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

BONDING IN ORGANIC CHEMISTRY

- 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°.



• The valence electrons in carbon occupy the 2s and 2p orbitals, as shown below:

$$\frac{\uparrow\downarrow}{2s}$$
 $\frac{\uparrow}{2p}$ —

- Based on this configuration, one would expect carbon to form only two bonds. However, this would not allow carbon to achieve octet. Therefore, another explanation is required to account for the fact that carbon forms 4 covalent bonds.
- One explanation would be to promote one of the 2s electrons in carbon to occupy the empty 2 p orbital, making four unpaired electrons available for bonding.
- If this explanation were correct, one would expect the 4 bonds formed by carbon to be different from one another, since the orbitals used are different. Examination of carbon bonds formed indicates that the four bonds are identical in bond length and other properties.
- Another explanation that would account for this observation is the concept of *hybrid* orbitals, that is mixed orbitals formed by combining atomic orbitals. This concept is referred to as *hybridization* and was first introduced by Linus Pauling in 1931.
- A more advanced bonding theory, *Valence Bond* theory (*VB*) utilizes the concept of hybridization to develop a more comprehensive knowledge of the bonds in a molecule.

HYBRIDIZATION

- Using the concept of hybridization, the bonding in organic molecules can be classified as shown below.
- Carbon can form single, double and triple bonds with other atoms, including other carbons. Single bonds are referred to as *σ(sigma)* bonds. Multiple bonds (double or triple) consist of one *σ* bond and one or two *π(pi)* bonds.



- The hybridization of C, N and O can be easily found by the following scheme:
 - > If the atom only forms single bonds (σ), then it is sp³ hybridized and forms a tetrahedral electron-pair geometry.
 - > If the atom forms double bond $(1 \sigma \text{ and } 1 \pi)$, then it is sp² hybridized and forms a trigonal planar electron-pair geometry.
 - > If the atom forms triple bond $(1 \sigma \text{ and } 2 \pi)$ or two double bonds, then it is sp hybridized and forms a linear electron-pair geometry.



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:

$$H H H \\ | | \\ H - C - C - O - H$$
(Ethanol)
$$| | \\ H H$$

• 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.



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Examples:

b)

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) CH₃CH₂CHCH₂CH₃ | CH₃

Cl | CH₃CHCH₂CHCH₂CH₃ | CH₃

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 ₂ с — сн ₂ |
| Alkyne | -c≡c- | НС≡СН |
| Alcohol | | CH ₃ CH ₂ OH |
| Amine | | CH ₃ CH ₂ NH ₂ |
| Ether | $-\mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{O}$ | CH ₃ OCH ₃ |
| Acid | о —С—ОН | CH ₃ CO ₂ H |
| Amide | О -С—NH ₂ | CH ₃ CONH ₂ |
| Ester | $-\mathbf{c} - \mathbf{o} - \mathbf{c} - \mathbf{c}$ | CH ₃ COOCH ₃ |
| Aldehyde | о —С— н | CH ₃ CHO |
| Ketone | | CH ₃ COCH ₃ |

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 | | | Malagular | Condensed Structural | |
|--------------|--------|---------|----------------|---|--|
| Atoms | Prefix | Name | Formula | Formula | |
| 1 | Meth | Methane | CH_4 | CH_4 | |
| 2 | Eth | Ethane | C_2H_6 | CH ₃ —CH ₃ | |
| 3 | Prop | Propane | C_3H_8 | CH ₃ —CH ₂ —CH ₃ | |
| 4 | But | Butane | C_4H_{10} | CH_3 — CH_2 — CH_2 — CH_3 | |
| 5 | Pent | Pentane | $C_{5}H_{12}$ | CH_3 — CH_2 — CH_2 — CH_2 — CH_3 | |
| 6 | Hex | Hexane | C_6H_{14} | CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — 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 | $C_{8}H_{18}$ | $\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_3$ | |
| 9 | Non | Nonane | $C_{9}H_{20}$ | $\mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_3$ | |
| 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.

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

Examples:

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

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

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:

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

- 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_nH_{2n+1} 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. CH₃CH₂CH₂CHCH₃ CH_3

2. CH₃CH₂CH₂CHCH₃ CH₃CHCH₃

3. CH₃CHCH₃ Ċl

4.

 CH_3 CH₃CHCH₂CHCH₃ CH_2CH_3

UNSATURATED HYDROCARBONS

- The *unsaturated* hydrocarbons consist of three families of *homologous* compounds that contain *multiple bonds* between carbon atoms.
- Alkenes contain carbon-carbon double bonds. Double bonded carbons possess an angle of 120° and hybridization of sp².
- Alkynes contain carbon-carbon triple bonds. Triple bonded carbons possess an angle of 180° and hybridization of sp.
- Aromatic compounds contain benzene rings. Benzene rings are six membered rings that contain alternate double bonds and are represented by any of the structures shown below:



Representations of Benzene

- Benzene compounds are unlike other unsaturated compounds (alkenes and alkynes) and have their own characteristic properties and reactions.
- Some organic molecules contain several benzene rings and are called polycyclic aromatic compounds. Some examples of are shown below:



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.





