Organic chemistry is the study of compounds that contain carbon. It is one of the major branches of chemistry.

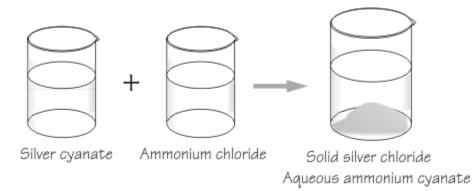
The history of organic chemistry can be traced back to ancient times when medicine men extracted chemicals from plants and animals to treat members of their tribes. They didn't label their work as "organic chemistry", they simply kept records of the useful properties and uses of things like willow bark which was used as a pain killer. (It is now known that willow bark contains acetylsalicylic acid, the ingredient in aspirin - chewing on the bark extracted the aspirin.) Their knowledge formed the basis of modern pharmacology which has a strong dependence on knowledge of organic chemistry.

Organic chemistry was first defined as a branch of modern science in the early 1800's by Jon Jacob Berzelius. He classified chemical compounds into two main groups: **organic** if they originated in living or once-living matter and **inorganic** if they came from "mineral" or non-living matter. Like most chemists of his era, Berzelius believed in **Vitalism** - the idea that organic compounds could only originate from living organisms through the action of some vital force.

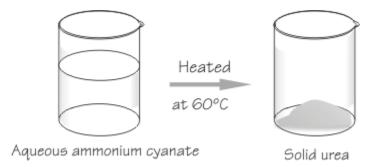
It was a student of Berzelius' who made the discovery that would result in the abandonment of Vitalism as a scientific theory. In 1828, Frederich Wöhler discovered that urea - an organic compound - could be made by heating ammonium cyanate (an inorganic compound).

Wöhler mixed silver cyanate and ammonium chloride tp produce solid silver chloride and aqueous ammonium cyanate:

 $AgOCN_{(aq)} + NH_4Cl_{(aq)} \rightarrow AgCl_{(s)} + NH_4OCN_{(aq)}$



He then separated the mixture by filtration and tried to purify the aqueous ammonium cyanate by evaporating the water.



To his surprise, the solid left over after the evaporation of the water was not ammonium cyanate, it was a substance with the properties of urea! Wöhler's observation marked the first time an organic compound had been synthesized from an inorganic source.

 $\begin{array}{ll} \text{NH}_4\text{OCN}_{\,(\text{aq})} \ \rightarrow \ (\text{NH}_2)_2\text{CO}_{\,(\text{s})} \\ \\ \text{inorganic} & \text{organic} \end{array}$

A Turning Point in Science History

Wöhler's discovery was a turning point in science history for two reasons. First, it undermined the idea of Vitalism because an organic compound was produced from an inorganic one. However, it also represented the discovery of **isomerism** - the possibility of two or more different structures (ammonium cyanate crystals and urea crystals) based on the same chemical formula (N_2H_4CO).

Chemists started searching for reasons to explain isomerism. That in turn led to theories about the structure of chemical compounds. By the 1860's, chemists like Kékulé were proposing theories on the relationship between a compound's chemical formula and the physical distribution of its atoms. By the 1900's chemists were trying to determine the nature of chemical bonding by developing models for electron distribution. During all of this time the number of known organic compounds was increasing rapidly year by year.

During the 20th century, organic chemistry branched into sub-disciplines such as polymer chemistry, pharmacology, bioengineering, petro-chemistry, and numerous others. During that century, millions of new substances were discovered or synthesized. Today over 98% of all known compounds are organic.

Your study of organic chemistry begins at a time when the number of organic compounds and the number of reactions they undergo is nothing short of bewildering! Your study of organic chemistry begins with a study of the classification system, naming rules, and some key reactions that organic compounds undergo.

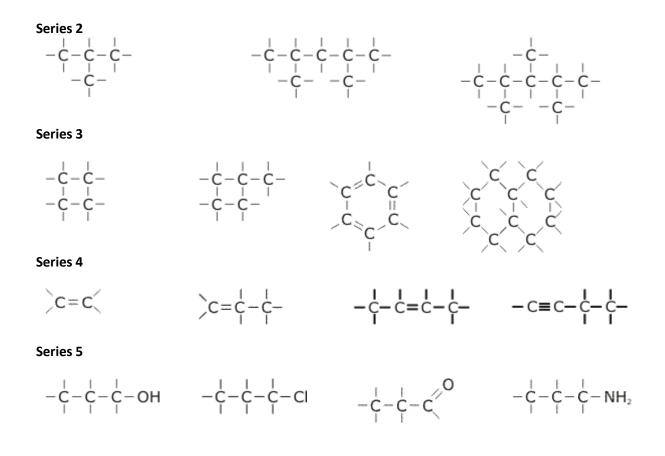
Uniqueness of Carbon

What bonding properties of carbon might account for the tremendous diversity of organic compounds?

Have a look at each series of structural formulas. The hydrogen atoms have been omitted from the structural formulas for simplicity - this is standard practice when drawing structural formulas for organic compounds. Look for trends in each series and then respond to the items that follow.

Series 1

$$- \overset{i}{C} - \qquad - \overset{i}{C} - \overset{i}{C} - \qquad - \overset{i}{C} - \overset{i}{C} - \overset{i}{C} - \qquad - \overset{i}{C} -$$



Stability of Carbon to Carbon Bonds

Carbon atoms form stable covalent bonds with other carbon atoms. Carbon to carbon bonds are very strong - a lot of energy is required to break them compared to other covalent bonds.

The tremendous diversity of organic compounds is due mainly to the ability of carbon atoms to form stable chains, branched chains, rings, branched rings, multiple rings, and multiple bonds (double and triple bonds). Add to this the ability to bond to many other nonmetal atoms, and you can certainly see why organic compounds outnumber all other classes of compounds combined by a huge margin!

Hydrocarbons

Hydrocarbons are pure substances that contain carbon and hydrogen atoms only. There are two main classes of hydrocarbons: the aliphatics and the aromatics. The key difference between the two classes is the presence of a benzene ring in aromatics.

Hydrocarbons are typically low melting point nonpolar substances. They are important as fuels and as starting materials in a variety of industries, in particular, the plastics industry.

Alkanes

Propane, butane and octane are just three examples of organic compounds that are classified as alkanes. **Alkanes** are hydrocarbons in which the carbon atoms have single bonds to other atoms. They have the general formula C_nH_{2n+2} where *n* is a natural number. For example, an alkane containing five carbon atoms (n=5) will have 2n + 2 or 12 hydrogen atoms. Its formula will be C_5H_{12} .

(Count the number of carbon and hydrogen atoms to convince yourself that the diagram conforms to the general formula for an alkane. Note that in structural formulas for organic compounds the symbols for hydrogen atoms may be omitted.)

Nomenclature (Naming) of Alkanes

The International Union of Pure and Applied Chemistry (IUPAC) has existed since 1920. One of its goals is to have international agreement on the rules of nomenclature so that every compound has the same chemical name and formula throughout the world. Widespread use of these rules has helped to minimize the confusion associated with the use of non-systematic names. Yet even today, many compounds are still known better by "common" rather than systematic IUPAC names. For example, ammonia versus nitrogen trihydride.

The nomenclature system for organic compounds is based on sets of prefixes and suffixes. You already know that the suffix "-*ane*" means single bonded carbon atoms, and you have probably already deduced that *meth-*, *eth-*, *prop-*, and *but-* mean 1, 2, 3, and 4 respectively. These prefixes are used throughout organic nomenclature, so you must memorize them.

Table 1: IUPAC prefixes for use in organic nomenclature.

meth	eth	prop	but	pent	hex	hept	oct	non	dec
1	2	3	4	5	6	7	8	9	10

Naming Simple Alkanes

To name continuous-chain (simple) alkanes from either a chemical or structural formula:

- make sure that the number of carbon and hydrogen atoms matches the general formula C_nH_{2n+2} .
- count the number of carbon atoms and indicate this number using the appropriate prefix.
- add the -*ane* ending to the prefix to indicate that the compound is an alkane.

Name these continuous-chain hydrocarbons.

1.
$$C_{6}H_{14}$$
 $-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-\overset{i}{C}-$
2. $C_{10}H_{22}$ $-\overset{i}{C}-\overset{i$

You should be able to draw the structure of any continuous-chain alkane given either its chemical formula or its name.

The steps are straight-forward:

- determine the number of carbon atoms in the molecule by looking at the subscript in the chemical formula.
- draw the carbon atoms in a straight line. Draw a line between each atom to represent a single covalent bond.
- draw single lines from carbon atoms to hydrogen atoms. Each carbon atom should have four single bonds and each hydrogen must have just one single bond.

Example 2

Draw the structural formula for heptane, C_7H_{16} .

Methods for Drawing Organic Molecules

(1) Structural Diagrams / Skeleton Diagrams (See above)

(2) Condensed Structural Formulas (I don't like these)

Another common way to represent a hydrocarbon is to use a condensed structural formula. For example, the chemical formula of C_4H_{10} can be represented as:

$$CH_3CH_2CH_2CH_3$$
 or $CH_3-CH_2-CH_3$ or $CH_3-(CH_2)_2-CH_3$
(dashes are optional)

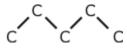
A condensed structural formula provides more information about the bonds in a molecule than a molecular formula does but it is sometimes harder to interpret than a complete structural formula.

(3) Line-Angle Drawings (best)

Structural formulas show you the bonds in a molecule, but they cannot represent molecules threedimensionally.



Notice that a carbon "skeleton" is not perfectly straight, but zigzagged. Each carbon atom is bonded to four other atoms. VSEPR theory predicts that each of the single bonds involving carbon points to a corner of a tetrahedron to give bond angles of about 109.5°. A carbon chain in which each carbon is bonded to another by single bonds has a zigzagged shape.



A really compact way of representing this structure is to use a line drawing. You will use these kinds of drawings when representing alicyclic hydrocarbons in a later lesson. Nonetheless, it is worth noting how these drawings are made in the event that you encounter them in your readings.



The end of each segment represents a carbon atom. Single lines represent single covalent bonds. The presence of hydrogen atoms is assumed and bonds to them are not shown.

Alkyl Groups

Alkyl groups have the general formula C_nH_{2n+1} . They have one less hydrogen atom than a corresponding alkane. For example the methyl group, -CH₃, has one less hydrogen than methane, CH₄.

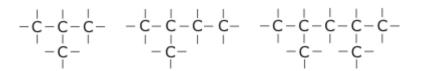
The prefixes used in alkane nomenclature are the same as those used to name alkyl groups. The suffix for an alkyl group, as you may have gathered, is *-yl*. Here are the ones you will use frequently - it is a good idea to memorize them:

- methyl: -CH₃
- ethyl: -C₂H₅ or -CH₂CH₃
- propyl: -C₃H₇ or -CH₂CH₂CH₃
- butyl: -C₄H₉ or -CH₂CH₂CH₂CH₃
- pentyl: -C₅H₁₁ or -CH₂CH₂CH₂CH₂CH₃

Alkyl groups are examples of **substituents**: atoms or groups of atoms that replace a hydrogen atom on a chain or ring of carbon atoms.

Branched alkanes contain one or more alkyl groups. You can identify the alkyl groups by finding the longest continuous chain and then locating any carbons that do not appear to be part of the chain.

Each of the structures below represents a branched alkane. The left and middle structures have one substituent each. The structure on the right consists of five carbons with methyl groups at the second and fourth carbons.



Naming Branched Alkanes

Writing a IUPAC name for a structural formula is an important skill to master. It involves following strict sets of rules. Different rules exist for different classes of organic compounds; however, there are two rules that are used throughout organic nomenclature.

- First, the name of a molecule is based on the longest continuous chain of carbon atoms containing a functional group.
- Second, numbers are used to indicate the location of substituents or functional groups on the continuous chain.

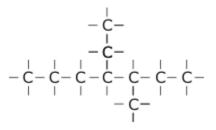
Steps to Name a Branched Alkane:

- 1. Find the longest continuous chain of carbons in the molecule and name it. This is the **parent** chain of the molecule. Be careful, the longest continuous chain is not always obvious because it may zigzag. (HINT! highlight the parent chain in some way.)
- 2. Number the carbons in the parent chain. Designate the carbon at the end to which branching is closest as number 1.
- 3. List the alkyl groups present.
- 4. If there is more than one type of alkyl group in the molecule you list their names in alphabetical order.
- 5. If an alkyl group occurs more than once, use a Latin prefix to indicate the number present. The Latin prefixes are di = 2, tri = 3, tetra = 4, penta = 5, and so on.
 - e.g. two methyl groups would be represented as *dimethyl*
- 6. Use a number to indicate the location of each alkyl group on the parent chain.
- 7. Use proper punctuation: commas are used to separate numbers, and hyphens are used to separate numbers and letters.

Important Points About Naming Branched Alkanes:

- 1. An alkyl group cannot be located on the terminal carbon of a continuous chain because such an "alkyl" group would serve to extend the chain further.
- 2. Note that the longest continuous chain may not be obvious, make sure you have located it by testing the length of all possible parent chains!
- 3. Alkyl groups must be assigned the lowest numbers possible.
- 4. Adding a prefix to an alkyl group's name does not change its order in the alphabetized listing of alkyl groups in a name.

Write an IUPAC name to represent this structural formula.



More Examples:

Drawing Structural Formulas for Branched Alkanes

You may be asked to draw a structural formula for a branched alkane given its name. The steps involve decomposing the name into the parent chain and the alkyl groups, and then arranging the alkyl groups on the structural formula of the parent chain based on their numbers.

Steps for Drawing a Structural Formula

- 1. Draw the parent chain.
- 2. Add the alkyl groups (substituents).
- 3. Make sure each carbon atom has an octet (e.g. four single covalent bonds).

Draw the structural formula for 3-ethyl-2,4-dimethylhexane.

More Examples

Isomers

Structures that have the same molecular formula but different structural formulas are called **structural isomers**.

The possibility of more than one structure for a single molecular formula is called **isomerism**. It is a key reason for the tremendous diversity of organic compounds. For example, there are 75 possible isomers of $C_{10}H_{22}$; 366, 319 possible isomers of $C_{20}H_{42}$; and 4, 111, 846, 763 possible isomers of $C_{30}H_{62}$. Note the use of the word "possible". It is used because relatively few of the isomers for these molecular formulas have actually be isolated.

Draw and name all the possible isomers of C₅H₁₂.

Alkenes and Alkynes

In organic chemistry, the term **saturated** refers to organic compounds which contain single carbon to carbon bonds or which have the maximum number of hydrogen atoms bonded to carbon atoms. Alkanes are saturated hydrocarbons.

Hydrocarbons whose molecules contain double or triple carbon to carbon bonds (multiple bonds) are said to be **unsaturated**. Alkenes and alkynes are unsaturated hydrocarbons - they possess at least one double or triple bond respectively. As a result, alkenes and alkynes have a higher carbon to hydrogen ratio than alkanes.



Your study of alkenes and alkynes will be restricted to compounds containing only one multiple bond per molecule. This allows you to make the generalization that with each extra shared pair of electrons between two carbons, the number of hydrogen atoms per molecule decreases by two. The general formulas for alkenes and alkynes reflect this generalization. Respectively, they are: C_nH_{2n} and C_nH_{2n-2} .

Functional group: special group of atoms that makes the molecule different from an alkane.

Naming Alkenes and Alkynes

Consider these structural formulas for isomers of C₅H₁₀:

If you follow the rules introduced in the study of alkanes, then both isomers would be named pentene. Can you see a problem with this? Roll your mouse over each structural formula above to see how IUPAC (International Union of Pure and Applied Chemistry) deals with the issue?

When naming alkenes and alkynes, a number is used to designate the location of the multiple bond. In fact, priority in the numbering of the longest continuous chain in unsaturated hydrocarbons is given to the location of the multiple bond. Consider these examples:

If the structural formula on the left was named using the rules for branched alkanes, the parent chain would be numbered from right to left and the methyl group would be located at carbon #2. However, since priority is given to the location of the multiple bond, the parent chain is numbered from left to right and the structure is named 4-methyl-1-pentene.

The suffixes *-ene* and *-yne* are used to name the parent chains in alkenes and alkynes respectively.

Rules for Naming Alkenes and Alkynes

The rules for naming alkyl branches in alkenes and alkynes are the same as those introduced when you studied alkanes.

Here is a summary of the rules to be applied:

- 1. Count to find the longest continuous chain of carbon atoms that contains the multiple bond. Number the carbons by giving the multiple bond the lowest possible number.
- 2. List and number the alkyl groups present. Assign Latin prefixes if necessary. List them alphabetically. (For the purpose of alphabetizing, ignore the prefixes *di, tri*, etc.)
- 3. Write the name using proper punctuation. Commas are used to separate numbers, and hyphens are used to separate numbers and letters.

Examples:

Structural Formulas for Alkenes and Alkynes

The process of translating the name of an alkene or alkyne into a structural formula requires the same kind of systematic approach introduced in your study of alkanes. Decompose the name from right to left beginning with the name of the parent chain, the location of the multiple bond and then the location(s) of the alkyl group(s). Consider these examples.

Example

Draw a structural formula for 2-ethyl-1-pentene

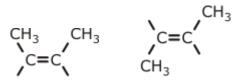
More Examples:

Isomers of Alkenes and Alkynes

```
Draw and name all possible isomers of C_4H_{10}
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Other isomers called **geometric isomers** are possible in alkenes. The labels *cis*- and *trans*- are used to distinguish between them. Think of *cis* as meaning the same side and *trans* as meaning across.

Example:



Cyclic Hydrocabons

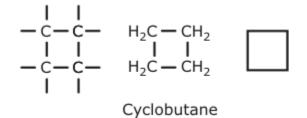
A ring of three or more carbons connected by single bonds is called a **cyclic alkane** or a **cycloalkane**. Cyclic alkanes have two less hydrogen atoms than their corresponding continuous-chain alkanes. The general formula for a cyclic alkane is C_nH_{2n} which is the same as the general formula for an alkene that has one double bond.

Cyclic alkenes are rings that possess a double carbon to carbon bond. They are sometimes referred to as cycloalkenes.

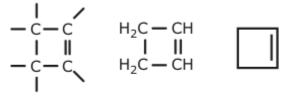
Cyclic aliphatics may have one or more alkyl groups; however, in this course, you will focus on structures that have only one substituent.

Structural Formulas for Cyclic Aliphatics

There are at least three acceptable methods of representing a cyclic aliphatic structure: full structural formula, condensed structural formula, and line drawing.



All three ways are acceptable, but line drawings are preferred. In a line drawing, each point or corner represents the location of a carbon atom.



Cyclobutene

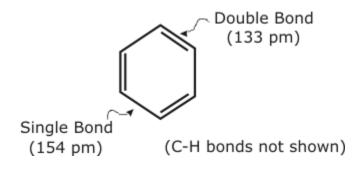
Examples

Draw a structural diagram for cyclopentane.

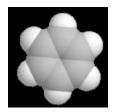
Carbon to Carbon Bonds in Benzene

The benzene ring consists of six carbon atoms, each of which is bonded to a hydrogen atom.

One way to satisfy the octet rule for carbon atoms in the benzene ring is to show the carbons with alternating single and double bonds. That way, each carbon atom has four bonds: a double bond (C=C), a single bond (C-C), and another single bond (C-H).



Double carbon to carbon bonds are 14% shorter than single carbon to carbon bonds, yet *x*-ray crystallography studies show that all six carbon to carbon bonds in benzene ring are the same length (about 139 pm). The benzene ring is actually a flat hexagonal structure as illustrated by this image.



This structure suggests that all six of the carbon to carbon bonds are the same length. In other words, a distorted, unsymmetrical ring is not a suitable model for benzene.

The problem of producing a structural formula for benzene that is consistent with the flat ring observations has been addressed using the concept of resonance. It is a pretty simple idea.

Resonance means that there are two or more possible distributions of bonding electrons for a compound. The **resonance structure** (sometimes called resonance hybrid) is an average of the electron distributions.

Diagram:

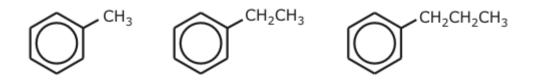
Naming Aromatic Hydrocarbons

One or more hydrogen atoms of a benzene molecule may be substituted with an alkyl group. The resulting compound is called an **alkyl benzene**.

Although all six of benzene's hydrogen atoms can be replaced by substituents, you will focus on those in which just one or two are replaced.

Monosubstituted Alkyl Benzenes

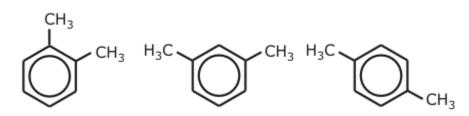
A benzene compound in which one hydrogen is replaced by an alkyl group is called a monosubstituted alkyl benzene. Consider these examples:



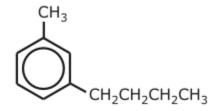
Naming monosubstituted alkyl benzene compounds requires a similar approach to the one you used for simple branched aliphatic compounds. The benzene ring is the parent and the alkyl group is the substituent. The ring carbon where the substituent is located is designated as carbon #1. This number is not included in the name.

Disubstituted Alkyl Benzenes

When two hydrogen atoms on the benzene ring are replaced by alkyl groups, the result is a **disubstituted alkyl benzene**. The two alkyl groups may be the same or different. Consider these examples:



Example: Provide an IUPAC name for this structural formula.

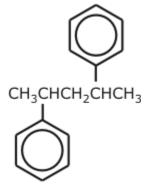


When Benzene is the Substituent

There are instances when a benzene ring is bonded to a non-terminal carbon of an alkyl group and others where more than one benzene ring is connected to an alkyl group. In these cases, the alkyl groups become the parents and the benzene rings become the branches.

As a branch, the benzene ring is called a **phenyl** group.





More Examples:

Hydrocarbon Derivatives

The ability of carbon atoms to form stable bonds with various other elements contributes to the tremendous diversity of organic compounds. In this section, you will learn about organic compounds that contain other non-metallic elements such as the halogens, nitrogen, oxygen, and sulfur. These compounds are classified as hydrocarbon derivatives.

Each class of hydrocarbon derivatives is defined by a **functional group** - an atom or group of atoms that give the hydrocarbon derivative its unique chemical and physical properties. In addition to learning to recognize and classify compounds on the basis of their functional groups, you will discover some of the properties associated with each class of compounds.

An <u>organic halide</u> is a compound that contains one or more halogen atoms as part of its molecular structure.

Organic halides have many important uses including:

- fire retardation
- anaesthesia
- plastics manufacturing
- refrigeration/cooling systems



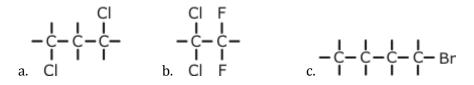
The term **alkyl halide** is often used to represent organic halides derived from hydrocarbons. The general formula of an alkyl halide is *R*-*X* where *R* represents an alkyl group and *X* represents a halogen substituent.

Naming Alkyl Halides

Naming alkyl halides is a lot like naming branched alkanes. Here are the steps to follow:

- Identify and name the longest continuous chain of carbon atoms.
- Identify and name the halogen substituent(s). Assign lowest possible numbers to the substituents:
 - \circ F Fluoro
 - Cl Chloro
 - o Br Bromo
 - o I Iodo
- List the substituents in alphabetical order using appropriate prefixes.
- Write the full name of the compound beginning with the names of the substituents and ending with the name of the parent.

Provide an IUPAC name for each structural formula.



Mores Examples:

The approach to writing structural formulas for alkyl halides is much the same as writing structural formulas for branched aliphatic compounds.

- Draw the parent chain
- Add a symbol for each halogen atom based on the information on its position in the name.

Example

Write a structural formula for 1-chloro-1,2-difluoroethane.

More Examples:

Production of Organic Halides: Substitution Reactions

A **substitution** reaction occurs when a hydrogen atom is removed from the hydrocarbon and replaced by a halide substituent. The products are a hydrocarbon derivative and a hydrogen halide. A key point to remember about substitution reactions is that a hydrogen atom has to be removed from the hydrocarbon before a substituent can be added.

Example: Methane + Bromine

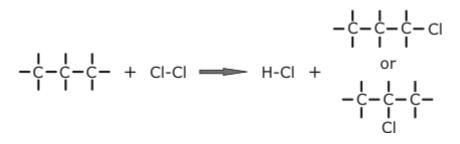
In this example, a substitution reaction involving methane and bromine occurs. The product is bromomethane. When a bromine molecule absorbs energy, the covalent bond is broken resulting in the formation of bromine atoms. These atoms are good examples of **radicals** - very unstable and highly reactive particles.

One of the bromine atoms removes a hydrogen atom to form hydrogen bromide while the other one bonds to the carbon from which hydrogen was removed. The reaction can be summarized by this equation.

$$-\overset{l}{C} + Br-Br \longrightarrow H-Br + -\overset{l}{C} - Br$$

A question you might have at this point is: "Can more than one hydrogen atom be substituted?" That is a good question. The answer is yes. All four of the hydrogen atoms in methane can be replaced by bromine atoms.

Structural isomerism is the existence of two or more structural formulas for one chemical formula. Single step or multi-step substitution reactions can result in the production of structural isomers. Consider the reaction between propane and chlorine.



If a hydrogen on carbon #1 is replaced, then the product is 1-chloropropane; however, if a carbon #2 hydrogen is replaced, then the product is 2-chloropropane. Is 3-chloropropane a third possibility?

Substitution: Two-Stage Reactions

If a propane molecule reacts with two chlorine molecules, then there are several possible isomeric products!

Example: Draw and name the structural formulas for possible isomeric products of a reaction between propane and two molecules of chlorine.

Stage 1: The first chlorine molecule reacts with propane.

$$-c^{-}-c^{-}-c^{-}-c^{-}-c^{-}$$

 $-c^{-}-c^{-}-c^{-}-c^{-}$
 $-c^{-}-c^{-}-c^{-}-c^{-}$

The products of the first step of the reaction are 1-chloropropane or 2-chloropropane.

Stage 2a: If the second chlorine molecule reacts with 1-chloropropane;

$$- \dot{c} - \dot{c}$$

then the possible isomers are: 1,1-dichloropropane, 1,2-dichloropropane, and 1,3-dichloropropane.

Stage 2b: If the second chlorine molecule reacts with 2-chloropropane;

then the possible isomers are: 1,2-dichloropropane and 2,2-dichloropropane.

Thus there are four different isomeric products possible for this two-step substitution reaction. As you can imagine, a higher ratio of chlorine to propane results in even higher numbers of possible isomers.

Examples:

Production of Organic Halides: Addition Reactions

Alkenes and alkynes are unsaturated hydrocarbons containing at least one double or triple bond respectively. They do not undergo substitution reactions; instead, they undergo **addition** - a reaction in which substituents are added to both carbons involved in the multiple bond. Alkenes and alkynes are chemically more reactive than alkanes because of the presence of the multiple carbon to carbon bonds.

When halogens are added to an alkene or alkyne, the halogen atoms are added at the location of the multiple bonded carbon atoms. The reaction is spontaneous unlike substitution reactions which require light energy to break the covalent bonds in the diatomic halogen molecules.

a. The product is 1,2-dichloroethane.

 $\begin{array}{rcl} CH_2CHCH_2CH_3 & + & CI-CI & \longrightarrow & CH_2CICHCICH_2CH_3 \\ b. & 1-butene & & 1,2-dichlorobutane \end{array}$

The product is 1,2-difluorocyclohexane.

In addition reactions, no hydrogen atoms are removed from the hydrocarbon. Substituents are bonded to the hydrocarbon using the bonding electrons that make up the multiple bond. In alkenes, a double bond is reduced to a single bond and in alkynes, a triple bond is reduced to either a double or a single bond depending on the amount of the substituent available for addition.

Example: Predict the products of addition reactions between:

- a. one molecule of ethyne and one molecule of chlorine
- b. one molecule of ethyne and two molecules of chlorine

Example: Predict the product of a reaction between ethene and hydrogen chloride.

added to the multiple bond. This results in isomeric products.

More Examples

Elimination Reactions

Halogen substituents can be removed from an alkyl halide in a reaction involving a base. The organic product of an elimination reaction is an unsaturated hydrocarbon.

Example

Write a chemical equation to show the conversion of 2-chlorobutane to an unsaturated hydrocarbon.

Answer

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Hydroxide ions (OH⁻) give a substance the properties of a base (e.g. high pH).

In this elimination reaction, it removes a hydrogen from either carbon #1 or carbon #3.

- If a hydrogen is removed from carbon #1, then 1-butene is produced.
- If a hydrogen is removed from carbon #3, then 2-butene is produced.

The hydroxide ion combines with the hydrogen to produce water, and the eliminated chlorine atom becomes a chloride ion.

More Examples:

Benzene

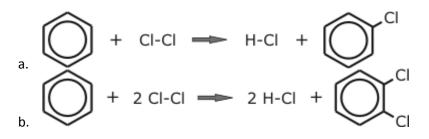
In the lesson on aromatic hydrocarbons, you read about the special carbon to carbon bonds in the benzene ring. One piece of evidence cited to support the theory of delocalized bonding electrons was the chemical behaviour of benzene.

Benzene behaves chemically like an alkane (a saturated compound) and not like the alkenes and alkynes (unsaturated compounds.) This is because the hybrid carbon to carbon bonds of the benzene ring are very stable and are not easily broken like the double bonds in alkenes and triple bonds in alkynes. Since the hybrid bond is not easily broken, reactions between halogens and benzene result in the substitution of hydrogen with halogen atoms. In other words, benzene behaves chemically like a saturated compound because it undergoes substitution reactions.

Example: Write an equation using structural formulas to illustrate a reaction between

- a. benzene and chlorine
- b. one benzene molecule and two chlorine molecules

Answer



Are there other possible isomeric products in item b?

More Examples:

Alcohols and Ethers

Alcohols are defined by the functional group called **hydroxyl** (<u>-OH</u>). The general formula for an alcohol is R-OH where R represents an alkyl group.

Ethers are defined by the functional group known as **ether** (*-O-*). The general formula for an ether is R-O-R' where R and R' represent alkyl groups.

$$-\stackrel{l}{\underset{\scriptstyle \mathsf{L}}{\overset{\scriptstyle \mathsf{O}}}}-\stackrel{l}{\underset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}}}-\stackrel{l}{\underset{\scriptstyle \mathsf{C}}{\overset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}}}-\stackrel{l}{\underset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}{\overset{\scriptstyle \mathsf{O}}}}}$$

In an ether, the alkyl groups can be the same or different. In the above example, the alkyl groups are *methyls* (-CH₃).

Naming and Drawing Structural Formulas for Alcohols

What do the names methanol, ethanol and 1-propanol have in common? It should be pretty obvious - they all end in *-ol*.

The *-ol* suffix in a chemical name identifies a compound as an alcohol; in other words, it signals the presence of a hydroxyl group.

When you are given a structural formula that contains the hydroxyl group, follow these steps to name the compound:

- 1. Count to find the number of carbon atoms in the longest continuous chain (the alkyl stem).
- 2. Name the continuous chain of carbons in the same way you would name a corresponding alkane.
- 3. Change the *-e* ending of the alkane name to *-ol*.
- 4. Indicate the location of the hydroxyl group using the lowest possible number. Attach the number to the name with a hyphen. (Alcohols containing one or two carbon atoms have only one possible location for the hydroxyl group, so the position number can be omitted in those cases.)
- **5.** If the alkyl group is branched, priority in the numbering of the parent goes to the location of the hydroxyl group.

Naming Alcohols

Example: Write the IUPAC names that correspond to these structural formulas.

$$- \overset{I}{\overset{C}{}}_{\overset{C}{}} \overset{I}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}}_{\overset{C}{}} \overset{OH}{\overset{C}{}} \overset{OH}{\overset{C}} \overset{OH}{\overset{OH}} \overset{O$$

More Examples:

Structural Formulas for Alcohols

To draw a structural formula when you are given the name of an alcohol,

- 1. draw a chain of one or more carbons based on the name of the alkyl parent;
- 2. then situate the hydroxyl group (and any other groups) based on the assigned number(s) in the name.

Example: Draw a structural formula for each alcohol.

- a. 2-propanol
- b. 3-pentanol
- c. 2-methyl-2-butanol

Phenol is an alcohol in which the hydroxyl group is a substituent of a benzene ring.



The name consists of the root of the word *phenyl* (which is used to identify benzene rings) and the suffix *ol* which represents a hydroxyl group.

Naming and Drawing Structural Formulas for Ethers

Ethers are hydrocarbon derivatives that contain an oxygen atom bonded to two alkyl groups. They have the general formula of R-O-R'where R and R'are alkyl groups. The alkyl groups can be either the same or different.

When you are given the structural formula for an ether,

- determine whether the alkyl groups are the same or different.
- if they are different, name and list them in alphabetical order as <u>one word</u>, and add the word ether to make a phrase.
- If they are the same, add the prefix *di* to the alkyl name, and then write the word ether to complete the phrase.

Example: Provide an IUPAC name for each ether.

To draw the structural formula of an ether, draw the oxygen atom symbol and attach the alkyl groups to it.

Example: Draw a structural formula for each ether.

- a. dimethyl ether
- b. butylmethyl ether

More Examples:

Reactions of Alcohols...

Addition Reactions

Addition reactions are an alternative to fermentation as a means of producing alcohols. These reactions proceed in much the same way as the addition reactions that produce alkyl halides except that water is added at the location of the double bond. Consider this example:

The water molecule splits into hydrogen and a hydroxyl. These species are added to ethene at the location of the double bond. The product is ethanol. This reaction is an important synthetic source of ethanol.

Elimination Reactions

Alkenes can be produced by elimination of a water molecule from an alcohol. This reaction involves the use of an acid catalyst. A catalyst is a substance that speeds up a chemical reaction without being consumed. The acid catalyst in the example below is represented by the symbol H⁺.

$$-\overset{I}{C}-\overset{I}{C}-\overset{I}{C}-OH \xrightarrow{H^+} -\overset{I}{C}=\overset{I}{C}-\overset{I}{C}- + H_2O$$

Can you see why this reaction is classified as elimination? It should be obvious that a hydroxyl group and a hydrogen atom are being eliminated from the alkyl parent. The result is the formation of an unsaturated hydrocarbon and water.

Examples:

Properties of Alcohols and Ethers

The properties of alcohols are a function of the hydrogen bonding associated with the highly polar "OH" bond.

Short chain alcohols like methanol, ethanol, and propanols have the unique property of being soluble in nonpolar and polar solvents. This makes them very useful for cleaning oily, greasy, or waxy materials. The alkyl component of these alcohols dissolves in nonpolar oils, grease, or wax while the hydroxyl end dissolves easily in water.

dissolves in water dissolves the grease

The higher melting and boiling points of alcohols compared to corresponding aliphatic hydrocarbons is due to the strong hydrogen bonds that form between alcohol molecules and the slightly greater London dispersion forces due to the higher number of electrons per molecule. For example, ethane boils at -88.5°C whereas ethanol boils at 78.5°C.

The properties of ethers are a function of the stable ether link between the alkyl groups. Aside from being highly flammable, ethers are generally unreactive. Ethers are volatile - they evaporate more easily than alcohols because they lack hydrogen bonding. This property makes them useful as anaesthetics, propellants (in spray cans), and solvents for varnishes and lacquers. Ethers have lower melting and boiling points than their alcohol isomers because they lack hydrogen bonding.

Aldehydes and Ketones

Aldehydes and ketones are two more groups of hydrocarbon derivatives. What do they have in common? How are they different? How can they be distinguished from each other.

Aldehydes and ketones both contain the functional group **carbonyl** (-C=O). The carbonyl group consists of a carbon atom and an oxygen atom joined together by a double bond. The location of the carbonyl group in a carbon chain determines whether the hydrocarbon derivative is an aldehyde or a ketone.

A functional group gives a compound its unique chemical and physical properties. Based on this definition, you would think that aldehydes and ketones have similar properties.

Aldehydes

Aldehydes have a terminal carbonyl group - that is, the carbonyl group is located at the end of the molecule. A good way to remember this fact is that the name *al*dehyde begins with "*al*" and the word termin*al* ends in "*al*".

The general formula of an aldehyde is *R-CHO* where *R* represents a single hydrogen atom or a chain of carbon atoms (usually and alkyl group).

The simplest aldehyde is methanal, H_2CO . The carbon of the carbonyl group is the only carbon atom in the molecule.

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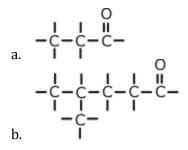
Naming Aldehydes

To name an aldehyde from a structural formula:

- 1. Identify the longest continuous chain of carbon atoms (including the carbon atom in the carbonyl group).
- 2. Write the name of the corresponding alkane and replace the *-e* ending of the alkane name with *-al*.

Note that the carbon of the carbonyl group is counted as part of the carbon chain for naming purposes.

Provide a name for each structural formula.



Examples:

Structural Formulas of Aldehydes

Drawing structural formulas for aldehydes involves determining the number of carbon atoms in the carbon chain, adding any alkyl groups listed in the name, and drawing a double bond to an oxygen atom on the terminal carbon.

Provide structural formulas for these aldehydes.

- a. heptanal
- b. 2-methylbutanal

Ketones

Ketones also contain the functional group called carbonyl; however, unlike the aldehydes, the carbonyl group in ketones is located on a non-terminal carbon. This means the simplest possible ketone is propanone: CH₃COCH₃.



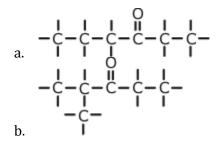
The general formula for ketones is *R*-*CO*-*R*', where *R* and *R*'represent alkyl groups. The carbon of the carbonyl group is counted as part of the carbon chain for naming purposes. The shortest carbon chain in a ketone is three carbons in length.

Naming Ketones

To name a ketone from a structural formula:

- 1. Identify the longest continuous chain of carbon atoms (including the carbon atom in the carbonyl group).
- 2. Write the name of the corresponding alkane and replace the *-e* ending of the alkane name with *-one*.
- 3. If the carbon chain is five carbon atoms or longer, indicate the position of the carbonyl group by assigning it the lowest number possible.

Provide names for these ketones.



Examples:

Structural Formulas for Ketones

Writing structural formulas for ketones follows a similar sequence of steps to those used for aldehydes above.

- Determine the number of carbon atoms in the carbon chain from the alkane component of the name.
- Locate the carbonyl group from the number that precedes the alkane part of the name.
- Draw in any alkyl groups that precede the ketone name.

Provide structural formulas for these ketones.

- a. butanone
- b. 3-ethyl-4-methyl-2-hexanone

Some Properties and Uses of Aldehydes and Ketones

Many aldehydes and ketones have pleasant odours. For example, <u>benzaldehyde</u> gives almonds their distinctive flavour while <u>cinnamaldehyde</u> gives the aroma associated with oil of cinnamon. These compounds, like many other aldehydes and ketones, occur in nature but they may also be synthesized in a lab from alcohols.

Methanal (commonly known as formaldehyde) is by far the most common aldehyde. As formalin (a 40% solution of methanal and water), it is used as a tissue preservative in biology and hospital laboratories and as embalming fluid in funeral homes.

Perhaps the most widely recognized ketone is propanone (commonly known as acetone). It is found in substances such as nail polish remover, varnish, and liquid cleaners. Propanone, like some alcohols, dissolves polar and nonpolar solutes and is commonly used as a cleaner in organic chemistry laboratories.

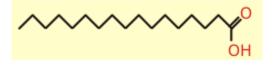
Isomerism

How many possible structures are there for the molecular formula C_3H_6O ? The answer is several. Of the possible structures, how many are aldehydes and/or ketones?

Organic Acids and Esters

Organic acids are common. The one you are probably the most familiar with is ethanoic acid which is also known as acetic acid or simply vinegar (a 5% by volume solution of aqueous acetic acid).

You have probably heard of the term *fatty acids* as well. Fatty acids are long chain hydrocarbons that have a carboxyl group at one end. They are found in animal fats and vegetable oils.





Carboxylic Acids

The functional group that gives organic acids, also known as carboxylic acids, their chemical and physical properties is the **carboxyl** group, **-COOH.**

You can think of a carboxyl group as a *carb*onyl group and a hydr*oxyl* group rolled into one.

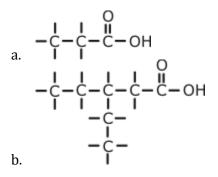
The general formula for the carboxylic acids is *RCOOH* where *R* represents a hydrogen atom or alkyl group.

Unlike carbonyl and hydroxyl groups, carboxyl groups are *always* terminal. The carbon atom of the carboxyl group is considered to be part of the alkyl stem.

Naming Carboxylic Acids

- 1. name the longest continuous chain of carbons, including the carbon of the carboxyl group, using an alkane name. The carbon atom in the carboxyl group is carbon #1.
- 2. if present, list the names of any alkyl branches and assign each a number. Build the name as you would for a branched hydrocarbon.
- 3. replace the *-e* ending of the hydrocarbon name with the suffix *-oic*.
- 4. add the word *acid* to the first name to make a phrase.

Provide a IUPAC name for each structural formula.



Examples

Structural Formulas for Carboxylic Acids

To draw the structural formula for a carboxylic acid,

- 1. draw the main carbon chain.
- 2. attach any alkyl groups listed in the name.
- 3. situate a carboxyl group at the end of the carbon chain.

Draw a structural formula for each carboxylic acid.

- a. butanoic acid
- b. 2-methyloctanoic acid

Esters

Esters are abundant in nature. Many of the pleasant odours you associate with flowers and berries are due to esters as are the scents of bath oils, shampoos, soaps, and room fresheners, etc. Esters are soluble in oils but not water. In the heyday of the whaling industry, whale blubber was boiled down to make the oils in which esters from plants were dissolved.

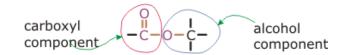


Esters are relative to synthesize in a lab. Nowadays, when you see the phrase "artificially flavoured" on the packaging of your favourite snack or candy, chances are that the flavour is due to a synthesized ester.

The functional group of an ester is actually a combination of a carbonyl group from an organic acid and an ether link from an alcohol.

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Esters are produced by reacting carboxylic acids with alcohols.



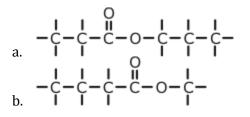
The general formula of an ester is *RCOOR*'where *R* represents hydrogen or a carbon chain/alkyl group and *R*'represents an alkyl group.

Naming Esters

To name an ester from a structural formula:

- 1. count to find the number of carbon atoms in the *-OR*' component of the structural formula (the part derived from an alcohol) and and assign it an alkyl group name.
- 2. count the number of carbon atoms in the *R*-*C*=*O* component of the structural formula (the part derived from the carboxylic acid) and assign it an alkane name with an *-oate* ending in place of the *-oic* ending.
- 3. combine the names to make a phrase.

Provide a IUPAC name for each structural formula.



Examples:

Structural Formulas for Esters

To draw a structural formula of an ester from a name,

- 1. draw carbon chains using the alkyl prefixes from the name and join them using an ether bridge.
- 2. add a double bonded oxygen to carbon #1 of the carboxylic acid component of the structure.

Example 4

Provide a structural formula for each ester.

- a. butyl ethanoate
- b. phenyl ethanoate

Esterification

Esters are often classified as derivatives of carboxylic acids. Esters are produced when alcohols and carboxylic acids are reacted in the presence of an acid catalyst.

Examples:

Example: Which alcohol and carboxylic acid are needed in order to produce the following esters? Write esterification reactions for each.

- a) ethyl propanoate
- b) octyl benzoate
- c) methyl pentanoate

Isomerism

At this point, you should be noticing a pattern in the organization of hydrocarbon derivatives in this section. Can you show that esters are isomers of carboxylic acids? Try drawing structural formulas for ethanoic acid and methyl methanoate and count up the number of carbon, oxygen, and hydrogen atoms per molecule.

Amines and Amides

You might recall that esters tend to have pleasant scents. Well, the same cannot be said for amines and amides. Their scents are characteristically unpleasant. <u>Urea</u> is one of many common examples.

Amines

Amines are derived from ammonia (NH₃) when more of the hydrogen atoms is replaced by a hydrocarbon group. A nitrogen atom is the functional group.

In this course, you will focus on *primary* amines or those that consist of one hydrocarbon group bonded to an **amino** group (-NH₂). These amines have the general formula *RNH*₂ where *R* represents an alkyl group.

To name an amine, identify the alkyl group and add the suffix *-amine* to its name.

Examples:

To draw a structural formula for an amine, determine the length of the carbon chain from the alkyl name and add an amino group to a terminal carbon.

Provide a structural formula for ethylamine.

Amides

The functional group of an **amide** consists of a carbonyl group and an amino group.

An amide can be produced by reacting a carboxylic acid with ammonia (NH₃).

$$H = C = OH + H = H = H = H = C = H + H = OH$$

The general formula for amides is RCONR'R'', where R, R', and R'' represent alkyl groups or hydrogen. However, in this course, we will restrict discussion of amides to the general formula $RCONH_2$ where R represents hydrogen or an alkyl group.

To name an amide, write the name for the carbon chain containing the carbonyl group, drop the *-e* ending, and add the suffix *-amide*.

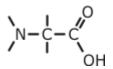
Provide a name for this structural formula.
$$-C - C - C - NH_2$$

Examples:

Write a structural formula for propanamide.

Amino Acids

Amino acids are the building blocks of proteins. Proteins are the stuff of life! See if you can identify the amino and the carboxylic acid components in this structural formula.



Polymers

One of the best analogies for a polymer is the average train.

A train consists of many individual cars joined together at the ends. A **polymer** is a huge molecule that is formed when hundreds or thousands of small molecules called **monomers** are bonded together.

Polymers are literally everywhere. Paper is mainly a natural polymer called cellulose. Cotton, wool, and protein are other examples of natural polymers. Synthetic polymers are things like Dacron®, Teflon®, nylon, polyvinyl chloride (PVC), polyethylene, polypropylene and polystyrene. Synthetic polymers are so common now that you probably can't imagine a world without them. Just think of it - no plastic bags, pipes or containers, no modern carpeting, no high-tech polishes and waxes - the list is extensive. About half of all synthetic polymers are the products of addition polymerization reactions. Natural polymers and the remainder of the synthetic polymers are formed by condensation polymerization.

Addition polymerization is the joining of hundreds or thousands of unsaturated hydrocarbon molecules (the monomer) under specific reaction conditions to form one very long molecule (the polymer).

You know from the bonding unit that a double bond is two pairs of electrons shared by two atoms, in this case, two carbon atoms. This carbon to carbon bond is fairly strong, but when other molecules such as those which tend to strongly attract electrons (radicals) are near, one pair of electrons in the double bond is vulnerable to attack.

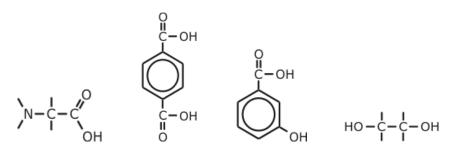
During an attack, the double bond of the monomer is broken to make bonding electrons available. These electrons become shared by the original monomer and another one. Repetition of the process results in the joining of many monomers to make a polymer in a way analogous to the joining of rail cars to make a train. Examples:

Condensation Polymerization

The term *condensation* usually means a phase change from the gas state to the liquid state; however, in organic chemistry, it also describes a type of chemical reaction in which a by-product molecule is formed as two molecules are joined together. Esters and amides are produced by condensation reactions.

A condensation polymer is the product of condensation chain reaction. With each monomer that becomes part of the polymer, a by-product molecule is produced. Unlike addition polymers which can only grow at one end, a condensation polymer can grow in two or more directions at once.

Here are some examples of molecules involved in condensation polymerization reactions:



What do these molecules have in common? How do they differ from molecules that undergo addition polymerization?

Monomers are molecules that are chemically combined at the location of their functional groups. View the following animation to see a generalized condensation polymerization reaction.

Examples: