Chapter 7
Structure and Synthesis of Alkenes

Introduction

• Hydrocarbon with carbon-carbon double bonds
• Sometimes called olefins, “oil-forming gas”
• Planar
• Pi bond is the functional group.
• More reactive than sigma bond (more exposed).
• Bond dissociation energies:
  ➢ C=C BDE \ 611 \text{kJ/mol}
  ➢ C-C BDE \ -347 \text{kJ/mol}
  ➢ Pi bond \ 264 \text{kJ/mol}
Orbital Description

- Sigma bonds around C are \( sp^2 \) hybridized.
- Angles are approximately 120 degrees.
- No nonbonding electrons.
- Molecule is planar around the double bond.
- Pi bond is formed by the sideways overlap of parallel \( p \) orbitals perpendicular to the plane of the molecule.

Bond Lengths and Angles

- Hybrid orbitals have more \( s \) character.
- Pi overlap brings carbon atoms closer.
- Bond angle with pi orbital increases.
  - Angle C=C-H is 121.7°
  - Angle H-C-H is 116.6°
Pi Bond

- Sideways overlap of parallel $p$ orbitals.
- No rotation is possible without breaking the pi bond (264 kJ/mole).
- Cis isomer cannot become trans without a chemical reaction occurring.

Elements of Unsaturation

- A saturated hydrocarbon: $C_nH_{2n+2}$
- Each pi bond (and each ring) decreases the number of H’s by two.
- Each of these is an element of unsaturation.
- To calculate: find number of H’s if it were saturated, subtract the actual number of H’s, then divide by 2.
Propose a Structure:
for \( \text{C}_5\text{H}_8 \)

- First calculate the number of elements of unsaturation.
- Remember:
  - A double bond is one element of unsaturation.
  - A ring is one element of unsaturation.
  - A triple bond is two elements of unsaturation.

Heteroatoms

- Halogens take the place of hydrogens, so add their number to the number of H’s.
- Oxygen doesn’t change the C:H ratio, so ignore oxygen in the formula.
- Nitrogen is trivalent, so it acts like “half” a carbon.
Structure for C$_6$H$_7$N?

• Since nitrogen counts as half a carbon, the number of H’s if saturated is 
  $2(6.5) + 2 = 15$.
• Number of missing H’s is $15 - 7 = 8$.
• Elements of unsaturation is $8 \div 2 = 4$.

IUPAC Nomenclature

• Parent is longest chain containing the double bond.
• -ane changes to -ene (or -diene, -triene).
• Number the chain so that the double bond has the lowest possible index number.
• In a ring, the double bond is assumed to be between carbon 1 and carbon 2.
• Place numbers in front of suffix to indicate where double bond is.
**Name These Alkenes**

1. CH$_2$=CH–CH$_2$–CH$_3$
   - 1-butene
   - but-1-ene

2. CH$_3$–C=CH–CH$_3$
   - 2-methyl-2-butene
   - 2-methylbut-2-ene

3. C$_3$H$_5$
   - 3-methylcyclopentene

4. CH$_2$=CH–CHCH$_2$CH$_3$
   - 2-sec-butyl-1,3-cyclohexadiene
   - 2-sec-butylcyclohexa-1,3-diene

5. C$_6$H$_3$
   - 3-n-propyl-1-heptene
   - 3-n-propylhept-1-ene

---

**Alkene Substituents**

- = CH$_2$
  - methylene
  - (methylene)

- - CH = CH$_2$
  - vinyl
  - (ethenyl)

- - CH$_2$ - CH = CH$_2$
  - allyl
  - (2-propenyl)

Name:

- \[
\begin{align*}
&\text{CH}_2=\text{CH} \\
&\text{(methylene)}
\end{align*}
\]

- \[
\begin{align*}
&\text{CH} = \text{CH}_2 \\
&\text{(vinyl)}
\end{align*}
\]

- \[
\begin{align*}
&\text{CH}_2 - \text{CH} = \text{CH}_2 \\
&\text{(allyl)}
\end{align*}
\]

- \[
\begin{align*}
&\text{(2-propenyl)}
\end{align*}
\]
# Common Names

- Usually used for small molecules.
- Examples:

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>ethylene</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CH}-\text{CH}_3 )</td>
<td>propylene</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{C} \cdots \text{CH}_3 )</td>
<td>isobutylene</td>
</tr>
</tbody>
</table>

# Cis-trans Isomerism

- Similar groups on same side of double bond, alkene is cis.
- Similar groups on opposite sides of double bond, alkene is trans.
- Cycloalkenes are assumed to be *cis* for rings less than 8.
- *Trans* cycloalkenes are not stable unless the ring has at least 8 carbons (and even here *trans* is rare).
Name these:

- \( \text{trans-2-pentene} \)
- \( \text{cis-1,2-dibromoethene} \)
- \( \text{trans-pent-2-ene} \)

What about this?

**E-Z Nomenclature**

- Use the Cahn-Ingold-Prelog rules to assign priorities to groups attached to each carbon in the double bond.
- If high priority groups are on the same side, the name is *Z* (for *zusammen*).
- If high priority groups are on opposite sides, the name is *E* (for *entgegen*).
Example, \textit{E-Z}

\begin{align*}
\text{H}_2\text{C} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{CH} - \text{CH}_3 \\
\end{align*}

\text{2Z} \quad \text{5E}

\textit{3,7-dichloro-(2Z, 5E)-2,5-octadiene}

\textit{3,7-dichloro-(2Z, 5E)-octa-2,5-diene}

\textbf{Commercial Uses: Ethylene}

\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{O} & \quad \text{H}_2\text{O} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\end{align*}

polyethylene

\begin{align*}
\text{CH}_3 & \quad \text{C} \\
\text{O} & \quad \text{H} \\
\end{align*}

acetaldehyde

\textit{oxidize}

\begin{align*}
\text{CH}_3 & \quad \text{C} \\
\text{O} & \quad \text{H} \\
\end{align*}

acetic acid

\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{O}_2 & \quad \text{Ag catalyst} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\end{align*}

ethylene oxide

\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}

ethylene

\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{C} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\end{align*}

ethylene dichloride

\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\end{align*}

ethylene glycol

\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{OH} & \quad \text{OH} \\
\end{align*}

ethanol

\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{C} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\end{align*}

vinyl chloride

\text{Copyright © 2005 Pearson Prentice Hall, Inc.}
Commercial Uses: Propylene

\[
\begin{align*}
\text{H}_2\text{C} & \text{CH} \text{CH}_3 \xrightarrow{\text{propylene oxide}} \text{H}_2\text{C} & \text{CH} \text{CH}_3 \\
\text{H}_2\text{O} & \xrightarrow{\text{H}^+} \text{H}_2\text{C} & \text{CH} \text{CH}_3 \\
\text{OH} & \text{OH} & \text{OH}
\end{align*}
\]

(propylene glycol)

\[
\begin{align*}
\text{CH}_2 & \text{CH} \text{CH}_3 \
\text{OH} & \text{OH} & \text{OH}
\end{align*}
\]

(isopropyl alcohol)

\[
\begin{align*}
\text{CH}_3 & \text{CH} \text{CH}_3 \
\text{OH} & \text{OH} & \text{OH}
\end{align*}
\]

(acetone)

Other Polymers

\[
\begin{align*}
\text{H} & \text{C} = \text{C} \text{CH}_3 \
\text{H} & \text{C} = \text{C} \text{H} \
\text{H} & \text{C} = \text{C} \text{Cl}
\end{align*}
\]

(propylene (monomer))

\[
\begin{align*}
\text{H} & \text{C} = \text{C} \text{CH}_3 \\
\text{H} & \text{C} = \text{C} \text{Cl}
\end{align*}
\]

(vinyl chloride)

\[
\begin{align*}
\text{F} & \text{C} = \text{C} \text{F} \
\text{F} & \text{C} = \text{C} \text{F}
\end{align*}
\]

(tetrafluoroethylene)

\[
\begin{align*}
\text{H} & \text{C} = \text{C} \text{CH}_3 \\
\text{H} & \text{C} = \text{C} \text{CH}_3 \\
\text{H} & \text{C} = \text{C} \text{Cl} \\
\text{H} & \text{C} = \text{C} \text{Cl}
\end{align*}
\]

(polypropylene (polymer))

\[
\begin{align*}
\text{H} & \text{C} = \text{C} \text{CH}_3 \\
\text{H} & \text{C} = \text{C} \text{Cl} \\
\text{H} & \text{C} = \text{C} \text{Cl}
\end{align*}
\]

(poly(vinyl chloride))

PVC, "vinyl"

\[
\begin{align*}
\text{F} & \text{C} = \text{C} \text{F} \\
\text{F} & \text{C} = \text{C} \text{F}
\end{align*}
\]

(poly(tetrafluoroethylene))

PTFE, Teflon®
Stability of Alkenes

• Measured by heat of hydrogenation:
  \[
  \text{Alkene} + H_2 \rightarrow \text{Alkane} + \text{energy}
  \]
• More heat released, higher energy alkene.

Substituent Effects

• More substituted alkenes are more stable.
  \[
  \text{H}_2\text{C}=\text{CH}_2 < \text{R-CH}=\text{CH}_2 < \text{R-CH}=\text{CH-R} < \text{R-CH}=\text{CR}_2 < \text{R}_2\text{C}=\text{CR}_2
  \]
  unsub. < monosub. < disub. < trisub. < tetra sub.
• Cis vs Trans vs terminal
• Alkyl group stabilizes the double bond.
• Alkene less sterically hindered.
Disubstituted Isomers

- Stability: cis < geminal < trans isomer
- Less stable isomer is higher in energy, has a more exothermic heat of hydrogenation.

<table>
<thead>
<tr>
<th>Cis-2-butene</th>
<th>CH₃-C=C-CH₃</th>
<th>-120 kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylene</td>
<td>(CH₃)₂C=CH₂</td>
<td>-117 kJ</td>
</tr>
<tr>
<td>Trans-2-butene</td>
<td>H-C=C-CH₃</td>
<td>-116 kJ</td>
</tr>
</tbody>
</table>

Relative Stabilities
Cycloalkene Stability

- \textit{Cis} isomer more stable than \textit{trans}.
- Small rings have additional ring strain.
- Must have at least 8 carbons to form a stable \textit{trans} double bond.
- For cyclodecene (and larger) \textit{trans} double bond is almost as stable as the \textit{cis} (‘floppy’ rings).

Bredt’s Rule (Bridgehead Alkenes)

- A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms.
- Examples:

Unstable. Violates Bredt’s rule

Stable. Double bond in 8-membered ring.
Physical Properties

- Low boiling points, increasing with mass.
- Branched alkenes have lower boiling points.
- Less dense than water.
- Slightly polar
  - Pi bond is polarizable, so instantaneous dipole-dipole interactions occur.
  - Alkyl groups are electron-donating toward the pi bond, so may have a small dipole moment.

Polarity Examples

\[
\begin{align*}
\text{cis-2-butene, bp } 4^\circ \text{C} & \quad \mu = 0.33 \text{ D} \\
\text{trans-2-butene, bp } 1^\circ \text{C} & \quad \mu = 0
\end{align*}
\]
Alkene Synthesis:
Overview

Simple preparation involves *Elimination reactions*:

- E2 dehydrohalogenation (-HX)
- E1 dehydrohalogenation (-HX)
- Dehalogenation of vicinal dibromides (-X₂)
- Dehydration of alcohols (-H₂O)

Removing HX via E2

- Strong base abstracts H⁺ as X⁻ leaves from the adjacent carbon.
- Tertiary and hindered secondary alkyl halides give good yields (S₉2 is retarded).
- Use a bulky base if the alkyl halide usually forms substitution products (such as isopropoxide or t-butoxide).
- Zaitsev product preferred if possible
E2 Mechanism

- Lewis base approaches molecule; removal of H is more facile than substitution:

\[
\begin{array}{c}
\text{Nu}^- \\
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\xrightarrow{d}
\begin{array}{c}
\text{H} \\
\text{Br} \\
\end{array}
\]

- Rate bond making = rate bond breaking
- H being removed and X leaving must be periplanar;
- Anti periplanar preferred to syn periplanar

Some Bulky Bases

- tert-butoxide
- diisopropylamine
- 2,6-dimethylpyridine
- triethylamine
Hofmann Product

- Bulky bases abstract the least hindered H⁺
- Least substituted alkene is major product.

\[
\text{Zaitsev product} \quad \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{Br} \\
\text{Br} \\
\text{H} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{OCH}_2\text{CH}_3} \quad \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{CH}_3 \\
\text{H} \quad \text{CH}_3
\end{array}
\xrightarrow{\text{H}_2\text{O}} \quad \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{CH}_3 \\
\text{H} \quad \text{CH}_3
\end{array}
\]

\[
\text{Hofmann product} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{OCH}_2\text{CH}_3} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{H}_2\text{O}} \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3
\end{array}
\]

E2: Diastereomers

\[
\begin{array}{c}
\text{Ph} \\
\text{Br} \\
\text{H} \\
\text{H} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{Ph}}
\begin{array}{c}
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\text{Ph} \\
\text{Ph}
\end{array}
\]

Stereospecific reaction: \((S, R)\) produces only trans product,
\((R, R)\) produces only cis.
E2: Cyclohexanes

Leaving groups must be trans diaxial. =>

E2: Vicinal Dibromides

- Remove Br₂ from adjacent carbons.
- Bromines must be anti-coplanar (E2).
- Use NaI in acetone, or Zn in acetic acid.
Removing HX via E1

- Secondary or tertiary halides.
- Formation of carbocation intermediate.
- May get rearrangement.
- Weak nucleophile.
- Usually have substitution products, too.

=>

Dehydration of Alcohols

- Reversible reaction.
- Use concentrated sulfuric or phosphoric acid, remove low-boiling alkene as it forms.
- Protonation of OH converts it to a good leaving group, HOH.
- Carbocation intermediate, like E1.
- Protic solvent removes adjacent H⁺.

=>
Dehydration Mechanism

Industrial Methods

- Catalytic cracking of petroleum
  - Long-chain alkane is heated with a catalyst to produce an alkene and shorter alkane.
  - Complex mixtures are produced.
- Dehydrogenation of alkanes
  - Hydrogen (H₂) is removed with heat, catalyst.
  - Reaction is endothermic, but entropy-favored.
- Neither method is suitable for lab synthesis.
End of Chapter 7