## HISTORY OF ORGANIC CHEMISTRY

- In the early days of chemistry, scientists classified chemical substances into 2 groups:
  - 1. **Inorganic**: those that were composed of **minerals**, such as rocks and nonliving matter.
  - 2. **Organic**: those that were produced by **living organisms**, hence the name "organic".
- At the time, scientists believed that a "vital force", only present in living organisms, was necessary to produce organic compounds.
- In 1828, German chemist **Friedrick Wöhler** disproved this theory by producing urea, an organic compound found in urine, from inorganic compounds.



• Now **organic** chemistry is defined as the study of compounds containing **carbon atom**. There are currently about 10 million organic compounds known to man.



Aspirin

Sulfa drug

Some examples of organic molecules

# **PROPERTIES OF ORGANIC COMPOUNDS**

• **Organic** compounds differ from **inorganic** compounds in many ways. The table below summarizes these differences.

	A Comparison of Properties of Organic and Inorganic Compounds			
Property		Organic Compounds	Inorganic Compounds	
•	Bonding within molecule	Usually covalent	Mostly ionic	
•	Forces between molecules	Generally weak	Very strong	
•	Physical states	Gas, liquids, or low melting solids	High melting solids	
•	Flammability	Often flammable	Nonflammable	
•	Solubility in water	Often low	Often high	
•	Conductivity of aqueous solutions	Nonconductor	Conductor	
•	Rate of chemical reactions	Usually slow	Usually fast	

## **Examples:**

1. Identify each compound below as organic or inorganic:

A)  $CaCl_2$  B)  $C_4H_{10}$  C)  $C_2H_5Cl$  D)  $Na_2CO_3$ 

- 2. Match the following properties with the compounds ethane,  $C_2H_6$  or sodium bromide, NaBr.
  - a) boils at –89°C
  - b) burns vigorously
  - c) dissolves in water
  - d) solid at 250°C

## STRUCTURE OF ORGANIC COMPOUNDS

• An **expanded structural formula** shows all the **atoms present** in a molecule and the **bonds** that connect them together. For example:



• A **condensed structural formula** shows the arrangement of the atoms, but shows each carbon atom and its attached hydrogen atoms as a group. For example:



• A stick formula is a short-hand method of showing large and complex molecules easily. In these diagrams the non-terminal carbon atoms are displayed as joints and the non-terminal hydrogens are deleted.



- Many organic compounds contain carbon bonded to 4 other atoms through single bonds.
- The VSEPR theory predicts that these molecules should have a tetrahedral geometry with bond angles of 109.5°.



## Examples:

1. Draw condensed structural formulas and determine molecular formula for each of the following stick structures:



- 2. Draw stick structures and determine molecular formulas for each of the following condensed structures:
  - a) CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub> | CH<sub>3</sub>

b) Cl | CH<sub>3</sub>CHCH<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub> | CH<sub>3</sub>

# **FUNCTIONAL GROUPS**

• Organic compounds are classified by common units called functional groups. Functional groups undergo similar chemical reactions. The simplest functional group is the alkyl group.

$$-CH_3 = R$$

• Some of the other important functional groups include:

Name	Structure	Example
Alkene	_c=c<	н <sub>2</sub> с — сн <sub>2</sub>
Alkyne	-c≡c-	НС≡СН
Alcohol		CH <sub>3</sub> CH <sub>2</sub> OH
Amine		CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>
Ether	$-\mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{O} - \mathbf{C}$	CH <sub>3</sub> OCH <sub>3</sub>
Acid	о    —С—ОН	CH <sub>3</sub> CO <sub>2</sub> H
Amide	О    -С—NH <sub>2</sub>	CH <sub>3</sub> CONH <sub>2</sub>
Ester	$-\mathbf{c} - \mathbf{o} - \mathbf{c} - \mathbf{c} - \mathbf{c}$	CH <sub>3</sub> COOCH <sub>3</sub>
Aldehyde	о    —С— Н	CH <sub>3</sub> CHO
Ketone		CH <sub>3</sub> COCH <sub>3</sub>

**Examples:** Identify the functional groups in each of the following famous molecules:



# HYDROCARBONS

• **Hydrocarbons** are organic compounds composed of only **carbon** and **hydrogen**. Hydrocarbons are further broken down into several groups:



- **Saturated hydrocarbons** are those that contain only **carbon-carbon single bonds**. Ethane is an example of a saturated hydrocarbon.
- Unsaturated hydrocarbons are those that contain carbon-carbon double and triple bonds. Ethylene and acetylene are examples of unsaturated hydrocarbons.

## ALKANES

- Alkanes are hydrocarbons that contain only carbon-carbon single bond (saturated).
- Alkanes have the general molecular formula  $C_nH_{2n+2}$ , and can be straight chain or branched.



• Smaller alkanes were originally named in a random fashion, but larger alkanes are named by the IUPAC system. The first ten alkanes are named as shown below:

Number of Carbon Atoms	Prefix	Name	Molecular Formula	Condensed Structural Formula
1	Meth	Methane	$CH_4$	$CH_4$
2	Eth	Ethane	$C_2H_6$	CH <sub>3</sub> —CH <sub>3</sub>
3	Prop	Propane	$C_3H_8$	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>3</sub>
4	But	Butane	$C_4H_{10}$	$CH_3$ — $CH_2$ — $CH_2$ — $CH_3$
5	Pent	Pentane	$C_5H_{12}$	$CH_3$ — $CH_2$ — $CH_2$ — $CH_2$ — $CH_3$
6	Hex	Hexane	$C_6H_{14}$	$\mathbf{CH}_{3} - \mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{3}$
7	Hept	Heptane	$C_7H_{16}$	$\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_3$
8	Oct	Octane	$C_8H_{18}$	$\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_3$
9	Non	Nonane	$C_{9}H_{20}$	$\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_3$
10	Dec	Decane	$C_{10}H_{22}$	$\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_3$

## STRUCTURAL ISOMERS

- Compounds with the same molecular formula but *different structural formulas* are called *isomers*.
- Most organic compounds have isomers. For example, butane has 2 isomers; pentane has 3 isomers, and hexane has 5 isomers. The two isomers of butane are shown below:



• In recognizing isomers of a compound, it is important to recognize molecules that might appear to have different structures, but are really the same.

$$\begin{array}{ccc} C & C & Both of these structures \\ C - C - C - C & C - C - C \end{array} \qquad Both of these structures represent the same compound. \end{array}$$

### **Examples:**

1. Identify all the isomers of  $C_3H_7Br$  from the choices given below:

$$\begin{array}{ccccccc} CH_3CH_2CH_2 & CH_3CH_2CH_2 & CH_3CHCH_3 \\ & & & & & & \\ Br & Br & Br & Br \\ & & & \\ CH_2CH_2CH_3 & Br--CH_2CH_2CH_3 \end{array}$$

2. Draw structural formulas for all the isomers of  $C_4H_9Cl$ .

# **CLASSIFICATON OF CARBONS & HYDROGENS**

Carbons in alkane molecules can be classified as one of 3 types:

- Primary (1°) carbons are those that are attached to only one other carbon atom.
- Secondary (2°) carbons are those that are attached to two other carbon atoms.
- Tertiary (3°) carbons are those that are attached to three other carbon atoms.

#### **Examples:**

1. Identify the primary, secondary and tertiary carbon atoms in the skeleton structure shown below:

- Hydrogens in an alkane can be similarly classified as primary, secondary or tertiary.
- Primary (1°) hydrogens are those bonded to a primary carbon. Secondary (2°) hydrogens are those bonded to a secondary carbon. Tertiary (3°) hydrogens are bonded to a tertiary carbon.

### Examples:

2. Draw all hydrogens missing in the skeleton structure above and classify as primary, secondary or tertiary.

$$\begin{array}{c} c \\ c - c - c - c - c - c - c - c \\ \downarrow \\ c - c \end{array}$$

## NAMING ORGANIC COMPOUNDS

- Many organic compounds have common names that are used because of convenience and long usage. The majority of organic compounds however, are named systematically by the IUPAC system.
- In order to name compounds by the IUPAC system, a familiarity with common alkyl groups is necessary. Alkyl groups have the general formula C<sub>n</sub>H<sub>2n+1</sub> and are named based on the corresponding alkanes. Some common alkyl groups include:

$$\begin{array}{cccc} CH_3 & CH_3 CH_2 - & CH_3 CH_2 CH_2 - \\ methyl & ethyl & n-propyl \end{array} \\ & & CH_3 \\ & | \\ CH_3 CHCH_3 & CH_3 CHCH_2 - \\ & isopropyl & isobutyl \end{array}$$

### **IUPAC Rules for Naming Alkanes:**

- 1. Select the longest continuous chain of carbons as the parent compound. All the other groups are considered side chains.
- 2. Number the carbon atoms in the parent chain so that the side chains fall on the smallest numbers.
- 3. Name each side chain alkyl group and designate its position on the parent chain by the carbon number. Side chains should be listed in alphabetical order.
- 4. Each side chain must possess a number designating its position on the parent chain. When the same side chains are present, use prefixes di-(2), tri-(3), etc.



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**Examples:** Name each compound shown below using the IUPAC system:

1. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>3</sub>  $CH_3$ 

2. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>3</sub> CH<sub>3</sub>CHCH<sub>3</sub>

3. CH<sub>3</sub>CHCH<sub>3</sub> Ċl

4.

CH<sub>3</sub> CH<sub>3</sub>CHCH<sub>2</sub>CHCH<sub>3</sub> CH<sub>2</sub>CH<sub>3</sub>

# **PROPERTIES OF ALKANES**

- The first four alkanes-methane, ethane, propane and butane-are gases at room temperature and are widely used as heating fuels. Alkanes having 5 to 8 carbon atoms (pentane, hexane, heptane and octane) are liquid at room temperature and are volatile, which makes them useful as fuels such as gasoline.
- Liquid alkanes with 9 to 17 carbon atoms have higher boiling points and are found in kerosene, diesel and jet fuels. Alkanes with 18 or more carbon atoms are waxy solids at room temperature. These alkanes, known as paraffins, are used as waxy coatings added to fruits and vegetables to retain moisture.
- Larger alkanes become more viscous and are commonly used as petroleum jelly, Vaseline and various lubricants.
- Alkanes have the lowest melting and boiling points of all the organic compounds. This occurs because they contain only contain non-polar C–C and C–H bonds. As a result, the attraction between the alkane molecules are very weak and are called dispersion forces.
- As the number of carbon atoms in alkanes increases, there is also an increase in the number of electrons, which increase the dispersion forces. Therefore, alkane with larger masses have higher melting and boiling points. For example,



## **REACTIONS OF ALKANES**

• The carbon–carbon single bonds in alkanes are difficult to break, so the alkanes are one the least reactive family of organic compounds. However, alkanes readily burn in oxygen to form carbon dioxide, water and release energy as heat (combustion reaction).

Alkanes (g) +  $O_2(g) \rightarrow CO_2(g) + H_2O(g) + energy$ 

• Halogens can also react with alkanes in presence of light to *substitute* for a hydrogen and form *mono-substituted alkyl halides*.

• Halogenation of propane can yield two isomers of chloropropane.

$$\begin{array}{rrrr} CH_{3}CH_{2}CH_{3} \ + \ Cl_{2} & \xrightarrow{\ \ \ light} & CH_{3}CH_{2}CH_{2}Cl \ + \ \ CH_{3}CHClCH_{3} \ + \ HCl \\ & 1\ \ chloropropane & 2\ \ chloropropane \end{array}$$

## **Examples:**

- 1. In each of the following pairs of hydrocarbons, which do you expect to have the higher boiling point?
  - a) pentane or heptane
  - b) hexane or 2-methylpentane
- 2. Write a balanced equation for the complete combustion of each of the following alkanes:
  - a) dimethylpropane
  - b) cyclobutane

- 3. Write structures and names for all mono-chlorosubstituted products formed from each reaction shown below:
- a)  $CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{light}$

b)  $\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_2 - CH_3 + Cl_2 \end{array} \rightarrow \begin{array}{c} \text{light} \end{array}$ 

## **UNSATURATED HYDROCARBONS & AROMATIC COMPOUNDS**

- The *unsaturated* hydrocarbons consist of two families of *homologous* compounds that contain *multiple bonds* between carbon atoms.
  - 1. Alkenes contain carbon-carbon double bonds. Double bonded carbons possess an angle of  $120^{\circ}$  and hybridization of sp<sup>2</sup>.
  - 2. Alkynes contain carbon-carbon triple bonds. Triple bonded carbons possess an angle of 180° and hybridization of sp.



• Alkenes and alkynes names are similar to those of the alkanes with the same number of carbon atoms. A comparison of the naming of the 3 families is given below:

## NAMING ALKENES

- Alkenes have the general formula  $C_nH_{2n}$ .
- To use the IUPAC rules for naming alkenes:
  - 1. Select the longest continuous carbon-carbon chain that contains the double bond.
  - 2. Name this parent compound as you would an alkane, but change the *-ane* ending to *-ene*.
  - 3. Number the carbon chain of the parent compound starting with the end nearer to the double bond. Use the smaller of the two numbers on the double-bonded carbon atoms to indicate the position of the double bond. Place this number in front of the alkene name.
  - 4. Branch chains and other groups are treated as in naming alkanes, by numbering and assigning them to the carbon atom to which they are bonded.



### **Examples:**

- 1. Write a structural formula for 4-methyl-2-pentene.
- 2. Write a structural formula for 7-methyl-2-octene.
- 3. Name the compound shown :



# **GEOMETRIC ISOMERS**

- Compounds containing a carbon-carbon double bond have restricted rotation about that double bond. This restricted rotation in a molecule gives rise to a type of isomer known as *geometric isomer*.
- Isomers that differ from each other only in the geometry of their molecules and not in the order of their atoms are known as *geometric isomers*. They are also called *cis-trans isomers*.



• An alkene shows cis-trans isomerism when each carbon atom of the double bond has two different kinds of groups attached to it.



cis isomer



• An alkene *does not show* cis-trans isomerism if one carbon of the double bond has two identical groups attached to it.



## **GEOMETRIC ISOMERS**

• Shown below are some examples of alkenes that do not have cis/trans isomers.



## **Examples:**

1. Identify each of the molecules below as cis or trans isomers.



2. Name the following compound:

3. Is the compound shown below cis or trans isomer? Name this compound.



4. Draw structure for cis-5-chloro-2-hexene.

## **REACTIONS OF ALKENES**

• Alkenes can undergo addition reactions of the following four types:

Addition of H <sub>2</sub>	(hydrogenation)	Symmetrical addition
Addition of H <sub>2</sub> O Addition of HX	(hydration) (hydrohalogenation)	Unsymmetrical addition
Polymerization	(addition of alkene to its	elf)

#### Addition of H<sub>2</sub>



## Addition of H<sub>2</sub>O



#### Addition of HX



Name of Addition Reaction	Reactants	Catalysts	Product
Hydrogenation	Alkene + H <sub>2</sub>	Pt, Ni, or Pd	Alkane
Hydration	Alkene + H <sub>2</sub> O	H <sup>+</sup> (strong acid)	Alcohol
Polymerization	Alkenes	High temperature, pressure	Polymer

# UNSYMMETRICAL ADDITION TO ALKENES

• When an unsymmetrical molecule such as HCl is added to an alkene, two products are theoretically possible. For example, when HCl adds to propene, 1-chloropropane and 2-chloropropane are possible.



- Experimentally, however, we only find one product formed (2-chloropropane). The reason for this selectiveness lies in the *reaction mechanism*, the pathway by which a reaction occurs.
- In an unsymmetrical addition, the prevalent product is formed by H bonding to the carbon with the most number of hydrogens attached. For example, when H<sub>2</sub>O adds to propene, the major product is 2-propanol.



## **ADDITION OF ALKENES (POLYMERIZATION)**

- A polymer is a large molecule that consists of many small repeating units called • monomers. The plastics industry has made many synthetic polymers that are in many materials we use every day (see list in table below). Polymers also have many uses in the medical, aerospace and other important industries.
- Many of the synthetic polymers are made by addition reaction of small alkene monomers. •



Ethene (ethylene) monomers

Some Alkenes and Their Polymers



Examples: 1. Draw the condensed structural formula for the major product that forms in the following reactions:

a) 
$$CH_3 - CH_2 - CH_2 - CH = CH_2 + H_2O \xrightarrow{H^+}$$

b) 
$$CH_3 - CH = CH_2 + H_2 \xrightarrow{Pt}$$

c) 
$$(H^+)$$
 + HCl  $\xrightarrow{H^+}$ 

$$_{d)} \xrightarrow{Pt} + H_2 \xrightarrow{Pt}$$

e) 
$$H_2C = CH_2 - CH_3 + H_2O \xrightarrow{H^+}$$

# **AROMATIC COMPOUNDS**

• <u>Benzene</u> is a six-membered ring with molecular formula  $C_6H_6$ . It has alternating double bonds, and is represented by the following structures:



- Because many compounds containing benzene had fragrant odors, the family of benzene compounds became known as *aromatic compounds*. Some common examples of aromatic compounds that we use for flavor are shown below.
- Removal of a H from a benzene ring results in an *aryl group* with formula  $C_6H_5$  called *phenyl*.



## NAMING AROMATIC COMPOUNDS

• Simple monosubstituted aromatic compounds can be named as benzene derivatives. For example:



• Some other simple aromatic compounds that have special names are shown below:



• Compounds with benzene rings that cannot be easily named as benzene derivatives are named with phenyl groups. For example:



3-chloro-2-phenylpentane

• When two substituents occur on a benzene ring, three isomers are possible. These isomers are named either by numbering of the ring atoms or the Greek prefixes ortho (o), meta (m) and para (p).



1,2- or ortho- 1,3- or meta

**Examples:** Name the following aromatic compounds by at least 2 different names:



3. Name the following compounds:



CH<sub>3</sub>