Chapter 11 Introduction to Organic Chemistry

The Chemistry of Carbon Compounds

Mid-1700s
Organic substance: from plants and animals, could not be prepared and manipulated
Inorganic substance: from minerals

Mid-1800s
No definite line can be drawn between organic and inorganic chemistry
(NH₄)⁺[OCN]⁻ ammonium cyanate
H₂N-C(≡O)NH₂ urea

Organic substances contain C
Organic substances are NOT all from living organisms

Organic vs. Inorganic

The only distinguishing characteristic of organic compounds is that all contain carbon (C).

Six elements (C, H, N, O, P and S) make up over 95% of all living biological molecules. The key element is CARBON. In biological molecules, carbon acts like a backbone to which many other elements are attached.

No other good criteria to distinguish organic and inorganic, including solubility in water.
Cells are 70-90% water, biochemical reactions are almost always aqueous.

Water soluble organic compounds: alcohol, carbohydrate, carboxylic acid, amino acid, nucleic acid, protein, antibiotics, even some polymers, etc.

Organic vs. Inorganic

Typical Examples

Propane CH₃-CH₂-CH₃
Covalent bonding Individually

Sodium Chloride NaCl
Ionic bonding Infinite network
Organic Compounds: the importance in Everyday Life

- Food, food additive, cotton, wool, silk, dyes, shampoos, perfume, plastic, polyester, nylon, etc.

Organic Compounds: the importance in Fuel

- Crude oil
- Distillation tower
- Natural gas
- C1-C4
- C5-C10
- C11-C14
- C14-C25
- Vacuum distillation

Organic Compounds: the importance in In Biological System

- Tumor-specific carbohydrate antigens
Organic Compounds: the importance of Drugs

Lipitor (Hypercholesterolemia)
Plavix (Atherosclerotic)
Nexium (GRED, gastric ulcers)
Advair (Asthma)
Norvasc (Hypertension)
Zyprexa (Schizophrenia)
Prevacid (GRED, gastric ulcers)

Other Well-Known Ones

Vitamin C
Penicillin
Cocaine
Nicotine
Heroin
Jasmine odor
Vanillin

Carbon
- Carbon has 4 valence electrons; hydrogen has 1.
  - C
  - H
- To achieve an octet, carbon forms four bonds.
  H : C : H
  H : C : H
  CH₄
  methane

Lewis Structure
Kekule Structure
Expanded formula
Molecular formula
Chemical name

Covalent bond: Shared-electron bond, first proposed in 1916 by G.N. Lewis

2005 Top Eight Pharmaceutical Drugs

As Drugs

GRED: Gastroesophageal reflux disease

Carbon has 4 valence electrons; hydrogen has 1.
To achieve an octet, carbon forms four bonds.
CH₄: Methane
1874, Van’t Hoff suggested the tetrahedral geometry:
When a carbon atom has four single covalent bonds, the bonds and their atoms are arranged in a tetrahedral shape.

In molecules with two or more carbon atoms, each carbon atom with four single bonds has a tetrahedral shape.

### Covalent Bonds

<table>
<thead>
<tr>
<th>Element</th>
<th>Group</th>
<th>Covalent Bonds</th>
<th>Structure of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1A</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4A</td>
<td>4</td>
<td>Alkane, alkene, alkyne, aromatic</td>
</tr>
<tr>
<td>N</td>
<td>5A</td>
<td>3</td>
<td>Amine, amide</td>
</tr>
<tr>
<td>O, S</td>
<td>6A</td>
<td>2</td>
<td>Alcohol, ether, epoxide, aldehyde, ketone, carboxylic acid</td>
</tr>
<tr>
<td>F, Cl, Br, I</td>
<td>7A</td>
<td>1</td>
<td>(X = F, Cl, Br, I)</td>
</tr>
</tbody>
</table>

---
Line Bond Structures

| Table 1.2 Levels and Keleal Structures of Some Simple Molecules |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Name            | Levels structure | Keleal structure | Name            | Levels structure | Keleal structure |
| Water (H₂O)     | H—O—H           | H₂O             | Methane (CH₄)   | H—C—H           | CH₄             |
| Ammonia (NH₃)   | H—N—H           | NH₃             | Methanal (CH₂O) | H—C—O           | CH₂O            |

Polarity of Organic Molecules affects physical properties

- The covalent bond C-C is nonpolar.
- Covalent bonds in which C bonds with H, O, N, F, Cl, or Br are polar.
- Organic molecules are nonpolar when dipoles cancel and polar when dipoles do not cancel.

<table>
<thead>
<tr>
<th>Element</th>
<th>F</th>
<th>O</th>
<th>N</th>
<th>Cl</th>
<th>Br</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>4.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
<td>2.5</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

Learning Check

Complete the structure of the organic molecule by adding the correct number of hydrogen atoms.

C-C-C-C

C—C—C—O

C

C- C- C
Learning Check

Draw the molecular formulas for the following structures:

\[
\begin{align*}
\text{Structure 1:} & \quad \text{H} - \text{H} - \text{H} - \text{H} \\
\text{Structure 2:} & \quad \text{H} - \text{H} - \text{H} - \text{H} \\
\text{Structure 3:} & \quad \text{H} - \text{H} - \text{H} - \text{H} \\
\end{align*}
\]
Constitutional (or Structural) Isomers

Constitutional isomers:

- Compounds with the *same molecular formula* but different structures.
- Isomers have *different names*.
- Isomers have *different* physical and chemical properties.

Constitutional Isomers

Give the molecular formulas and draw the Kekule structures for the following molecules:

\[ \text{CH}_3(\text{CH}_2)_3\text{CH}_3 \quad \text{CH}_3\text{CH}(_\text{CH}_3)\text{CH}_2\text{CH}_3 \]

Why are the structural formulas below constitutional isomers?

\[ \text{O-H} \]

\[ \text{CH}_3\text{CH}-\text{CH}_3 \quad \text{CH}_3\text{CH}-\text{O}-\text{CH}_3 \]

**Functional group**: the structural features that make it possible to classify compounds by reactivity
A Functional Group is:

A group of atoms with a molecule that has a characteristic chemical behavior. Chemically, a given functional group behaves in nearly the same way in every molecule it is a part of.

- The chemistry of every organic molecule, regardless of size and complexity, is determined by the functional groups it contains.
- A way to classify families of organic compounds.

Some Functional Groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=CF</td>
<td>Carbon-carbon triple bond</td>
</tr>
<tr>
<td>R=H</td>
<td>Simple hydrocarbon chain</td>
</tr>
<tr>
<td>R=CH3</td>
<td>Ethane group</td>
</tr>
<tr>
<td>R=OH</td>
<td>Hydroxyl group</td>
</tr>
<tr>
<td>R=NH2</td>
<td>Amino group</td>
</tr>
<tr>
<td>R=CH3</td>
<td>Ethyl group</td>
</tr>
</tbody>
</table>

More Functional Groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=Cl</td>
<td>Chlorine atom</td>
</tr>
</tbody>
</table>
Learning Check

Identify the functional group in each.

1) \( \text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH} \)
2) \( \text{CH}_3\text{—O—CH}_2\text{—CH}_3 \)
3) \( \text{CH}_3\text{—CH}_2\text{—NH}_2 \)
4) \( \text{CH}_3\text{—C—O—H} \)
5) \( \text{CH}_3\text{—C—O—CH}_3 \)

### Alkanes

- **Functional group**: A way to classify families of organic compounds.
- **Alkanes**: The ONLY functional group in this class is alkyl.
  - Contain only C and H.
  - Have only single C—C bonds.
  - Have a general formula of \( \text{C}_n\text{H}_{2n+2} \).

<table>
<thead>
<tr>
<th>C Atoms</th>
<th>H Atoms</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2(1) + 2 = 4</td>
<td>( \text{CH}_4 )</td>
</tr>
<tr>
<td>3</td>
<td>2(3) + 2 = 8</td>
<td>( \text{C}_3\text{H}_8 )</td>
</tr>
<tr>
<td>6</td>
<td>2(6) + 2 = 14</td>
<td>( \text{C}<em>6\text{H}</em>{14} )</td>
</tr>
</tbody>
</table>

**International Union of Pure and Applied Chemistry**

- Greek prefixes indicate the number of carbon atoms in the chain
  - Penta (5), hexa (6), hepta (7)
- Suffix 'ane' indicates alkane

### Alkanes

- In plant and animal, e.g.
  - Waxy coating on cabbage leaves, \( \text{C}_{29}\text{H}_{60} \)

- Major sources:
  - Natural gas and petroleum deposits
  - From the decomposition of plant and animal matter
**Line-Bond Formulas**

- Because each C atom has a tetrahedral arrangement, the geometrical arrangement of carbon atoms is not a straight line.
- A line-bond formula abbreviates the carbon chain and shows only the zigzag pattern of bonds from carbon atom to carbon atom.

![Line-bond formula diagram]

**IUPAC System of Naming Alkanes**

- The IUPAC (International Union of Pure and Applied Chemistry) establishes the rules for naming organic compounds.
- Alkanes are named with –ane endings.
- The first four alkanes are **methane**, **ethane**, **propane**, and **butane**.
- The names of longer carbon chains use Greek prefixes such as **pent-** for 5 C atoms and **hex-** for 6 C atoms.

**Names of Continuous-Chain Alkanes**

![Table of continuous-chain alkanes]

- Table 12.1 IUPAC Names for the First Ten Continuous-Chain Alkanes
  
<table>
<thead>
<tr>
<th>Number</th>
<th>Carbon</th>
<th>Prefix</th>
<th>Name</th>
<th>Molecular Formula</th>
<th>Condensed Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td>CH₄</td>
<td>CH₄</td>
<td>CH₄</td>
<td>CH₄</td>
</tr>
<tr>
<td>2</td>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>CH₂CH₂</td>
<td>CH₃CH₂</td>
<td>CH₃CH₂</td>
</tr>
<tr>
<td>3</td>
<td>Propane</td>
<td>CH₃CH₂CH₃</td>
<td>CH₃CH₂CH₃</td>
<td>CH₃CH₂CH₃</td>
<td>CH₃CH₂CH₃</td>
</tr>
<tr>
<td>4</td>
<td>Butane</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₃</td>
</tr>
<tr>
<td>5</td>
<td>Pentane</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>6</td>
<td>Hexane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>7</td>
<td>Heptane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>8</td>
<td>Octane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>9</td>
<td>Nonane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>10</td>
<td>Decane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
</tbody>
</table>

*Table credits: General Organic and Biological Chemistry. Copyright © Pearson Education Inc., publishing as Benjamin Cummings.*
Learning Check
A. Give the name of each compound:
1) CH₃—CH₃
2) CH₃—CH₂—CH₃
3) CH₃—CH₂—CH₂—CH₂—CH₃

Alkanes
12.2 IUPAC Naming System for Alkanes
12.3 Drawing Structural Formulas

2,4-dimethylpentane

Branched-Chain Alkanes

- In a branched-chain alkane, a side group called a branch or a substituent is attached to a carbon chain.
Classification of Carbon Atoms

Carbon atoms are classified according to the number of attached carbon atoms.

- **Primary** (1°) bonds to one carbon atom.
- **Secondary** (2°) bonds to two carbon atoms.
- **Tertiary** (3°) bonds to three carbon atoms.

![Diagram of carbon atom classification]

Alkyl Groups

An alkyl group:

- Is composed of one or more carbon atoms attached to a carbon chain.
- Is derived from the corresponding alkane by removing one hydrogen.
- Is named by replacing the -ane ending of the corresponding alkane with -yl.
- Derived from methane is methyl and from ethane is ethyl.

![Table of alkyl groups]

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Name of Alkyl Group</th>
<th>Molecular Formula</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Methyl</td>
<td>CH₃</td>
<td>CH₃-CH₂-CH₃</td>
</tr>
<tr>
<td>Ethane</td>
<td>Ethyl</td>
<td>C₂H₅</td>
<td>CH₃-CH₂-CH₂-CH₃</td>
</tr>
</tbody>
</table>
Naming Branched-Chain Alkanes

In the IUPAC system:
1. The longest chain is named as the main chain.
2. Any carbon branches use their alkyl names.
3. Each branch is numbered by counting the main chain from the end nearest the first side group.
4. Branches are listed in alphabetical order.

Learning Check
Give the IUPAC name for each alkane.
A. \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \) 2,4-dimethylpentane
B. \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \) 5-ethyl-3,3-dimethylheptane

What Is In A Name?
Draw the structure from the IUPAC name.
2, 4-dimethylhexane
- Location of branches on main chain
- Two \( \text{CH}_3 \) groups attached
- 6 carbon main chain with single C-C bonds
Writing Isomers

The constitutional isomers for C₄H₁₀ can be written by first writing the continuous chain. Then remove one CH₃ and attach it as a branch.

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₃} \\
\text{CH₃} & \quad \text{CH₂} & \quad \text{CH₂} & \quad \text{CH₃} & \quad \text{CH₃}
\end{align*}
\]

Butane 2-Methylpropane

Learning Check

Write 3 constitutional isomers of C₅H₁₂ and name each.

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₃} & \quad \text{CH₂} & \quad \text{CH₂} & \quad \text{CH₃} & \quad \text{pentane} \\
\text{CH₃} & \quad \text{CH₃} & \quad \text{CH₂} & \quad \text{CH₂} & \quad \text{CH₃} & \quad \text{2-methylbutane} \\
\text{CH₃} & \quad \text{CH₃} & \quad \text{CH₂} & \quad \text{CH₂} & \quad \text{CH₃} & \quad \text{2,2-dimethylpropane}
\end{align*}
\]

Cycloalkanes

Cycloalkanes:
- Are rings of carbons that can be drawn as geometric figures.
- Have a general formula of CₙH₂ₙ or 2 H less than the alkane.
- Are named with the prefix cyclo- in front of the corresponding alkane name.
Formulas of Cycloalkanes

Naming Cycloalkanes
A cycloalkane with:
- One substituent is named by placing the name of the substituent in front of the cycloalkane name.
- Two or more substituents is named by numbering the ring in the direction that gives the lower numbers to the substituents.

Cycloalkanes with Side Groups

- methylcyclopentane
- 1,2-dimethylcyclopentane
- 1,2,4-trimethylcyclohexane
Constitutional Isomers

- The rigid ring in a cyclic structure prevents rotation of substituents bonded to the ring.
- A cyclic structure with two substituents has two isomers called cis-trans isomers.
- The cis isomer has two substituents on the same side of the ring.
- The trans isomer has two substituents on opposite sides of the ring.

Cis-Trans Isomers

- The compound 1,2-dimethylcyclopropane has cis-trans isomers.

Physical Properties of Alkanes

Alkanes, including cycloalkanes:
- Are nonpolar and insoluble in water.
- Have densities between 0.65 – 0.70 g/mL; they float on water.
- Have low melting and boiling points compared to other families of organic compounds.
Boiling Points of Alkanes

Boiling points:

- Increase in larger alkane molecules due to increased dispersion forces.
- Are lower for branched alkanes because they have fewer contact points.
- Are higher for cycloalkanes because their rigid structures allow more contact and attraction between molecules.

Uses of Alkanes

- Methane, ethane, propane, and butane are gases at room temperature and used as fuels.
- Alkanes with 5-17 carbon atoms are liquids and found in gasoline, diesel, and jet fuels.
- Alkanes with 18 or more carbon atoms are solids and found in the waxy coatings of fruits and vegetables.

Chemical Properties of Alkanes

- Alkanes are typically not very reactive due to strong C-C single bonds.
- The most typical reaction is combustion, where an alkane reacts with oxygen to produce carbon dioxide, water, and energy.

\[
\text{alkane} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{energy}
\]

A fuel such as propane reacts with oxygen and burns, producing CO₂ and H₂O and energy, useful for cooking or warming a room.
Halogenation of Alkanes (Substitution)

- When alkanes react with halogens, a mixture of halogenated products is produced.
- In a reaction called substitution, one or more H atoms are replaced with a halogen usually Cl or Br.
- The equation for the reaction of ethane and chlorine to give the monosubstituted product is
  \[
  \text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl}
  \]

Common uses of halogenated alkanes: solvent, anesthetics, dry cleaning, etc.

Haloalkanes

- In IUPAC names, a halogen is named as fluoro, chloro, bromo, or iodo.
- \(\text{CH}_3\text{Br}\)  bromomethane (methyl bromide)
- \(\text{CH}_2\text{CH}_2\text{Cl}\)  2-chlorobutane (sec-butyl chloride)

Haloalkanes

- Methane compounds with two or more chlorine atoms are sometimes named by common names that do not reflect their structures.
Learning Check

Give the structures and names of the monosubstituted products for the reaction of propane with bromine in the presence of light.

\[
\begin{align*}
\text{CH}_3\text{—CH—CH}_2\text{—Br} & \quad \text{1-bromopropane} \\
& \quad \text{Br} \\
& \quad \text{CH}_3\text{—CH—CH}_2 \\
& \quad \text{2-bromopropane}
\end{align*}
\]

The name of this compound is:

1) 2,4-dimethylhexane
2) 3-chloro-5-methylhexane
3) 4-chloro-2-methylhexane

Two or more substituents are named in alphabetical order.

\[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{CH}_3\text{—CH—CH—CH—CH—CH}_3 & \\
& \quad \text{4-bromo-2-chlorohexane}
\end{align*}
\]
Give the IUPAC name for each.

A. CH₃CH₂—F

\[
\begin{array}{c}
\text{Br} \\
\text{Cl}
\end{array}
\]

fluoroethane

B. CH₃—CH—CH—CH₃

2-bromo-3-chlorobutane

Learning Check

Halothane is widely used as an anesthetic, which is a compound that decreases the ability of the nerve cells to conduct pain. What is the IUPAC name of halothane?

\[
\begin{array}{c}
\text{F} \\
\text{Br} \\
\text{F—C—C—Cl} \\
\text{F} \\
\text{H}
\end{array}
\]

2-bromo-2-chloro-1,1,1-trifluoroethane

Learning Check

Name each as a cis or trans isomer.

trans-1,2-dibromocyclopropane

cis-1,3-dichlorocyclobutane

trans-1-bromo-3-chlorocyclopentane
The ozone (O₃) layer in the atmosphere absorbs most of the sun’s harmful radiation.

- Chlorofluorocarbons (CFCs) cause reactions that destroy the ozone layer.
- CFCs such as Freon-12 (CF₂Cl₂) have been used in refrigeration, air conditioning, and foam insulation.
- The use of CFCs in spray cans is no longer allowed.

Chlorofluorocarbons and Ozone

- In the stratosphere, the CFCs are cleaved by the high-energy UV radiation from the sun.

\[ \text{CF}_2\text{Cl}_2 \xrightarrow{\text{UV light}} \text{CF}_2\text{Cl} + \text{Cl} \]

The Cl reacts with ozone (O₃). The ClO produced destroys another O₃ forming additional Cl. Thus one Cl can destroy many O₃ molecules.

\[ \text{Cl} + \text{O}_3 \quad \text{ClO} + \text{O}_2 \]
\[ \text{ClO} + \text{O}_3 \quad \text{Cl} + 2\text{O}_2 \]

Impact of Loss of Ozone

- According to the National Academy of Sciences, each 1% loss of ozone (O₃) increases the amount of UV radiation reaching the earth by 2%.
- More UV radiation means more skin cancer and cataracts in humans, more intense photochemical smog, and lower crop yields.
Saturated Hydrocarbons

Saturated hydrocarbons:
- Have the maximum number of hydrogen atoms attached to each carbon atom.
- Are alkanes and cycloalkanes with single C-C bonds.

\[ \text{CH}_3-\text{CH}_2-\text{CH}_3 \]

Unsaturated Hydrocarbons

Unsaturated hydrocarbons:
- Have fewer hydrogen atoms attached to the carbon chain than alkanes.
- Are alkenes with double bonds
- or alkynes with triple bonds.

Alkenes Have Double Bonds

In a double bond:
- One pair of electrons form a strong sigma (\(\sigma\)) bond.
- One pair of electrons in adjacent \(p\) orbitals overlap to form a \(\pi\) (\(\pi\)) bond.
Alkynes have Triple Bonds

In a triple bond:
- One pair of electrons form a strong sigma (σ) bond.
- Two pairs of electrons in adjacent π orbitals overlap to form two π (π) bonds.

Bond Angles in Alkenes and Alkynes

According to VSEPR theory:
- The three groups bonded to carbon atoms in a double bond are at angles of 120°.
- The two groups bonded to each carbon in a triple bond are at angles of 180°.

Naming Alkenes and Alkynes

- In the IUPAC system, the –ane ending of the corresponding alkane is changed to –ene for alkenes and to –yne for alkynes.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Alkene</th>
<th>Alkyne</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)C(=)CH(_2)</td>
<td>Ethene</td>
<td>Ethyne</td>
</tr>
<tr>
<td>H(_2)C(=)CH</td>
<td>Ethene (ethylene)</td>
<td>Ethyne (acetylene)</td>
</tr>
<tr>
<td>CH(_3)(=)CH(_2)</td>
<td>Propene</td>
<td>Propane</td>
</tr>
<tr>
<td>CH(_2)(=)CH(_2)</td>
<td>Propene</td>
<td>Propane</td>
</tr>
<tr>
<td>CH(_2)(=)CH (_2)</td>
<td>Propene</td>
<td>Propane</td>
</tr>
<tr>
<td>CH(_2)(=)CH</td>
<td>Propene</td>
<td>Propane</td>
</tr>
</tbody>
</table>
When the carbon chain has 4 or more C atoms, the chain is numbered to give the lowest number to the double or triple bond.

1. \( \text{CH}_2=\text{CH} \cdots \text{CH}_3 \) → 1-butene
2. \( \text{CH}_3 \cdots \text{CH}=\text{CH} \cdots \text{CH}_3 \) → 2-pentene
3. \( \text{CH}_3 \cdots \text{CH}_2 \cdots \text{C≡C} \cdots \text{CH}_2 \cdots \text{CH}_3 \) → 3-hexyne

### Learning Check

Write the IUPAC name for each:

A. \( \text{CH}_3 \cdots \text{CH} \cdots \text{C≡C} \cdots \text{CH}_3 \) → 2-pentyne

B. \( \text{CH}_3 \cdots \text{C}=\text{CH} \cdots \text{CH}_3 \) → 2-methyl-2-butene

C. \( \text{CH}_3 \)

### Cis-Trans Isomers

- There is no rotation around the double bond in alkenes.
- Groups attached to the double bond are fixed relative to each other.
- You can make a “double bond” with your fingers with both thumbs on the same side or opposite from each other.
Two isomers are possible when groups are attached to the double bond.

- In a cis isomer, groups are attached on the same side of the double bond.
- In the trans isomer, the groups are attached on opposite sides.

Insects emit tiny quantities of pheromones, which are chemicals that send messages. The silkworm moth attracts other moths by emitting bombykol, which has one cis and one trans double bond.

The prefixes cis or trans are placed in front of the alkene name when there are cis-trans isomers.
**Cis-Trans Isomerism**

Alkenes cannot have cis-trans isomers if a carbon atom in the double bond is attached to identical groups.

- **Identical**
  - 2-bromopropene
  - 1,1-dibromoethene

**Learning Check**

Name each, using cis-trans prefixes when needed.

- **A.**
  - cis-1,2-dibromoethene
  - trans-2-butene

- **B.**
  - 1,1-dichloropropene

**Addition Reactions**

- The pi (π) bond is easily broken, which makes double and triple bonds very reactive.
  - In the addition reaction, reactants are added to the carbon atoms in the double or triple bond.
In hydrogenation, hydrogen atoms add to the carbon atoms of a double bond or triple bond.

A catalyst such as Pt or Ni is used to speed up the reaction.

\[
\text{Hydrogenation} \quad \text{HC} = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{Pt}} \text{H}_2\text{C} = \text{CH}_2 \\
\text{HC} \equiv \text{CH} + 2\text{H}_2 \xrightarrow{\text{Ni}} \text{H}_2\text{C} \equiv \text{CH} 
\]

In halogenation, halogen atoms add to the carbon atoms of a double bond or triple bond.

\[
\text{Halogenation} \quad \text{H}_2\text{C} = \text{CH}_2 + \text{Br}_2 \rightarrow \text{H}_2\text{C} \equiv \text{CH}_2 \\
\text{HC} \equiv \text{C} - \text{CH}_3 + 2\text{Cl}_2 \rightarrow \text{H} - \text{C} - \text{C} - \text{CH}_3 
\]

Testing for Double and Triple Bonds

- When bromine (Br₂) is added to an alkane, the red color of bromine persists.
- When bromine (Br₂) is added to an alkene or alkyne, the red color of bromine disappears immediately.
Learning Check

Write the product of each addition reaction:

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

\[ + \text{Br}_2 \rightarrow \]

Hydrohalogenation

In hydrohalogenation, the atoms of a hydrogen halide add to the carbon atoms of a double bond or triple bond.

\[ \text{HCl} + \text{CH}_3\text{CH=CH—CH}_3 \rightarrow \text{ClCH}_2\text{CH=CH—CH}_3 \]

\[ + \text{HBr} \rightarrow \]

Markovnikov's Rule

When an unsymmetrical alkene undergoes hydrohalogenation, the H in HX adds to the carbon in the double bond that has the greater number of H.

\[ \text{Cl} + \text{CH}_2\text{=CH—CH}_2 \rightarrow \text{Does not form} \]

\[ \text{H} + \text{CH}_2\text{=CH—CH}_2 \rightarrow \text{Product that forms} \]
Hydration Adds Water

- In hydration, H and OH from water add to the carbon atoms of a double bond to form alcohols (OH).
- The reaction is catalyzed by acid H⁺.

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

Learning Check

Write the products of each reaction.

A. \( \text{CH}_3\text{CH}≡\text{CH}_2 + \text{Cl}_2 \)

B. \( \text{CH}_3\text{CH}≡\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \)

C. \( \text{C} + \text{H}_2 \xrightarrow{\text{Pt}} \)

Polymerization

- In polymerization, small repeating units called monomers are bonded to form a long chain polymer.

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

Ethylene monomers

Repeating monomer

Chain continues...

Polyethylene
Learning Check

What is the starting monomer for polyvinyl chloride (PVC)?

\[
\begin{align*}
\text{Polyvinyl chloride} & \quad \begin{array}{c}
\text{C} = \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{array} \\
\text{Chloroethene monomers} & \quad \begin{array}{c}
\text{C} = \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{array}
\end{align*}
\]
Polymers

Any of numerous natural and synthetic compounds of usually high molecular weight consisting of up to millions of repeated linked units, each a relatively light and simple molecule.

Benzene is an aromatic compound:
- A ring of 6 C atoms and 6 H atoms.
- A flat ring structure drawn with double bonds.
- Represented by two structures because the electrons move among the C atoms.

Aromatic Compounds

Benzene Structure

- Because the pi electrons in benzene are shared equally among the 6 C atoms, benzene can also be represented as a hexagon with a circle drawn inside.
Aromatic Compounds in Nature and Medicine

Some substituted benzene rings have common names that have been in use for many years.

- Toluene (Methylbenzene)
- Aniline (Benzenamine)
- Phenol (Hydroxybenzene)

A benzene with a single substituent is often named as a benzene derivative.

Methylbenzene
Chlorobenzene

Some Common Names

Naming Aromatic Compounds

Aromatic Compounds are common in natural and medicinal systems. Aromatic compounds are the building blocks of proteins in all living systems and are important in the formation of natural substances.
A benzene ring with two or more substituents is numbered to give the lowest numbers to the side groups.

Common names use the prefixes ortho- (1,2-), meta- (1,3-) and para- (1,4-).

1,2-dimethylbenzene  1,3-dichlorobenzene  4-chloromethylbenzene
(o-dibromobenzene)  (m-dichlorobenzene)  (p-chlorotoluene)

Select the correct name for each structure:

1) chlorocyclohexane  2) chlorobenzene  3) 1-chlorobenzene
4) 1,3-dichlorobenzene  5) o-dichlorobenzene  6) m-dichlorobenzene

Write the structural formula for each:

A. 1-bromo-4-chlorobenzene
B. o-chlorotoluene
Properties of Aromatic Compounds

Aromatic compounds:
- Have a stable aromatic bonding system.
- Are resistant to many reactions.
- Undergo substitution reactions, which retains the stability of the aromatic bonding system.

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{Cl}_2, \text{FeCl}_3} \text{Chlorobenzene} \\
\end{align*}
\]

Substitution Reactions

In a substitution reaction, a hydrogen atom on a benzene ring is replaced by an atom or group of atoms.

<table>
<thead>
<tr>
<th>Type of substitution</th>
<th>H on benzene replaced by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogenation</td>
<td>chlorine or bromine atom</td>
</tr>
<tr>
<td>Nitration</td>
<td>nitro group (—NO\textsubscript{2})</td>
</tr>
<tr>
<td>Sulfonation</td>
<td>—SO\textsubscript{3}H group</td>
</tr>
</tbody>
</table>

Halogenation

- Halogenation replaces a H on benzene by a chlorine or bromine atom.
- A catalyst such as FeCl\textsubscript{3} is used in chlorination; FeBr\textsubscript{3} in bromination.

\[
\begin{align*}
\text{Benzene} + \text{Cl}_2 & \xrightarrow{\text{FeCl}_3} \text{Chlorobenzene} + \text{HCl} \\
\end{align*}
\]
Nitration replaces a H on benzene by a nitro (—NO₂) group from HNO₃. An acid catalyst such as H₂SO₄ is used in nitration.

\[
\text{Benzene} + \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Nitrobenzene} + \text{H}_{2}\text{O}
\]

Sulfonation replaces a H on benzene by a —SO₃H group from SO₃. An acid catalyst such as H₂SO₄ is used in sulfonation.

\[
\text{Benzene} + \text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Benzenesulfonic acid} + \text{H}_2\text{O}
\]

Learning Check

Write the equation for the bromination of benzene, including catalyst.

\[
\text{Benzene} + \text{Br}_2 + \text{FeBr}_3 \rightarrow \text{BenzeneBr} + \text{HBr}
\]