Chapter 18 Organic Chemistry I: The Hydrocarbons

Aliphatic Hydrocarbons (Sections 18.1–18.7)

Key Concepts

hydrocarbons, types of hydrocarbons, aliphatic hydrocarbon, aromatic hydrocarbon, condensed structural formula, line structure, saturated hydrocarbon, unsaturated hydrocarbon, nomenclature of hydrocarbons, alkanes, cycloalkanes, alkenes, alkynes, isomers, structural isomers, connectivity, conformations, stereoisomers, geometrical isomers, optical isomers, chiral molecule, enantiomers, achiral molecule, racemic mixture, properties of alkanes, alkane substitution reactions, functionalization, properties of alkenes, elimination reactions, dehydrohalogenation reactions, electrophilic addition to alkenes, addition reactions, halogenation, hydrohalogenation, electrophile

Overview

• Hydrocarbons
  → Compounds containing only carbon and hydrogen (Study Guide, Section 3.7)
  → Hydrocarbons without benzene rings are aliphatic.
  → Saturated hydrocarbons with no multiple bonds are alkanes.
  → Unsaturated hydrocarbons with at least one double bond are alkenes and with at least one triple bond are alkynes.
  → Hydrocarbons with benzene rings are aromatic.
  → Complex molecules often have “aromatic parts” and “aliphatic parts.”

18.1 Types of Aliphatic Hydrocarbons

• Structural formula and line structure

<table>
<thead>
<tr>
<th>Example 18.1a</th>
<th>Write the structural formula and the line structure of NH₂CH₂CH₂OH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Answer</td>
<td>NH₂–CH₂–CH₂–OH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 18.1b</th>
<th>Write line structures for butane, 1-butene, and 1-butyne. The number indicates the position of the multiple bond.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Answer</td>
<td>Butane                                             1-Butene                1-Butyne</td>
</tr>
</tbody>
</table>

• Naming alkanes

<table>
<thead>
<tr>
<th>Example 18.1c</th>
<th>What is the name of the alkane CH₃(CH₂)₈CH₃?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>The alkane is unbranched with a total of 10 carbon atoms. The stem name is obtained by combining the prefix for ten (dec-) with the alkane suffix -ane to get the name decane.</td>
</tr>
</tbody>
</table>
Example 18.1d  What is the name of the branched alkane $\text{CH}_3(\text{CH}_2)_2\text{C(CH}_3)_2\text{CH}_2\text{CH}_3$?

Solution  The first step is to number the carbons of the longest carbon chain so that the substituents appear on the lowest numbered carbons.

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

The longest carbon chain contains six carbons, so the compound is a hexane. There are two methyl groups on carbon number 3. Combining all the information gives the name 3,3-dimethylhexane.

Example 18.1e  What is the name of the alkane $\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CH(CH}_2\text{CH}_3\text{)}\text{CH(CH}_3\text{)}\text{CH}_3$?

Answer  3-ethyl-2,4-dimethylhexane

- Naming alkenes

Example 18.1f  What is the name of the branched alkene $\text{CH}_3(\text{CH}_2)_2\text{C(CH}_3)\text{=}\text{CHCH}_3$?

Solution  The first step is to number the carbons of the longest carbon chain so that the double bond appears on the lowest numbered carbons.

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

The longest carbon chain contains six carbons, so the compound is a hexene. There is one methyl group on carbon number 3. Combining all the information gives the name 3-methyl-2-hexene.

Note: The location of the double bond is not numbered in the two unambiguous cases ethene, $\text{CH}_2\text{=}\text{CH}_2$, and propene $\text{CH}_3\text{CH=CH}_2$. The molecule 1-butene, $\text{CH}_3\text{=CHCH}_2\text{CH}_3$, is different than 2-butene, $\text{CH}_3\text{CH=CHCH}_3$.

Example 18.1g  What is the name of the alkene $\text{CHCl}_2\text{CH}_2\text{C(CH}_3\text{)}\text{=}\text{CHCH}_3$?

Answer  5,5-dichloro-3-methyl-2-pentene

(low number for the double bond takes precedence)

Example 18.1h  What is the name of the alkene $\text{CH}_3\text{CH=CHCH}_2\text{CH=CH}_2$?

Solution  The molecule contains two double bonds and six carbon atoms in a chain, so this compound is a hexadiene. Two numbers are required to locate the double bonds. The name with the lowest numbers is 1,4-hexadiene.

- Naming alkynes

Example 18.1i  What is the name of the branched alkyne $\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{C=CHCH}_3$?

Solution  The first step is to number the carbons of the longest carbon chain so that the triple bond appears on the lowest numbered carbons.

\[ \text{CH}_3 \]
\[ \text{CH}_3-\text{CH}_2-\text{CH=C=C=CH}_3 \]
The longest carbon chain contains six carbons, so the compound is a hexyne. There is one methyl group on carbon number 4. Combining all the information gives the name 4-methyl-2-hexyne.

**Note:** The location of the triple bond is not numbered in the two unambiguous cases ethyne, CH≡CH, and propyne CH₂C≡CH. The molecule 1-butyne, CH≡CCH₂CH₃, is different than 2-butyne, CH₃C≡CCH₃.

**Example 18.1j** What is the name of the alkyne CHCl₂CH(CH₃)C≡CH₃?

**Answer** 5,5-dichloro-4-methyl-2-pentyne (low number for the triple bond takes precedence)

**Example 18.1k** What is the name of the alkyne CH₃C≡CCH₂C≡CH?

**Solution** The molecule contains two triple bonds and six carbon atoms in a chain, so this compound is a hexadiyne. Two numbers are required to locate the triple bonds. The name with the lowest numbers is 1,4-hexadiyne.

**Note:** A molecule with a double and triple bond is 1-butene-3-yne, CH₂=CH−C≡CH, with the lowest number given preferentially to the location of the double bond.

### 18.2 Isomers

- **Structural isomers**

**Example 18.2a** Without referring to the text, draw all the structural isomers that have the formula C₅H₁₂.

**Solution** First draw the different possible arrangements of five carbon atoms then add the required hydrogen atoms. Start with the five carbons bonded in a straight chain, and then move one or more of the carbons to branched positions. Arrangements that may be interconverted by rotating the carbon framework are *not* structural isomers. The three possible carbon frameworks are

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

Three other structures may be drawn that are equivalent to the center one. These are *not* different structural isomers. They are formed by rotating the center structure. The three “rotated” structures shown are ignored.

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

To complete the drawings of the three structural isomers, add the 12 hydrogen atoms and recall that each carbon atom must have four bonds. For clarity, the branched C–C bonds are stretched.
Example 18.2b The carbon frameworks for six alkanes with the formula $\text{C}_6\text{H}_{14}$ are shown in the figure. Which are distinct structural isomers and which represent the same compound?

\[ \text{C–C–C–C–C–C} \quad \text{C–C–C–C–C–C} \quad \text{C–C–C–C–C–C} \]

I  II  III

\[ \text{C–C–C–C–C} \quad \text{C–C–C–C–C} \quad \text{C–C–C–C–C} \]

IV  V  VI

Answer I, II, IV, and V are distinct; I and III are the same; IV and VI are the same.

- Geometrical isomers

Example 18.2c Draw stick structures for the two geometrical isomers of 3-hexene.

Solution The double bond in 3-hexene is located on carbon 3. There is an ethyl group attached to carbon 3 and another to carbon 4. These two groups may be arranged in either a cis or trans fashion. The two isomers are

\[ \text{cis-3-hexene} \quad \text{trans-3-hexene} \]

Note: Remember that the restriction on rotation applies only to the C=C bond. The C–C single bonds are not restricted and relatively free rotation about them can occur. Also, if three of the four groups (or all four) bonded to the double-bonded carbon atoms are the same, then cis-trans isomers are not possible.

- Chiral properties

Example 18.2d Test each of the following organic molecules for chiral properties.

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

I  II  III

Solution In molecule I, the second carbon atom from the right has four different groups attached to it (ethyl, methyl, chloro, and bromo) and constitutes the stereogenic center. Molecule I is chiral. In molecule II, each carbon atom has at least two of the same groups attached. Molecule II is achiral. In molecule III, the second carbon atom from the left has four different groups attached to it (methyl, ethyl, bromo, and a hydrogen atom). Molecule III is chiral.
Example 18.2e  Draw a stick structure for the chiral molecule, 3-methylhexane, and identify the stereogenic center.

Solution  The stick structure is 3. Carbon atom 3 has four different groups attached to it (ethyl, propyl, methyl, and a hydrogen atom), and constitutes the stereogenic center.

18.3 Properties of Alkanes

Example 18.3  Describe the physical and chemical properties of alkanes. Also, provide an example of a substitution reaction.

Solution  An alkane with a long, unbranched chain tends to have a higher melting point, boiling point, and heat of vaporization than its branched structural isomer. Molecules with unbranched chains can get closer together than molecules with branched chains. As a result, molecules with branched chains have weaker intermolecular forces than their isomers with unbranched chains. As an example, butane containing an unbranched chain has a higher boiling point (−0.5°C) than its structural isomer, methylpropane, containing a branched chain (−11.6°C).

Alkanes are not very reactive chemically. They were once called paraffins, derived from the Latin “little affinity.” Alkanes are unaffected by concentrated sulfuric acid, by boiling nitric acid, by strong oxidizing agents such as potassium permanganate, and by boiling aqueous sodium hydroxide. The C–C bond enthalpy, 348 kJ⋅mol⁻¹, and the C–H bond enthalpy, 412 kJ⋅mol⁻¹, are large, so there is little energy advantage in replacing them with most other bonds. Notable exceptions are C=O, 743 kJ⋅mol⁻¹, C–OH, 360 kJ⋅mol⁻¹, and C–F, 484 kJ⋅mol⁻¹.

Reaction of methane, CH₄, and chlorine, Cl₂, is an example of a substitution reaction. In the presence of ultraviolet light or temperatures above 300°C, the gases react explosively:

\[
\text{CH}_4(g) + \text{Cl}_2(g) \xrightarrow{\text{light or heat}} \text{CH}_3\text{Cl}(g) + \text{HCl}(g)
\]

Chloromethane, CH₃Cl, is one of four products; the others are dichloromethane, CH₂Cl₂, trichloromethane, CHCl₃, and tetrachloromethane, CCl₄. The properties and uses of the chloromethanes are given in the following table.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Common name</th>
<th>Boiling point</th>
<th>Dipole moment</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Cl</td>
<td>methyl chloride</td>
<td>−24.2°C</td>
<td>1.87 D</td>
<td>refrigerant</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>methylene chloride</td>
<td>40°C</td>
<td>1.60 D</td>
<td>dry cleaning agent</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>chloroform</td>
<td>61.7°C</td>
<td>1.01 D</td>
<td>anesthetic</td>
</tr>
<tr>
<td>CCl₄</td>
<td>carbon tetrachloride</td>
<td>76.8°C</td>
<td>0</td>
<td>nonpolar solvent</td>
</tr>
</tbody>
</table>

Note: Tetrachloromethane is carcinogenic and its use is restricted. It once was used as a nonflammable fluid in certain fire extinguishers.
18.4 Alkane Substitution Reactions

Example 18.4  Describe the radical chain mechanism for the reaction of chlorine and methane gases.

Solution  Kinetic studies of the rate of the chlorine substitution reaction, as affected by concentration, catalyst, solvent, and temperature, suggest that alkane substitution reactions proceed by a radical chain mechanism (see Chapter 13). The initiation step is the dissociation of chlorine:

\[ \text{Cl}_2 \xrightarrow{\text{light or heat}} 2 \text{Cl}. \]

Chlorine atoms proceed to attack methane molecules and extract a hydrogen atom:

\[ \text{Cl} \cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot \text{CH}_3 \]

Because one of the products is a radical, this reaction is a propagation step. In a second propagation step, the methyl radical may react with a chlorine molecule:

\[ \text{Cl}_2 + \cdot \text{CH}_3 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}. \]

The chlorine atom formed may take part in the other propagation step or attack a CH\(_3\)Cl molecule to eventually form CH\(_2\)Cl\(_2\). A termination step occurs when two radicals combine to form a nonradical product, as in the reaction:

\[ \text{Cl} \cdot + \cdot \text{CH}_3 \rightarrow \text{CH}_3\text{Cl} \]

The substitution reaction is not very clean and the product is usually a mixture of compounds. One may limit the production of the more highly substituted alkanes by using a large excess of the alkane.

18.5 Properties of Alkenes

Example 18.5  Describe the properties of double bonds and give an example of an elimination reaction.

Solution  The carbon-carbon double bond, C=C, consists of a \(\sigma\)-bond and a \(\pi\)-bond. Each carbon atom is \(sp^2\) hybridized and one of the hybrid orbitals is used to form the \(\sigma\)-bond. The unhybridized \(p\)-orbitals on each atom overlap with each other to form a \(\pi\)-bond. All four atoms attached to the C=C group lie in the same plane and are fixed into that arrangement by the resistance to twisting of the \(\pi\)-bond (see Fig. 18.7 in the text). Alkene molecules cannot roll up into a compact arrangement as alkanes can, so alkenes have lower melting points. In C=C, the \(\pi\)-bond is weaker than the \(\sigma\)-bond (see Chapter 3). A consequence of this weakness is the reaction most common in alkenes, the replacement of the \(\pi\)-bond by two new \(\sigma\)-bonds.

In the petrochemical industry, abundant alkanes are converted to more reactive alkenes by a catalytic process called dehydrogenation:

\[ \text{CH}_3\text{CH}_3(g) \xrightarrow{\text{CrO}_2} \text{CH}_2=\text{CH}_2(g) + \text{H}_2(g) \]

This is an example of an elimination reaction, a reaction in which two groups or two atoms on neighboring carbon atoms are removed from a molecule, leaving a multiple bond (see Fig. 18.8 in the text).

18.6 Electrophilic Addition

Example 18.6  Estimate the reaction enthalpy for the hydrobromination reaction:

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

Solution  The following bonds are broken: C=C and H–Br.

\[ \sum n \Delta H_{\text{f}}(\text{bonds broken}) = 612 + 366 = 978 \text{ kJ}\text{mol}^{-1} \]
The following bonds are formed: C–C, C–H, and C–Br.
\[ \sum n \Delta H_b \text{(bonds formed)} = 348 + 412 + 276 = 1036 \text{ kJ mol}^{-1} \]
The final result is: \( \Delta H^\circ \approx 978 - 1036 = -58 \text{ kJ mol}^{-1} \)

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**Aromatic Compounds (Sections 18.7–18.8)**

**Key Concepts**
- arenes, nomenclature of arenes, aromatic hydrocarbons, benzene, phenyl group, naphthalene, anthracene, ring numbering, electrophilic substitution, mechanism

**Overview**
- **Definition**
  - Aromatic hydrocarbons are called *arenes*.
  - *Benzene*, \( \text{C}_6\text{H}_6 \), is the parent compound. The benzene ring is sometimes called the *phenyl* group, as in 2-phenyl-trans-2-butene, \( \text{CH}_3\text{C} \left( \text{C}_6\text{H}_5 \right) =\text{CHCH}_3 \).
  
  ![Benzene structure](image)

  \[ \begin{align*}
  &\text{1} \\
  &\text{2 (ortho)} \\
  &\text{3 (meta)} \\
  &\text{4 (para)} \\
  &\text{5} \\
  &\text{6}
  \end{align*} \]

- Aromatic compounds include those with fused benzene rings, such as naphthalene, \( \text{C}_{10}\text{H}_8 \), anthracene, \( \text{C}_{14}\text{H}_{10} \), and phenanthrene, \( \text{C}_{14}\text{H}_{10} \).

![Aromatic Compounds](image)

**18.7 Nomenclature of Arenes**

**Example 18.7** Describe the benzene ring numbering system and name the three possible dichlorobenzene molecules.

**Solution** Substituents on the benzene ring are designated by numbering the carbon atoms from 1 to 6 around the ring. Compounds are named by counting around the ring in the direction that gives the smallest numbers to the substituents. It is also common to use the prefixes, *ortho-, meta-,* and *para-* to denote substituents at carbon atoms 2, 3, and 4, respectively, relative to another substituent at carbon atom 1.
The three possible dichlorobenzene molecules are:

![Chemical structures of 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, and 1,4-Dichlorobenzene]

1,2-Dichlorobenzene  
1,3-Dichlorobenzene  
1,4-Dichlorobenzene

*ortho*-Dichlorobenzene  
*meta*-Dichlorobenzene  
*para*-Dichlorobenzene

Note: Numbering carbon atoms in fused ring systems is somewhat more complicated and is not covered in the text

### 18.8 Electrophilic Substitution

**Example 18.8** Describe substitution reactions of arenes.

**Solution** *Arenes* have delocalized $\pi$-electrons; but, unlike alkenes, arenes undergo predominantly *substitution* reactions, with the $\pi$-bonds of the ring unaffected. The reaction of benzene, $C_6H_6$, with chlorine produces chlorobenzene when one chlorine atom substitutes for a hydrogen atom:

$$C_6H_6 + Cl_2 \xrightarrow{Fe} C_6H_5Cl + HCl$$

The mechanism of substitution of a benzene ring is an electrophilic attack, so the reaction is called *electrophilic substitution*. The substitution reactions discussed in the text are halogenation, nitration, ortho- and para-directing activators, ortho- and para-directing deactivators, and meta-directing deactivators.

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### Impact on Materials: Fuels (Sections 18.9–18.10)

**Key Concepts**

gasoline, petroleum, fractional distillation, gasoline fraction, cracking, alkylation, octane rating, isomerization, aromatization, ethanol, coal, anaerobic conditions, coalification process, coal gas, coal tar, benzene, naphthalene

**Overview**

- **Gasoline**
  - Hydrocarbons in petroleum are separated by fractional distillation.
  - Petroleum is refined to increase the *quantity* and *quality* of the gasoline fraction ($C_5$ to $C_{11}$ hydrocarbons).
→ **Quantity** is increased by *cracking* (breakdown long hydrocarbon chains) and *alkylation* (combining small molecules to make larger ones).

→ **Quality** of gasoline is measured by the *octane number*, which is improved by increasing the branching of the molecules and by introducing unsaturation and rings.

→ In *isomerization*, straight chain hydrocarbons are converted into branched-chain isomers.

→ In *aromatization*, an *alkane* is converted into an *arene*.

→ *Ethanol* is used to reduce the demand for petroleum.

- **Coal**

  → End product of anaerobic decay of vegetable matter

  → Less environmentally friendly than gasoline, in part because it releases ash when burned

  → Contains many aromatic rings, and is primarily aromatic in nature

  → Fragments when heated in the absence of oxygen to yield coal tar which contains many aromatic hydrocarbons and their derivatives, consequently, coal is used as a raw material for other chemicals

  → Many pharmaceuticals, fertilizers and dyes are derived from coal tar.

  → Examples are naphthalene used for making indigo dyes (for blue jeans) and benzene used to make nylon, detergents and pesticides.