mercury(II) acetate.
  \[ \text{AcO-Hg-OAc} \rightarrow \text{AcO-Hg}^+ + \text{AcO}^- \]
  (an electrophile)

- **Step 2:** Formation of a bridged mercurinium ion intermediate; a two-electron three-center bond.
Oxymercuration/Reduction

- Step 3: Regioselective attack of H$_2$O (a nucleophile) on the bridged intermediate opens the three-membered ring.

- Step 4: Reduction of the C-HgOAc bond.
Oxymercuration/Reduction

- Anti stereoselective
  - Formation of a bridged mercurinium ion intermediate and anti attack of the nucleophile to open the three-membered ring.

- Regioselective (Hg goes to less substituted C)
  - The more substituted carbon of the mercurinium ion intermediate has the greater degree of partial positive character.
  - Computer modeling indicates that the C-Hg bond to the more substituted carbon of the bridged intermediate is longer than the one to the less substituted carbon.
  - The ring-opening transition state is reached more easily by attack at the more substituted carbon.