Chapter 21: Organic Chemistry

Section 21.1: Introduction to Organic Chemistry

Organic Chemistry is the study of carbon-based compounds. Carbon is the principal element around which the chemistry of life has evolved. Carbon has four electrons in its outer shell. Each of these electrons can be shared with electrons in other elements so they all complete their valence electronic shells. This results in the formation of covalent bonds.

Elements like nitrogen (N), hydrogen (H), and oxygen (O) bond to carbon in this fashion. The most distinguished feature of carbon atoms is their ability to share electrons with other carbon atoms to form covalent carbon-carbon bonds.

Carbon atoms form single, double and triple carbon-carbon bonds. Carbon atoms link up with each other in chains and ring structures.

Section 21.2: Introduction to Hydrocarbons

Hydrocarbons form the simplest class of organic compounds. Hydrocarbons are compounds containing only carbon and hydrogen.

There are four general types of hydrocarbons.

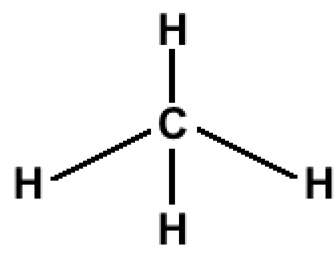
1. Alkanes
2. Alkenes
3. Alkynes
4. Aromatic Compounds

In this section, we will only discuss Alkanes.

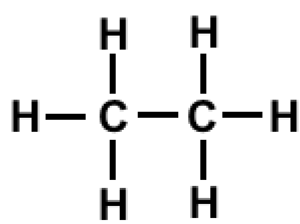
These hydrocarbons contain only single bonds. The general formula for alkanes is C_nH_{2n+2}, where n is the number of carbon atoms. Hence, the simplest alkane, obtained for n = 1, is CH_4. The name of this compound is **methane**.

Note: The name of alkanes always ends with –ane.

According to the VSEPR theory, the structure of methane is tetrahedral with bond angle of 109.5º. The C-atom is sp^3 hybridized.



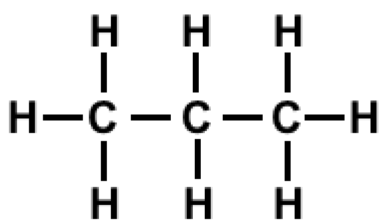
When n = 2, the formula is C_2H_6. In two dimensions, the structure of C_2H_6 is represented as:



The name of this compound is **ethane**.

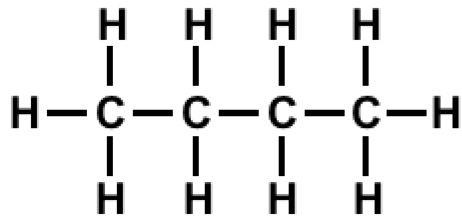
Note: In alkanes, all carbon atoms have a tetrahedral geometry and as sp^3 hybridized.

When n = 3, the formula is C_3H_8. In two dimensions, the structure of C_3H_8 is represented as:



The name of this compound is **propane**. The condensed structural formula of propane is $CH_3CH_2CH_3$.

When n = 4, the formula is C_4H_{10}. In two dimensions, the structure of C_4H_{10} is represented as:



The name of this compound is **butane**. The condensed structural formula of butane is $CH_3CH_2CH_2CH_3$.

n	Formula	Name
5	C_5H_{12}	Pentane
6	C_6H_{14}	Hexane
7	C_7H_{16}	Heptane
8	C_8H_{18}	Octane
9	C_9H_{20}	Nonane
10	$C_{10}H_{22}$	Decane

Note once again that all alkane names end with –ane. Alkanes are known as **saturated hydrocarbons**. This is because alkanes contain the largest possible number of hydrogen atoms per carbon atom. The alkanes discussed up to this point are **straight-chain** or **unbranched** hydrocarbons. In straight-chain hydrocarbons, C atoms are joined in a continuous chain.

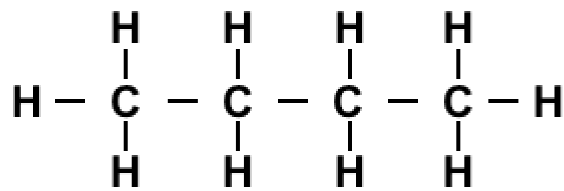
Straight-chain hydrocarbons up to butane exist as gases under standard conditions. From pentane ($n = 5$) to heptadecane ($n = 17$), they exist as liquids. Straight-chain hydrocarbons containing 18 or more carbon atoms are low-melting waxy solids. A mixture of these hydrocarbons is called a paraffin wax. Straight-chain hydrocarbons containing thousands of carbon atoms are known by the name polyethylene and belong to the family of plastics.

Sections 21.3 - 21.4: Structural Isomers of Alkanes

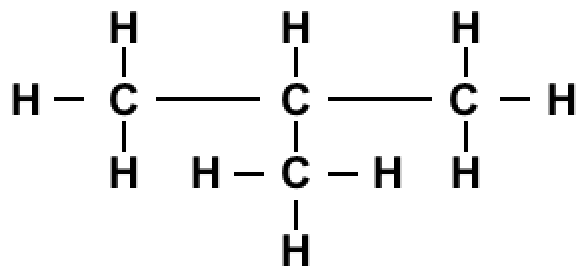
Alkanes consisting of four or more carbon atoms can also form branched chains.

Consider butane, C_4H_{10}:

The straight-chain hydrocarbon has a structural formula:



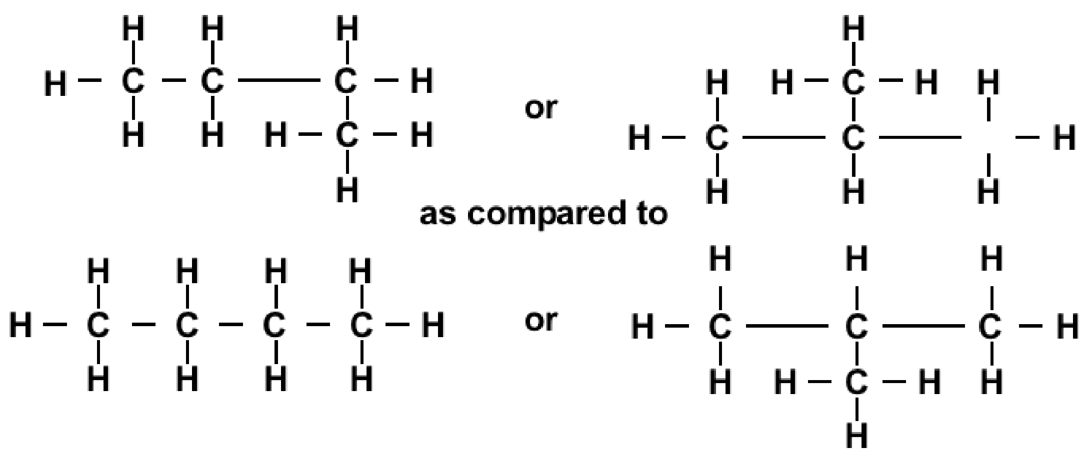
and the branched-chain hydrocarbon has a structural formula:



Note: Both structural formulas correspond to the same molecular formula, C_4H_{10}.

In the branched-chain structure, the atoms are bonded differently. Compounds with the same molecular formula, but different molecular structures are called **structural isomers**.

Now, one can think of arranging the carbon atoms in butane as:

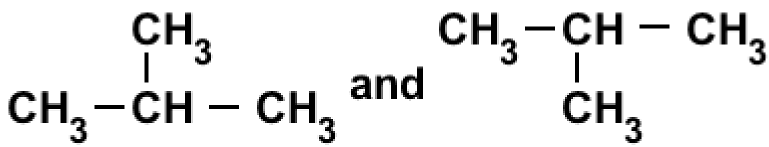


Compare the structures on the left. We write the condensed structural formula for these two molecules as:

$$CH_3-CH_2-CH_2-CH_3$$

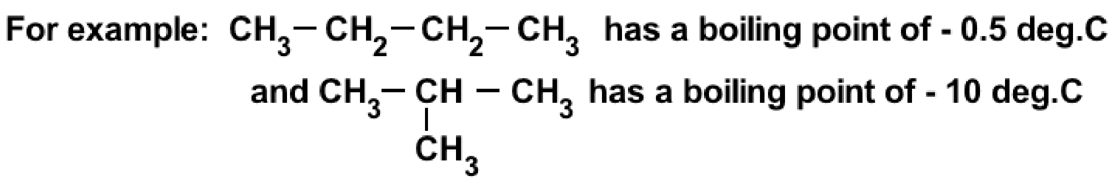
Thus, these structures are identical. Hence, they are not structural isomers.

Now, compare the structures on the right. The condensed structural formulas of these molecules are:



Thus, these structures are identical. Hence, they are not structural isomers. These structures are identical, even though they have CH_3 on opposite sides. Hence, neither of these molecules are structural isomers.

Different structural isomers have different names and different chemical and physical properties.



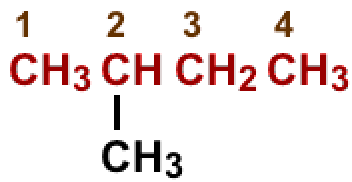
Branched molecules exhibit weaker intermolecular interactions than linear molecules of the same mass because they do not pack as densely in the liquid state. Hence, the branched isomer boils at lower temperature than the linear isomer.

In Section 21.4, practice the Interactive Problems.

Sections 21.5 - 21.6: Nomenclature of Alkanes

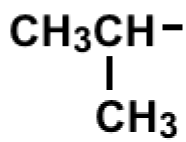
According to the IUPAC (International Union of Pure and Applied Chemistry), the longest carbon chain is numbered consecutively from one end to the other so that substituents on the chain have the lowest possible numbers.

For example:



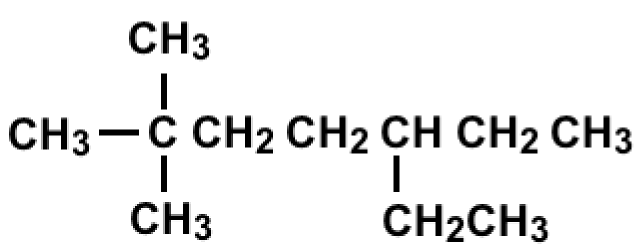
Number the longest chain from left to right. On the second carbon in the longest chain, there is a substituent group (i.e. CH_3). When the substituent group is a hydrocarbon, it is called an **alkyl** group.

The names for common alkyl groups are:

Group	Name
CH_3-	Methyl
CH_3CH_2-	Ethyl
$CH_3CH_2CH_2-$	n-propyl
	Isopropyl

The longest chain is the parent hydrocarbon. In the example, the longest chain consists of 4 carbons (i.e. C_4). The parent name for C_4 is butane. The substituent group is on the second carbon of the parent chain. The substituent group is CH_3-. Then name of this group is methyl. Therefore, the name of the compound is 2-methylbutane.

The rules for naming hydrocarbons are discussed next by considering the following example:



Rule 1: Find the longest continuous chain of carbon atoms. In this example, the longest continuous chain consists of seven carbon atoms. This gives the name of the parent hydrocarbon. Since there are seven carbon atoms, the name of the parent hydrocarbon is heptane.

Rule 2: Identify the number of substituent groups attached to the parent hydrocarbon. In this example, there are three substituent groups attached to the parent hydrocarbon.

Rule 3: Name each substituent group and place these names in alphabetical order before the name of the parent hydrocarbon. In this example, the name for the two CH_3 substituent groups is dimethyl (since there are two methyl groups). The name of the CH_2CH_3 substituent group is ethyl.
Note: Prefixes that denote the number of each group such as di, tri, etc. are not regarded when alphabetizing substituent groups.

Rule 4: Number the parent hydrocarbon chain in such a way to use the smallest numbers for the carbons to which substituent groups are attached. In the example, number the carbon atoms from left to right. This is because the second carbon atom has two substituent groups.

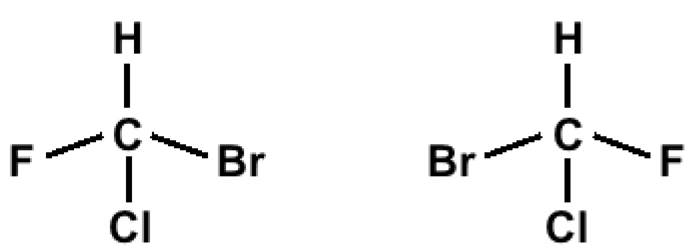
Rule 5: For each substituent group, add a numerical prefix that denotes the group's location of attachment. In this example, they are 2,2-dimethyl and 5-ethyl.

Combining these rules, you can now write the complete name of the compound. The name of the compound is: 5-ethyl-2,2-dimethylheptane.

In Section 21.6, practice the Interactive Problems.

Section 21.7: Optical Isomers of Substituted Alkanes

A tetrahedron whose central carbon atom bears four different substituents does not have a plane of symmetry. Consider the molecule CHFClBr. The geometry of the molecule could be represented by the schematic shown below on the left:



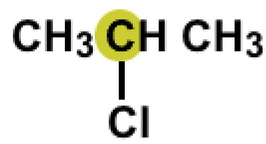
The mirror image of this molecule is represented above on the right.

The two arrangements, called configurations, are different. By different we mean that it is not possible to simultaneously superimpose all the atoms of the figure on the left on like atoms of the figure on the right. Thus, these two configurations are non-superimposable mirror images.

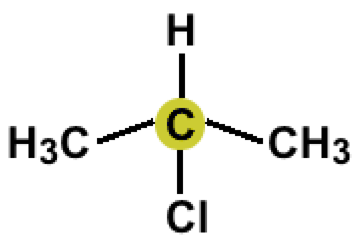
Non-superimposable mirror images result when four different groups are attached to the carbon atom. In such cases, the molecule is called a "**chiral**" molecule. A chiral molecule is asymmetric or a chiral molecule contains an **asymmetric** center (here, carbon). The two compounds that are related as non-superimposable mirror images are called **enantiomers**.

Experimentally, it is found that enantiomers possess identical physical properties, except that they rotate the plane of polarized light in opposite directions by equal amounts. Enantiomers are also called **optical isomers**.

Example: Consider the molecule



Examine the C atom to which Cl is attached. Draw the tetrahedral structure with this carbon atom as the central atom.



Are the four groups attached to the carbon atom different? The answer is no. Thus, this molecule is not chiral.

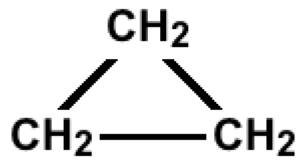
Remember: A molecule that is <u>not</u> chiral has a plane of symmetry. These molecules are related as superimposable mirror images.

Section 21.8: Cycloalkanes

Alkanes whose carbon atoms are connected in rings are called **cycloalkanes**. Cycloalkanes have a general formula C_nH_{2n}. The simplest cycloalkane has 3 carbon atoms.

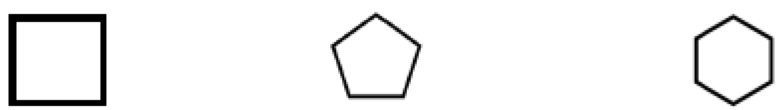
Rule: Unsubstituted monocyclic hydrocarbons are named by attaching the prefix “cyclo” to the name of the straight-chain alkane with the same number of carbon atoms.

Thus, a cycloalkane with 3 carbon atoms is called **cyclopropane**. The structure is cyclopropane is:



In shorthand, it is written as:

Similarly, cyclobutane, cyclopentane, and cyclohexane have the shorthand structures shown below:



Rings that contain 3 or 4 carbons are called small rings. Rings that contain 5-7 carbons are often called common rings. Rings that contain 8-11 carbons are called medium rings. Rings that contain 12 or more carbons are called large or macro rings.

The common and large ring compounds are like the alkanes in almost all of their physical and chemical properties. Both small and medium rings behave differently.

Small rings exhibit unusual characteristics because all carbon atoms in cycloalkanes are sp^3 hybridized. For sp^3 hybridization, the bond angle should be 109.5º. However, in small rings the bond angles are much smaller than 109.5º. Hence, small ring compounds experience angular strain. It is because of

angular strain that cycloalkanes with small rings behave differently than the corresponding alkanes.

Section 21.9: Alkenes and Alkynes

Alkenes and Alkynes are families of acyclic (i.e. open chain) hydrocarbons which contain less hydrogen per carbon atom than alkanes. Hence, alkenes and alkynes are called **unsaturated hydrocarbons**.

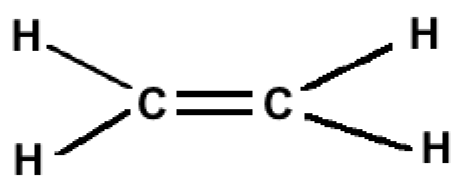
Alkenes have a general formula C_nH_{2n}

An alkene contains at least one carbon-carbon double bond. Alkenes are also called olefins.

The simplest alkene is obtained for n = 2 and has the formula C_2H_4. The common name of C_2H_4 is **ethylene** (IUPAC name: ethene).

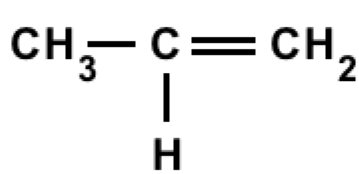
Note: The names of alkenes always end with "ene".

In two dimensions, the structure of ethylene is represented as:



Note: The double-bonded carbon atoms are sp^2 hybridized.

The next homolog in the alkene family after ethylene is **propylene**, C_3H_6. In two dimensions, the structure of propylene is represented as:



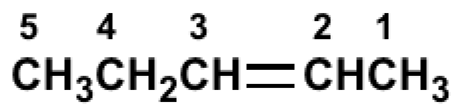
<u>IUPAC Names For Alkenes</u>

In naming alkenes beyond propylene one has to follow these rules:

For example: Consider: $CH_3CH_2CH{=}CHCH_3$

Rule 1: Select the longest carbon chain containing the double bond and assign it the parent name derived by changing the suffix <u>ane</u> of the alkane with same number of carbons to <u>ene</u>. In this example, the longest carbon chain containing the double bond has 5 carbon atoms.
Hence, the name of the alkane is pentane. Since the molecular formula contains a double bond, the compound is an alkene and the name is pentene.

Rule 2: Number the parent carbon chain from the end nearer the double bond. In the example, number the carbon atoms from right to left.



Rule 3: Indicate the position of the double bond by the number of the first double bonded carbon encountered. In this example, it is carbon number 2. Thus, the name of this compound is 2-pentene.

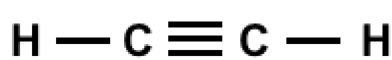
Rule 4: If there are substituents attached to the parent chain then indicate the positions and names of substituent groups. Place the substituent names in alphabetical order (i.e. according to the rules used in naming alkanes).

Alkynes have the general formula C_nH_{2n-2}

The simplest alkyne has the formula C_2H_2. The common name of C_2H_2 is acetylene. The IUPAC name of C_2H_2 is ethyne.

Thus, the name of alkynes always ends with "yne".

In two dimensions, the structure of ethyne is represented as:



Note: The triple-bonded carbon atoms are sp hybridized.

The naming of alkynes follows the same line as for alkanes. The parent chain must contain a triple bond. The suffix <u>ane</u> of the corresponding alkane is changed to <u>yne</u>. The position of the triple bond is indicated by the lowest possible carbon number.

In Section 21.9, practice the Interactive Problems.

Section 21.10: Geometric Isomers of Alkenes

Consider 2-butene. Its structural formula is:

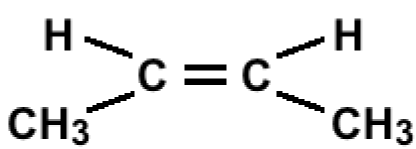
$$CH_3CH{=}CHCH_3$$

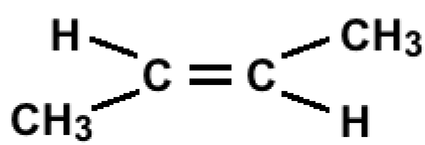
Note: The double bond between the middle two carbon atoms consists of a σ (sigma) bond and a π (pi) bond.

Imagine trying to rotate one of the $CHCH_3$ groups around the double bond. Rotation around the double bond would require breaking the π bond. Since breaking the π bond requires a large amount of energy, rotation around the π bond does not occur under the vast majority of experimental conditions.

Remember: Rotation around a double bond requires so much energy that it typically does not occur. Hence, molecules with a double bond may have two possible arrangements for the atoms or groups about the double bond.

For example, in 2-butene, the two possible arrangements for the atoms about the double bond are:





In the structure on the left, the two methyl groups are on the same side of the double bond. Hence, this molecule is called **cis-2-butene**.

In the structure on the right, the two methyl groups are on the opposite side of the double bond. Hence, this molecule is called **trans-2-butene**.

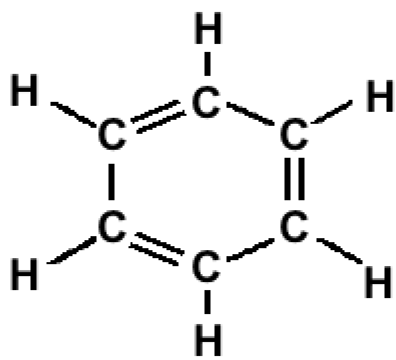
Cis-2-butene and trans-2-butene are called "**geometric isomers**". Geometric isomers often have different physical and chemical properties.

In Section 21.10, practice the Interactive Problems.

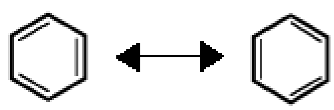
Section 21.11: Aromatic Hydrocarbons

A large group of compounds discovered in the 19th Century was given the general name "**aromatic**" compounds. The word "aromatic" was used because some of these compounds have a pleasant odor. The parent molecule of this family was found to be the hydrocarbon of molecular formula, C_6H_6 is called **benzene**.
Since this discovery, the connection between the structure of organic molecules and their odor has remained obscure. The term "aromatic compound" refers to unsaturated compounds that show a low degree of reactivity.

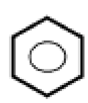
In 1865, Kekule proposed the structure of C_6H_6 as:



Kekule suggested that the double bonds were not rigidly fixed but constantly moved around the ring.



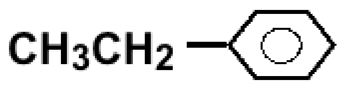
Since the real structure of benzene is intermediate between the two resonance forms, benzene rings are often drawn with a circle inside an hexagon.



Remember each carbon atom bears only one hydrogen atom.

Simple monosubstituted benzenes are named by adding the substituent name to benzene to form a one-word name. All positions on benzene are equivalent, so no number is needed to indicate the position of the substituent.

For example:

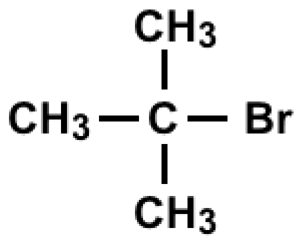


The attached substituent group is called ethyl. Therefore, the name of this compound is ethylbenzene.

Sections 21.12: Functional Groups in Organic Compounds: Alkyl Halides

An alkyl group is frequently symbolized by an "R" and halogens are often denoted by the symbol "X". Alkyl Halides, as a general class of compounds, can be represented by the shorthand notation "RX." The IUPAC names employ the substituent prefixes **bromo**, **chloro**, **fluoro** and **iodo**. The names otherwise follow the rules for naming the parent hydrocarbons (as discussed in the section on alkanes).

Example: Give the IUPAC name of the following alkyl halide:



The longest chain consists of 3 carbons. Hence, the parent name is propane. Two substituent groups (i) methyl and (ii) bromo are attached to the second carbon. Thus, arranging them in alphabetical order the compound name is: **2-bromo-2-methylpropane**

In Section 21.12, practice the Interactive Problems.

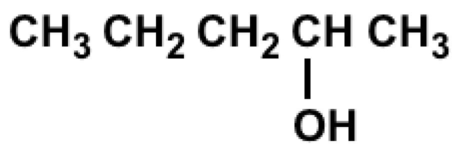
Sections 21.13: Functional Groups in Organic Compounds: Alcohols

An alcohol contains a hydroxyl functional group –OH. In the IUPAC name, the longest chain containing the hydroxyl group is used to determine the name of the parent hydrocarbon chain. The final –e of the hydrocarbon name is replaced by -ol. The position of the hydroxyl group is given by the lowest possible carbon number.

Note: Simple alcohols have a common name which consists of the name of the alkyl group followed by the word alcohol.

For example: CH_3OH is called methyl alcohol. The IUPAC name of methyl alcohol is **methanol**. Similarly, CH_3CH_2OH is called ethyl alcohol. The IUPAC name of ethyl alcohol is **ethanol**.

Example: Give the IUPAC name of the following alcohol:



The longest chain consists of 5 carbons. Hence, the name of the parent hydrocarbon is pentane. Since there is an –OH group, the –e from the alkane is dropped and the suffix –ol is added. The name becomes pentanol. –OH is attached to the second carbon. Therefore, the name of the compound is **2-pentanol**.

In Section 21.13, practice the Interactive Problems.

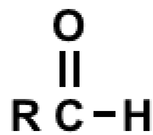
Sections 21.14: Functional Groups in Organic Compounds: Ethers

Ethers are organic molecules containing the R—O—R' linkage. Here R and R' are alkyl groups. Ethers are named by designating the alkyl groups attached to the oxygen atom, in alphabetical order, and adding the word "ether". For example, $CH_3OCH_2CH_3$ is named as **ethyl methyl ether**.

In Section 21.14, practice the Interactive Problems.

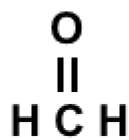
Sections 21.15: Functional Groups in Organic Compounds: Aldehydes and Ketones

Aldehydes are obtained by placing a carbonyl group C = O at one of the terminal positions of an alkane. The general formula of an aldehyde is,



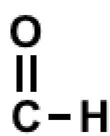
where R is an alkyl group.

Exception: Formaldehyde is the only aldehyde without an alkyl group. Formaldehyde has the following chemical formula:



Systematic IUPAC names of aldehydes are formed by replacing the final –e of the parent hydrocarbon name of –al.

The carbon in:



(often represented as –CHO) is always position 1. Hence, its position is not included in the name. For example: The name of the compound $CH_3CH_2CH_2CH_2CH_2CHO$ is **hexanal**.

Be careful when identifying functional groups.

Ketones contain a carbonyl group in an internal position of an alkane chain. The general formula of a ketone is:

where R and R' are alkyl groups. The IUPAC names for ketones are formed from the name of the longest continuous hydrocarbon chain containing the carbonyl group. The final –e of the alkane is replaced by the suffix –one.

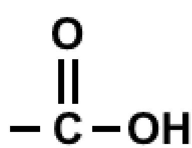
The location of the carbonyl group ($\overset{O}{\overset{||}{C}}$) is indicated by the lowest possible number placed just before the hydrocarbon name.

Thus, the name of $CH_3\overset{O}{\overset{||}{C}}CH_3$ is 2-propanone.

In Section 21.15, practice the Interactive Problems.

Sections 21.16: Functional Groups in Organic Compounds: Carboxylic Acids

Carboxylic acids are organic molecules containing the carboxyl group:



Carboxylic acids are commonly represented as RCOOH where R is an alkyl group.

Exception: Formic acid (HCOOH) is the only carboxylic acid that does not have an alkyl group.

Systematic IUPAC names are formed by
1) replacing the final “-e” in the name of the longest chain containing the carboxyl group –COOH by the suffix “-oic”
2) adding the word acid.

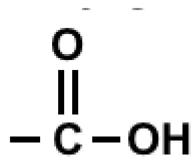
The carboxylic acids listed below are known by their well-established common names. Hence, they are accepted as IUPAC names.

Formula	Name
HCOOH	Formic acid
CH_3COOH	Acetic acid
CH_3CH_2COOH	Propionic acid
$CH_3CH_2CH_2COOH$	Butyric acid

Give the IUPAC name for the following organic molecule:

$CH_3CH_2CH_2CH_2COOH$

The continuous chain consists of five carbon atoms. Hence, the parent hydrocarbon chain is named pentane.

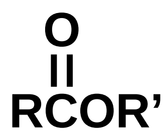


The above molecule is a carboxylic acid since it contains the carboxyl group. Hence, the compound is named as: **pentanoic acid**

In Section 21.16, practice the Interactive Problems.

Sections 21.17: Functional Groups in Organic Compounds: Esters

Esters have a general formula:



R and R' are alkyl groups. Esters are named as if they were alkyl salts of carboxylic acids.

For example:

CH_3COOH is acetic acid
CH_3COONa is sodium acetate
Then, CH_3COOCH_3 is methyl acetate

Note: Esters have two-word names.
The first word designates the alkyl group attached to the oxygen and the second word is derived from the name of the corresponding acid by dropping the " ic acid " and adding " ate ".

Example: Name the following ester: $CH_3CH_2COOCH_2CH_3$
Recall the first word designates the alkyl group attached to the oxygen atom. That group is called ethyl. The second word is derived from the name of the corresponding acid. The corresponding acid is propanoic acid since there are 3 carbons.

The "ic acid" is dropped and the "ate" is added.

The second word becomes propanoate.
Thus, the complete name of the ester is: **ethyl propanoate**.

In Section 21.17, practice the Interactive Problems.

Sections 21.18: Functional Groups in Organic Compounds: Amines

Amines are organic bases. Amines are divided into sub-classes according to the number of carbon atoms attached to the nitrogen.

RNH_2 is a primary amine.
R_2NH is a secondary amine.
R_3N is a tertiary amine.

Amines can be named by specifying the groups attached to the nitrogen as prefixes to the word amine.

In Section 21.18, practice the Interactive Problems.

Section 21.19: Summary of Functional Groups

Functional Group	Name
$>C=C<$	Carbon-Carbon double bond
$-C\equiv C-$	Carbon-Carbon triple bond
$-X$ (X = F, Cl, Br, I)	Alkyl halide
$-OH$	Alcohol
$>C=O$	Carbonyl (ketone)
$-C(=O)-OH$	Carboxyl (carboxylic acid)
$-C(=O)-O-R$	Ester
$-NR_2$	Amine

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