Organic Chemistry

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Alkenes I

Chapter 5
Unsaturated Hydrocarbons

- Unsaturated hydrocarbon: contains one or more carbon-carbon double or triple bonds
- Alkene: contains a carbon-carbon double bond and has the general formula $C_nH_{2n}$ (Ch 5-6)

\[
\text{H} \quad \text{H} \\
\text{C} \equiv \text{C} \\
\text{H} \quad \text{H}
\]

Ethylene (an alkene)
Unsaturated Hydrocarbons

Alkyne: contains a carbon-carbon triple bond and has the general formula \( C_nH_{2n-2} \) (Ch 10)

\[
\text{H-C} \equiv \text{C-H}
\]

Acetylene (an alkyne)
Unsaturated Hydrocarbons

- Arenes: benzene and its derivatives (Ch 19-20)

\[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} = \text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array} \]
We do not study benzene and its derivatives until Chapters 19 & 20.

But, we show structural formulas of compounds containing the phenyl group before that time.

The phenyl group is not reactive under any of the conditions we describe in Ch 6-19.

Alternative representations for the phenyl group.

Benzene

C₆H₅- Ph-
5 Structure of Alkenes

- The two carbon atoms of a double bond and the four atoms attached to them lie in a plane, with bond angles of approximately 120°.

- According to the MO model, a double bond consists of:
  - one sigma bond formed by overlap of sp² hybrid orbitals
  - one pi bond formed by overlap of parallel 2p orbitals
## Structure of Alkenes

- Length of C-C bonds: single > double > triple
- Strength of C-C bonds: triple > double > single

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C-C Orbital Overlap</th>
<th>Å</th>
<th>kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>$sp^3 - sp^3$</td>
<td>1.54</td>
<td>90</td>
</tr>
<tr>
<td>ethylene</td>
<td>$sp^2 - sp^2$, 2p-2p</td>
<td>1.34</td>
<td>172</td>
</tr>
<tr>
<td>acetylene</td>
<td>$sp - sp$, two 2p-2p</td>
<td>1.21</td>
<td>230</td>
</tr>
</tbody>
</table>
Because of restricted rotation about a C-C double bond, groups on adjacent carbons are either \textit{cis} or \textit{trans} to each other

\begin{align*}
\text{cis-2-Butene} & : & \text{mp } -139°C, \text{ bp } 4°C \\
\text{trans-2-Butene} & : & \text{mp } -106°C, \text{ bp } 1°C
\end{align*}
trans alkenes are more stable than cis alkenes because of nonbonded interactions
Use the infix -en- to show the presence of a C-C double bond

Number the parent chain to give the 1st carbon of the double bond the lower number

Follow IUPAC rules for numbering and naming substituents

For a cycloalkene, the double bond must be numbered 1,2
5 IUPAC Nomenclature

4-Methyl-1-hexene

2-Ethyl-3-methyl-1-pentene

3-Methylcyclopentene

1,6-Dimethylcyclohexene
### Alkenyl Groups

<table>
<thead>
<tr>
<th>Alkenyl Group</th>
<th>Common Name</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ =</td>
<td>methylene</td>
<td>CH$_2$=CHCH$_2$-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>methylenecyclohexane</td>
</tr>
<tr>
<td>CH$_2$=CH-</td>
<td>vinyl</td>
<td>CH$_2$=CHCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>vinyl chloride</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_2$-</td>
<td>allyl</td>
<td>CH$_2$=CHCH$_2$Cl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>allyl chloride</td>
</tr>
</tbody>
</table>
Despite the precision and universal acceptance of IUPAC nomenclature, some alkenes, particularly low-molecular-weight ones, are known almost exclusively by their common names.

**IUPAC:**
- Ethene
- Propene
- 2-Methylpropene

**Common:**
- Ethylene
- Propylene
- Isobutylene

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \text{CH}_3\text{CH}=\text{CH}_2 & \quad \text{CH}_3\text{C}=\text{CH}_2 \\
\text{Ethene} & \quad \text{Propene} & \quad \text{2-Methylpropene} \\
\text{Ethylene} & \quad \text{Propylene} & \quad \text{Isobutylene}
\end{align*}
\]
The *cis-trans* system: configuration is determined by the orientation of atoms of the main chain.

- **trans-3-Hexene**

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

- **cis-3,4-Dimethyl-2-pentene**

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{H}_3 \text{C} & \quad \text{CH} \left( \text{CH}_3 \right) _2 \\
\text{C} & \quad \text{C}
\end{align*}
\]
5 Configuration - E,Z

- The E,Z uses priority rules (Chapter 4)

- If groups of higher priority are on the same side, configuration is Z (German, zusammen)

- If groups of higher priority are on opposite sides, configuration is E (German, entgegen)
5 Configuration - E,Z

\[ \text{higher} \quad \text{lower} \quad \text{higher} \quad \text{lower} \]

\[ \text{Z (zusammen)} \quad \text{E (entgegen)} \]
Example: name each alkene and specify its configuration by the E,Z system

(a) \[ \text{H} - \text{C} = \text{C} - \text{CH}_3 \]
\[ \text{H}_3 \text{C} \quad \text{CH} (\text{CH}_3)_2 \]

(b) \[ \text{Cl} - \text{C} = \text{C} - \text{H} \]
\[ \text{H}_3 \text{C} \quad \text{CH}_2 \text{CH}_3 \]

(c) \[ \text{ClCH}_2 - \text{C} = \text{C} - \text{CH}_3 \]
\[ \text{H}_3 \text{C} \quad \text{CH}_2 \text{CH}_3 \]

(d) \[ \text{Cl} - \text{C} = \text{C} - \text{H} \]
\[ \text{Br} \quad \text{CH}_3 \]
Configuration of the double bond in cyclopropene through cycloheptene must be cis. Cyclopentene is planar.
5 Cis-Trans Isomerism in Cycloalkenes

- Cyclohexene is slightly puckered
trans-Cyclooctene is the smallest trans-cycloalkene stable at 25°C
- the cis isomer is 9.1 kcal/mol more stable than the trans isomer.
5 Physical Properties

- Alkenes are nonpolar compounds
- The only attractive forces between their molecules are dispersion forces
- The physical properties of alkenes are similar to those of alkanes
5 Terpenes

Terpene: a compound whose carbon skeleton can be divided into two or more units identical with the carbon skeleton of isoprene.

\[
\begin{align*}
\text{CH}_3 & \quad \text{tail} \\
\text{CH}_2=\text{C-CH=CH}_2 & \quad \text{head} \\
2\text{-Methyl-1,3-butadiene (Isoprene)} & \\
\end{align*}
\]
Myrcene, $C_{10}H_{16}$, a component of bayberry wax and oils of bay and verbena.
5 Terpenes

Menthol, from peppermint
α-Pinene, from turpentine, shown first without hydrogens, then with them.
Camphor, from the camphor tree
How many stereoisomers are possible for this triterpene alcohol?