Chapter 3: Organic Chemistry

Learning Outcomes:

1) Analyzing, Interpreting and naming organic functional groups using IUPAC nomenclature.
2) Interpreting different representations of organic structures
3) Recognize and predict the product of reagents with different functional groups

Essential Vocabulary

IUPAC, functional group, constitutional isomers, line angle (zig-zag) structures, aliphatic hydrocarbons, alicyclic hydrocarbons, saturated, unsaturated, parent chain, substituent, combustion reaction, aromatic hydrocarbon.

1.0 Introduction

Organic chemistry was originally designated as the branch of chemistry dedicated to the study of compounds obtained from living organisms (Animals and plants). In 1809, Jacob Berzelius proposed that organic compounds contained a "vital force", since they originated from living organisms, which could not be synthesized in the laboratory. This "vital force" theory was widely accepted by the scientific community.
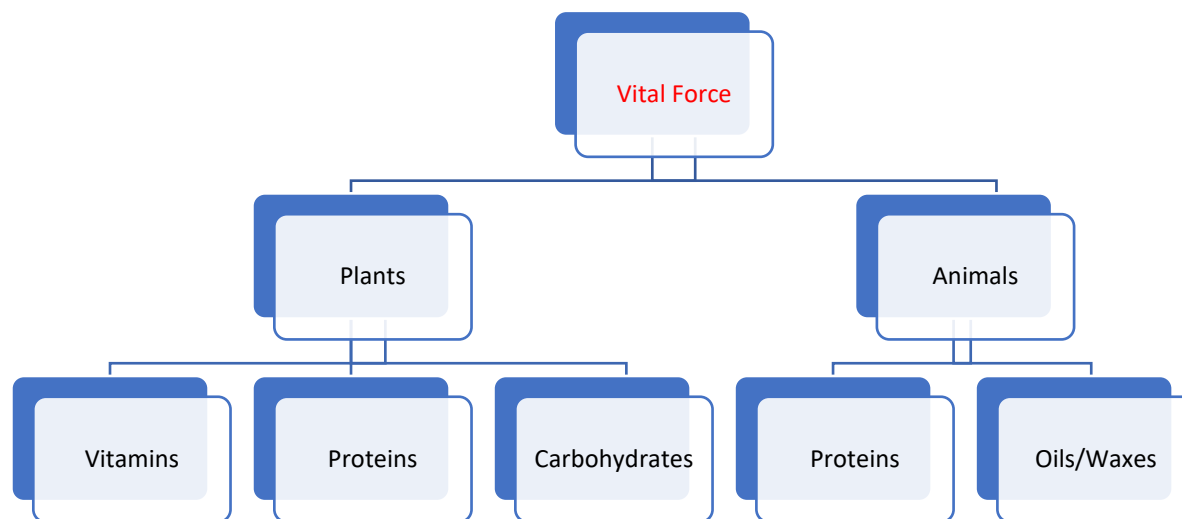

Figure 1: Illustration of Vital force theory

In 1829, German scientist Frederick Wohler reported the first successful synthesis of an organic compound under laboratory conditions using inorganic compounds. Wohler observed that when ammonium cyanate ($NH_4^+CNO^-$ an inorganic compound) was heated it produced urea (H_2NCONH_2-an organic compound found in waste products of animals).   This discovery earned Wohler the distinction of being called the father of modern organic chemistry.

$$NH_4^+CNO^- \xrightarrow{\text{Heat}} NH_2C(O)NH_2$$

<div style="text-align:center">

Ammonium Cyanate   Urea
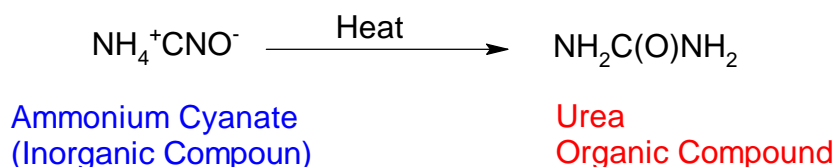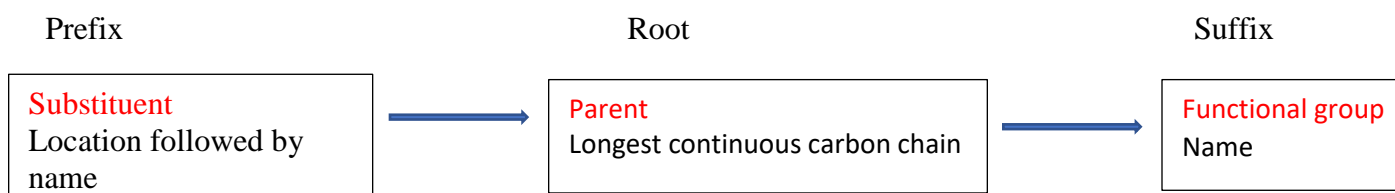(Inorganic Compoun)   Organic Compound

</div>

Figure 2: Reactions of Wohler's synthesis of Urea

Organic compounds are now defined as compounds that contain Carbon (except for carbonates, bicarbonates, oxides, cyanides and carbides).

1.1 Naming Compounds IUPAC Nomenclature

The most prevalent naming system of organic compounds is that which incorporates the IUPAC naming system. IUPAC stands for the International Union of Pure and Applied chemistry, established in 1919. The IUPAC is the world authority on naming rules of inorganic and organic compounds, standards and measurements and naming of new elements on the periodic table. Organic compounds are named by prefix, longest continuous chain (parent chain or root) and suffix. Below is an illustration of naming organic compounds using the IUPAC naming system.

Prefix	Root	Suffix
Substituent Location followed by name	Parent Longest continuous carbon chain	Functional group Name

IUPAC Root names are classified according to the longest continuous chain of carbons. Table 1 represents the root name of the first 10 longest continuous chain of carbons.

Table 1: Root names for first 10 longest continuous carbon chains

Longest continuous chain of carbons	Root name	Longest continuous chain of carbons	Root name
1	meth	6	hex
2	eth	7	hept
3	prop	8	oct
4	but	9	non
5	pent	10	dec

The prefix of a compound is determined by its substituents name and location attachment to the root or parent chain. Substituents are groups attached to the parent chain and not included in the longest chain of continuous carbons. Alkane substituents are named by replacing the *ane* of the suffix with *yl*. For instance, methane as a substituent is named methyl and ethane as a substituent becomes ethyl.

The name's suffix represents the functional group the compound consists of. ***Functional groups*** are groups of atoms that give molecules identical properties. These groups of atoms influence the chemical behavior of a molecule. Each functional group has a specific suffix that is unique.

1.2 Drawing Organic Structures (Representations)

The ability to draw and interpret organic structures is key to the understanding of organic chemistry. There are several ways of representing organic structures which include ***condensed structures***, complete structural formula (***Kekule or Lewis structures)*** and ***line angle (also called skeletal or zigzag).***

A condensed structural formula shows the hydrogen atoms right next to the carbon atoms to which they are attached. A complete structural formula shows all the carbon and hydrogen atoms and bonds and how they are attached to one another. A line-angle formula is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

Condensed structures show the order of the atoms of a molecule written in a straight, single line of text. These structures leave out all bonds and lone pairs on atoms. Carbons are drawn immediately followed by the hydrogens (or atoms) attached to it. Although condensed structures leave bonds and lone pairs on atoms out, when drawing condensed structures parentheses can be used. Parentheses can be used under the following conditions.

1. Repeating methylene groups (CH_2) connected to one another in the molecule. For instance, heptane has the condensed formula of $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$. Notice that this compound has five methylene units connected. We can simplify this condensed structure by writing $CH_3(CH_2)_5CH_3$.
2. The molecule has branching (single or multiple) in the molecule. Parentheses without a subscript indicate single branching on the chain while parentheses with subscripts indicate multiple branching. For example, the condensed formula $CH_3CH_2CH(CH_3)CH_3$ implies the presence of a CH_3 group branching off the **carbon** immediately to the left.
3. The presence of a carbonyl group (C=O) in the molecule. The oxygen of the carbonyl group is surrounded by parentheses. For example, $CH_3CH_2C(O)CH_2$ indicates that the carbon immediately to the left of the parentheses is doubly bonded to the oxygen of the condensed structure.

Complete structural formulas show all bonds in the molecule. all atoms in a neutral molecule having bonding patterns that must be followed when drawing. Let's review the bonding patterns of several elements that are commonly found in organic compounds.
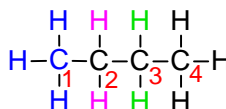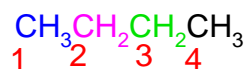
- H: Hydrogen is in Group IA and has 1 valence electron available for bonding. Hydrogen forms one single covalent bond.
- O: Oxygen is in group VIA and has 6 valence electrons. Oxygen forms two covalent bonds (2 single bonds or 1 double bond). Oxygen has two lone pairs of electrons
- N: Nitrogen is in Group VA and has 5 valence electrons. Nitrogen forms singles, double and triple bonds. Nitrogen has one lone pair of electrons.

- C: Carbon is in group in Group IV on the periodic table meaning and has 4 valence elections available for bonding (tetravalent). Because of a carbons tetravalency it can form 4 bonds (8 surrounding bonding electrons). A carbon atom can form covalent bonds (single, double and triple) with other carbons (called catenation) and other elements on the periodic table.
- Halogens: Halogens are in Group VIIA and have 1 valence electron available for bonding. Halogens form one single covalent bond.

The complete structural formula for butane which has a condensed formula of $CH_3CH_2CH_3$ is given below. When drawing the complete structural formula, notice that all carbons have 8 electrons (4 single bonds) obeying the octet rule and all hydrogens have single bonds. The structure is drawn in a straight chain of 3 carbons as indicated by the condensed formula.

The complete structural formulas for butane, which has both a straight chain (normal) and branch chain isomers is given below.

Condensed formula	Complete Structural Formula
$CH_3CH_2CH_2CH_3$ 1 2 3 4	 **Straight Chain**
$CH_3CH(CH_3)CH_3$ 1 2 3	 **Branched Chain**
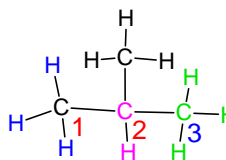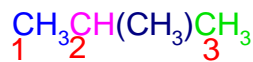
When representing larger organic molecules drawing each carbon and hydrogen can be a daunting task to say the least. Line angle (or skeletal formulas) is an easier and faster way of drawing organic molecules. Listed below are the general rules for drawing line angle structures
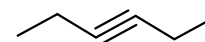
1. Carbon and hydrogens bonded to carbons are not shown
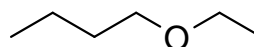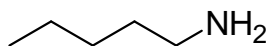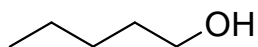2. Carbon atoms in a straight chain are drawn in a zig-zag format.
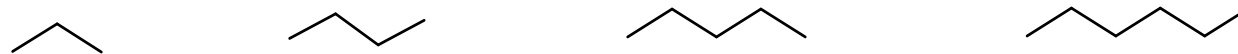
3. Single bonds are represented with one-line, double bonds are represented with two lines and triple bonds are represented with three lines.
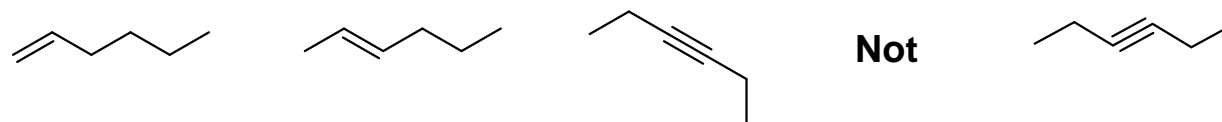
   Not

4. Atoms other than carbon and hydrogens (heteroatoms) must be shown explicitly. Hydrogens bonded to heteroatoms must also be shown.

## Converting Lewis Structures to line angle structures

Structural formulas can be easily converted to line angle structures. The step for converting structural formulas is as follows:

1. Find the longest continuous line of carbons in your Lewis structure, draw the bonds in a zigzag fashion, and remove all hydrogens bonded to carbons. For example, butane has a longest continuous chain of carbons equal to four.
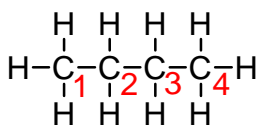
n-butane
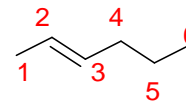
Lewis Structure
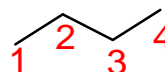
n-butane

Line Angle Structure

2. Add any multiple bonds (double or triple bonds) in the Lewis structure to the line angle structure
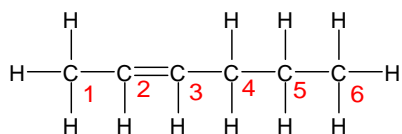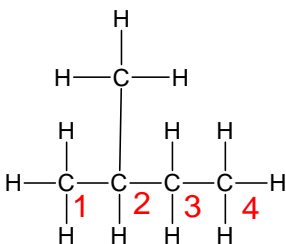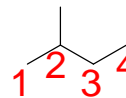

2-hexene

Lewis Structure

2-hexene

Line Angle Structure

3. Add any substituents to the carbon they are bonded to

2-methybutane

Lewis Structure

2-methylbutane

Line Angle Structure

1.3 Aliphatic Hydrocarbons

Hydrocarbons consist of only carbon and hydrogen atoms bonded together. The major classes of aliphatic (open chain hydrocarbons) and alicyclic (ring hydrocarbons). Aliphatic hydrocarbons

consist of alkanes (straight and branched), alkenes and alkynes. Alicyclic hydrocarbons consist of cycloalkanes, cycloalkenes and cycloalkynes. *It should be noted that aromatic hydrocarbons are cyclic, however we will address them separately due to their reactivity.*
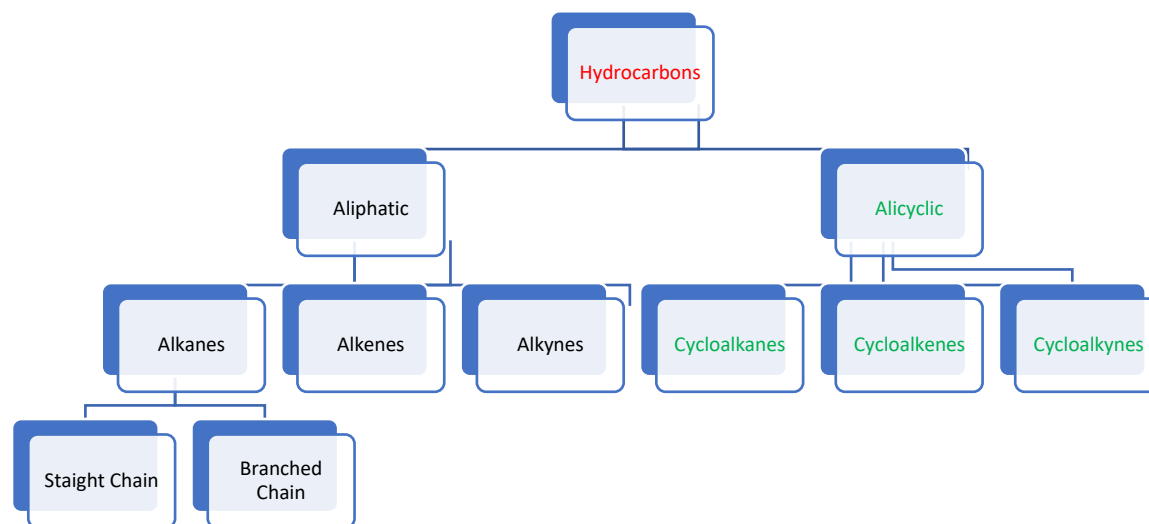

Figure 3: Illustration of major classification of hydrocarbons

1.4 Alkanes

Hydrocarbons that consist of only carbon-carbon single bonds are referred to as alkanes. Alkanes are commonly used for fuels such as methane, ethane, propane and octane. Alkanes are ***saturated*** *(no single or double bonds on carbons)* hydrocarbons. Straight and branched alkanes have the general formula of C_nH_{2n+2} (where n = the number of carbons). Straight alkanes, as the name implies have no attachments to the parent chain (longest continuous chain of carbons) and all carbons are sp^3 hybridized with a tetrahedral molecular shape. The boiling points of straight chained alkanes increase with the number of carbons in the chain (increase in molecular weight). Figure 3 gives the boiling point of the methane, ethane, propane, butane and pentane. Notice that the first four alkanes are gases at room temperature.

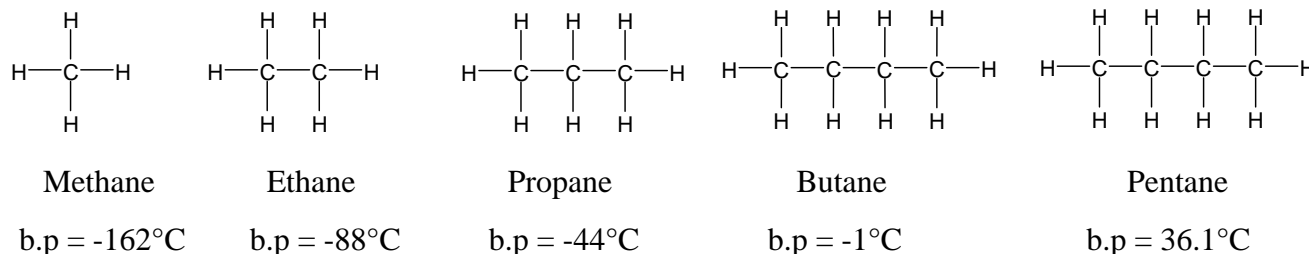| Methane	Ethane	Propane	Butane	Pentane
b.p = -162°C	b.p = -88°C	b.p = -44°C	b.p = -1°C	b.p = 36.1°C

Figure 4: Boiling points of the first five straight chain hydrocarbons

Branched alkanes have attachments that are not a part of the parent chain. These branches are referred to as ***substituents***. Branching on alkanes generally tends to decrease the boiling point of

alkanes due to the decrease of surface area. Figure 4 gives the boiling point of butane and its branched isomer 2-methylpropane

n-butane

b.p = -1°C

2-methylpropane

b.p = -11.7°C

Figure 5: Boiling points of n-butane and its constitutional isomer 2-methlypropane

Straight chain alkanes and branched chain alkanes with the same number or carbons and hydrogens are constitutional isomers. **Constitutional isomers** are molecules with the <u>same molecular formula</u> however their connectivity is different. For example, C_4H_{10} has two constitutional isomers, and they are n-butane and 2-methylpropane.

Carbons atoms of alkanes are classified by the substitution on the sp^3 hybridized carbons. The classifications are **primary** (carbon is singly bonded to one carbon), **secondary** (carbon is singly bonded to two carbons), **tertiary** (carbon is singly bonded to three carbons) and **quaternary** (carbon is singly bonded to four carbons). Primary carbons are denoted by 1°, secondary carbons are denoted by 2°, tertiary carbons are denoted by 3° and quaternary carbons are denoted by 4°. Hydrogen atoms of alkanes are classified by the classification of the carbon it is bonded to. The classifications are primary (hydrogen is bonded to a primary carbon), secondary (hydrogen is bonded to a secondary carbon), tertiary (hydrogen is bonded to a tertiary carbon). There are no quaternary hydrogens because this would violate the octet rule for carbon (5 single bonds = 10 electrons). As an example, let's again refer to the isomers of butane.
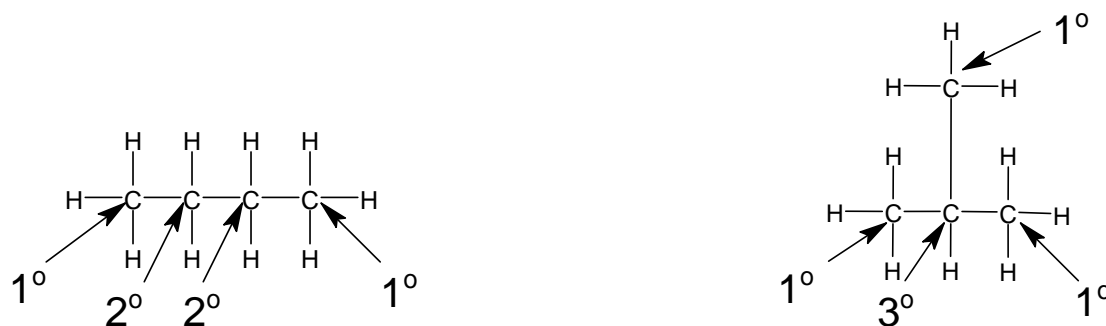

Figure 6: Classification of carbons of n-butane and its constitutional isomer 2-methlypropane

The IUPAC rules for naming alkanes are as follows.

1. Find the longest continuous chain of carbons to determine the parent name of the compound. The suffix for alkanes is (-**ane**)
2. Identify and name all alkyl groups attached to the longest continuous chain of carbons. These alkyl groups are called **substituents**.
3. Count the carbons in the direction that gives substituents the lowest possible number
4. Designate the location of each substituent relative to the parent chain by number.
5. Assemble the name, listing substituent groups in alphabetical order.
6. Insert a hyphen when going from number to letter. Use a comma when separating numbers.
7. If more than one of the same substituents is present in the compound, then numerical prefixes should be used. Table 2 illustrates first ten numerical prefixes

Table 2: First ten numerical prefixes

Number	Numerical Prefix	Number	Numerical Prefix
1	mono	2	di
3	tri	4	tetra
5	penta	6	hexa
7	hepta	8	octa
9	nona	10	deca

Below are several examples of alkanes named using the IUPAC system of naming organic compounds (Numbering according to IUPAC rules is illustrated in red).
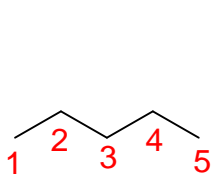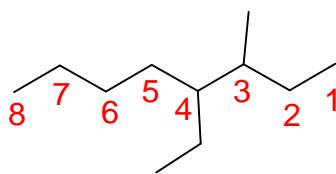

pentane   4-ethyl-3-methyloctane   2,5-dimethylheptane
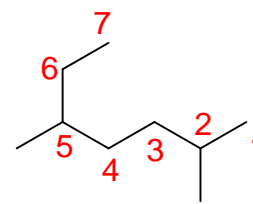
Alkanes are generally unreactive however they do participate in **combustion** reactions. In a combustion reaction the alkanes react with oxygen to produce carbon dioxide and water releasing energy. For example, when propane reacts with enough oxygen in heat the following reaction occurs.
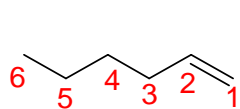
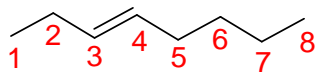$$CH_3CH_2CH_3 \quad + \quad 5O_2 \quad \longrightarrow \quad 3CO_2 \quad + \quad 4H_2O$$
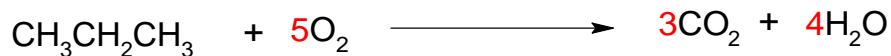
1.5 Alkenes

Hydrocarbons that contain one or more carbon-carbon double bonds are referred to as alkenes. Alkenes are *unsaturated* (contain a double bond) hydrocarbons. Alkanes have the general formula of C_nH_{2n}. The IUPAC rules for naming alkanes are as follows

1. Find the longest continuous chain of carbons that contains the double bond(s) to determine the parent name of the compound. The suffix for alkenes is (-**ene**)
2. Identify and name all alkyl groups attached to the longest continuous chain of carbons that contains the double bond(s). These alkyl groups are called *substituents*.
3. Count the carbons in the direction that gives the double bond the lowest possible number. When the double bond is equidistant from both ends of the parent chain, count in the direction that gives substituents the lowest possible number start (in most cases this is end closest to the nearest substituent).
4. Designate the location of each substituent relative to the parent chain by number.
5. Assemble the name, listing groups in alphabetical order.
6. If more than one carbon-carbon double bond is present in the compound, then numerical prefixes should be used. For instance, if the compound contains two carbon-carbon double bonds the prefix di is placed before the suffix ene (diene).
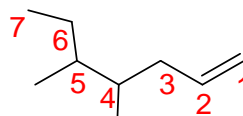
Below are several examples of alkenes named using the IUPAC system of naming organic compounds (Numbering according to IUPAC rules is illustrated in red).
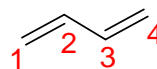

hexene   3-octene   4,5-dimethylheptene   1,3-butadiene

Alkenes can be reduced to saturated alkanes by reacting them with H_2 in the presence of a transitions metal catalyst (Ni, Pt, Pd). The result of this addition reaction is the loss of the double bond and addition of two hydrogen atoms (one atom to each carbon of the original carbon-carbon double bond). Notice when drawing the line angle product of this reaction we simply remove the double bond.
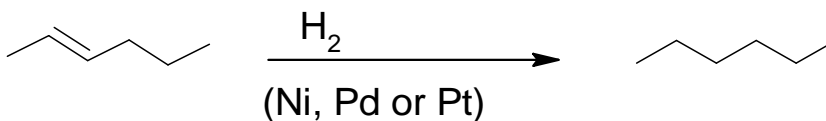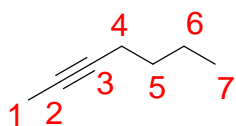

1.6 Alkynes

Hydrocarbons that contain one or more carbon-carbon triple bonds are referred to as alkynes. Alkynes are *unsaturated* (contain a triple bond) hydrocarbons. Alkynes have the general formula of C_nH_{2n-2}. The IUPAC rules for naming alkynes are as follows
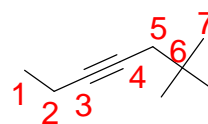
1. Find the longest continuous chain of carbons that contains the triple bond(s) to determine the parent name of the compound. The suffix for alkynes is (-**yne**)
2. Identify and name all alkyl groups attached to the longest continuous chain of carbons that contains the triple bond(s). These alkyl groups are called *substituents*.

3. Count the carbons in the direction that gives the triple bond the lowest possible number. When the triple bond is equidistant from both ends of the parent chain, count in the direction that gives substituents the lowest possible number start (in most cases this is end closest to the nearest substituent).
4. Designate the location of each substituent relative to the parent chain by number.
5. Assemble the name, listing groups in alphabetical order.
6. If more than one carbon-carbon triple bond is present in the compound, then numerical prefixes should be used. For instance, if the compound contains two carbon-carbon double bonds the prefix di is placed before the suffix yne (diyne).

Below are several examples of alkynes named using the IUPAC system of naming organic compounds (Numbering according to IUPAC rules is illustrated in red).
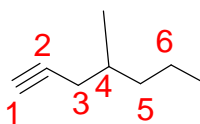
2-heptyne   4-methylheptyne   6,6-dimethyl-3-heptyne

Alkynes can be reduced to both alkenes and alkynes. There are two major reactions used in the reduction of an alkyne to an alkene. The first is the reaction of an alkyne with H_2 in the presence of Lindlar's catalyst. Lindlar's catalyst is Pd and barium sulfate poisoned with quinoline ($Pd/BaSO_4$ in quinoline). This reaction results in the formation of an alkene with *cis* hydrogens (on same side of double bond). The second is the reaction of an alkyne with sodium metal in liquid ammonia (NH_3). This reaction results in the formation of an alkene with trans hydrogens (on opposite side of the double bond). Like alkenes, alkynes can also be reduced to alkanes if reacted with H_2 in presence of transition metals (Ni, Pd or Pt), however two equivalents of H_2 must are used to ensure complete unsaturation.

$$\text{2 eq of } H_2$$
$$\xrightarrow{\hspace{2cm}}$$
$$(\text{Ni, Pd or Pt})$$
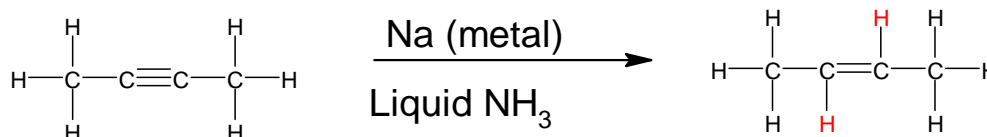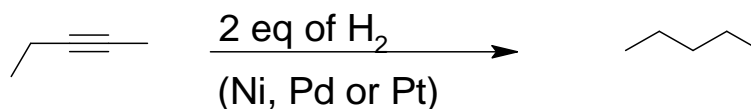
1.7 Cycloalkanes

Hydrocarbons that consist of only carbon-carbon single bonds in a ring structure are referred to as cycloalkanes. Cycloalkanes are **saturated** hydrocarbons. Cycloalkanes have the general formula of C_nH_{2n}. The IUPAC rules for naming alkanes are as follows.
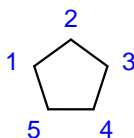
1. Count the number of carbons in the ring structure to determine the parent name of the compound. The prefix for cycloalkanes is (**cyclo**) and the suffix for is (**-ane**) Listed Below are the ring structures of the first ten cycloalkanes
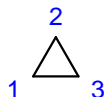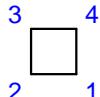
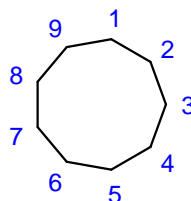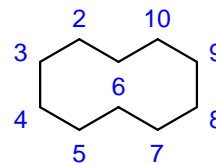cyclopropane   cyclobutane   cyclopentane   cyclohexane
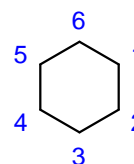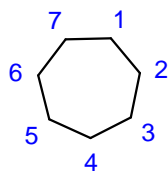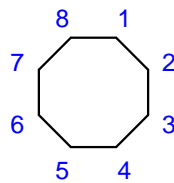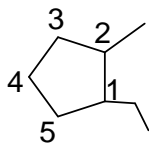
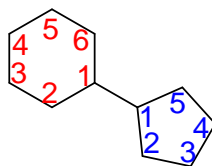cycloheptane   cyclooctane   cyclononane   cyclodecane

2. Identify and name all alkyl groups attached to the ring structure. The ring is considered the parent name if it contains more carbons than any of the alkyl substituent(s). If any alkyl group contains more carbons than the ring, then it is given the parent name and the ring structure is named as a substituent. For instance, cyclopropane, cyclobutane and cyclopentane become cyclopropyl, cyclobutyl and cyclopentyl respectively as substituents
3. If more than one ring structure is present, then the ring with the greater number of carbons is the given the parent name. The other ring(s) are named as cycloalkyl groups.
4. Count the carbons of the ring the direction that gives substituents the lowest possible number
5. If more than one of the same substituents is present in the compound, then numerical prefixes should be used.
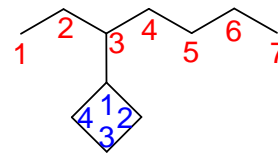
Below are several examples of cycloalkanes named using the IUPAC system of naming organic compounds.

1-ethyl-2-methylcyclopentane   cyclopentylcyclohexane   3-cyclobutylheptane

Cycloalkanes, like aliphatic alkanes, participate in **combustion** reactions. Cycloalkanes react with enough oxygen to produce carbon dioxide and water releasing energy. For example, when cyclobutane reacts with enough oxygen in heat the following reaction occurs.
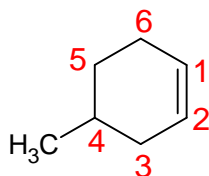
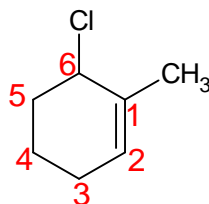$$\square \;\; + \;\; 6O_2 \longrightarrow 4CO_2 \;\; + \;\; 4H_2O$$

1.8 Cycloalkenes:

Hydrocarbons that have carbon-carbon double bond(s) in a ring structure are referred to as cycloalkenes. Cycloalkenes have the general formula of C_nH_{2n-2}. The IUPAC rules for naming cycloalkenes are as follows for alkenes. Then the naming of cycloalkenes is similar to alkenes. However, there are several other rules that must be applied to cyclohexenes. These rules are as follows:

1. When naming cycloalkenes if there is only one double bond its position is assumed to be 1
2.   Count the ring in the direction includes both carbons of the carbon-carbon double bond and gives the lowest possible number to the nearest substituent.
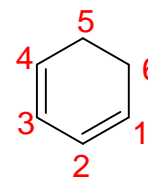3. If a carbon of the double bond has a substituent on it, it is in the one position

Below are several examples of cycloalkenes named using the IUPAC system of naming organic compounds.


4-methylcyclohexene   6-chloro-1-methylcyclohexene   cyclohexa-1,3-diene

Cycloalkenes react similarly to alkenes. Reacting cycloalkenes with H_2 in the presence of a transitions metal catalyst (Ni, Pt, Pd) results in cycloalkane formation. The result of this addition reaction is the loss of the double bond and addition of two hydrogen atoms (one atom to each

carbon of the original carbon-carbon double bond). As with alkenes, when drawing the line angle product of this reaction we simply remove the double bond.

4-methylcyclohexene $\xrightarrow{\text{H}_2 \atop \text{Pd, Pt or Ni}}$ methylcyclohexane
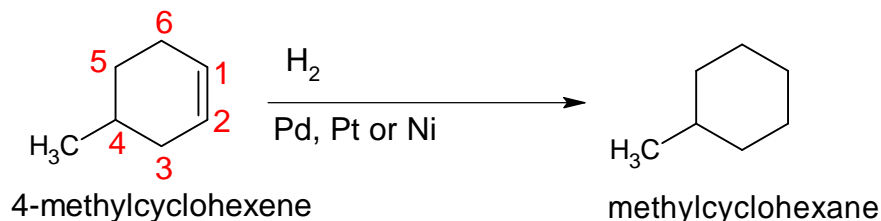
1.9 Cycloalkynes

Hydrocarbons that have carbon-carbon triple bonds(s) in a ring structure are referred to as cycloalkynes. Cycloalkanes have the general formula of C_nH_{2n-2}. Cycloalkynes are very unstable due to ring strain that must be overcome due to the linear geometry of the carbon-carbon triple bond. The IUPAC rules for naming cycloalkynes are like those for alkynes. When naming cycloalkynes if there is only one triple bond its position is assumed to be in position 1. Count the ring in the direction that includes both carbons the carbon-carbon triple bond and gives the lowest possible number for substituents.

Below are several examples of cycloalkynes named using the IUPAC system of naming organic compounds.

cyclooctyne 3-methylcyclononyne cyclodecyne
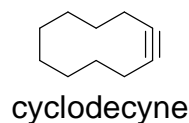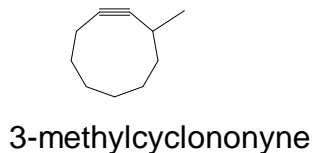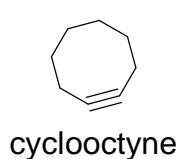
1.10 Alkyl halides

Alkyl halides are alkanes that have a sp3 carbon-halogen bond in the molecule structure. Halogens (Group VII elements) such as Fluorine, Chlorine, Bromine and Iodine contain seven valence electrons therefore they only singly bond to carbon in alkyl halides. Alkyl halides are used as industrial cleaners, organic solvents for reactions and as ingredients used in fire extinguishers.

Alkyl halides have the general formula of C_nH_{2n+1}. The IUPAC rules for naming alkyl halides are as follows

1. Find the longest continuous chain of carbons that contains the carbon-halogen bond to determine the parent alkane name of the compound.
2. Determine the location and identity of all halogens attached to the parent alkane and name as a halogen *substituent. Halogen substituents are named by replacing the "ine" of the halogen with "o"* (fluoro,chloro,bromo, iodo). The halogen substituent becomes the prefix for the parent alkane.

3. Count the carbons in the direction that gives the halogen substituents the lowest possible number.
4. Assemble the name, listing substituent groups in alphabetical order.
5. If more than one of the same substituents is present in the compound, then numerical prefixes should be used.

Below are several examples of alky halides named using the IUPAC system of naming organic compounds.

1-chloropentane   3-fluorohexane   2-bromo-3-iodobutane
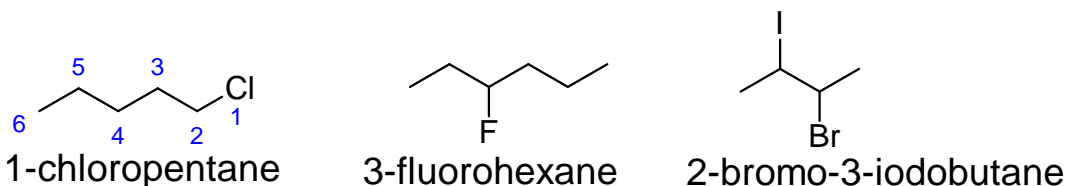
Alkyl halide classification: Alkyl halides are classified by the substitution of the carbon singly bonded to the halogen. The classifications are methyl (carbon bonded to halogen is singly bonded to zero carbons-only hydrogens), primary (carbon bonded to halogen is singly bonded to one carbon), secondary (carbon bonded to halogen is singly bonded to two carbons), and tertiary (carbon bonded to halogen is singly bonded to three carbons). There are **no** quaternary alkyl halides (carbon bonded to halogen is singly bonded to four carbons), because this would violate the octet rule on the carbon.

primary   secondary   tertiary
alkyl halide   alkyl halide   alky halide

Primary and secondary alkyl halides can be reduced to alkanes using the reducing reagent LiAlH4 (Lithium Aluminum Hydride).

$$LiAlH_4$$
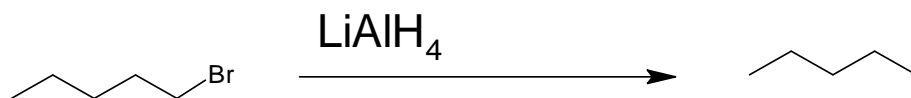
Primary alky halides can also be converted to alkenes via a dehydrohalogenation reaction. When a primary alkyl halide is reacted with strong, bulky bases such as tert-butoxide in the presence of heat alkene formation occurs

.

$$\frac{\text{tert-butoxide}}{\text{heat}}$$
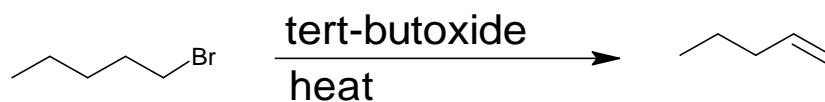
1.11 Alcohols

Alcohols have a sp3 carbon bonded to hydroxyl group (OH) the molecule structure. This carbon is referred to as the carbinol carbon. Alcohol is commonly used as disinfectants. Alcohol is also used in liquors, beer and wine.
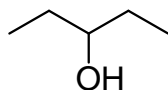
Alcohol has the general formula of $C_nH_{2n+1}OH$. The IUPAC rules for naming alkyl halides are as follows

1. Find the longest continuous chain of carbons that contains the carbon bonded to the OH group to determine the parent name of the compound. The suffix for alcohols is (**-ol**)
2. Count the carbons in the direction that gives the hydroxyl group (OH) the lowest possible number.
3. Assemble the name, listing and numbering all substituent groups in alphabetical order.
4. If more than one hydroxyl group is present in the compound, then the numerical prefix should be used. The prefix is inserted on the suffix (ol) For instance 2 hydroxyl groups = (diol)

Alcohol is classified by the substitution on the sp^3 hybridized carbon singly bonded to the hydroxyl group (also referred to as the carbinol). The classifications are ***methyl*** (carbon bonded to the hydroxyl group is bonded to three hydrogens), ***primary*** (carbon bonded to hydroxyl is singly bonded to one carbon), ***secondary*** (carbon bonded to hydroxyl is singly bonded to two carbons), and tertiary (carbon bonded to the hydroxyl is singly bonded to three carbons). There are **no** quaternary alcohols (carbon bonded to hydroxyl is singly bonded to four carbons), because this would violate the octet rule on the carbon.
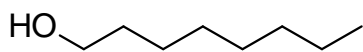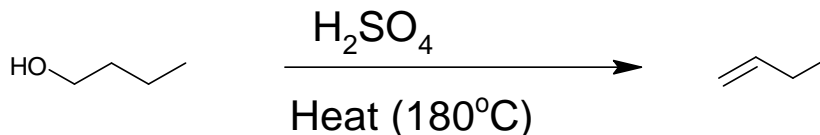

| primary alcohol | secondary alcohol | tertiary alcohol |

Primary alcohols can be reduced to alkenes using dehydration reactions. In the dehydration of an alcohol, the products of the reaction are an alkene and H_2O. When an alkene is treated with concentrated sulfuric acid (H_2SO_4) in the presence of heat (approximately 180°C) the alcohol is converted to an alkene.

1.12 Amines

Amines have a sp3 nitrogen single bonded to 1,2,3 or 4 in carbons the molecule structure. The general formula is dictated by the amine classification. The IUPAC rules for naming amines are as follows

1. Find the longest continuous chain of carbons that contains the nitrogen determine the parent name of the compound. The suffix for amines is (-**amine**)
2. Count the carbons in the direction that gives the amine group (NH_2) the lowest possible number.
3. Assemble the name, listing and numbering all substituent groups in alphabetical order.
4. If more than one amine group is present in the compound, then the numerical prefixes should be used to indicate the number. The prefix inserted on the suffix (amine) For instance 2 amine groups = (diamine)

Amine classification: Amines are classified by the substitution on the sp3 hybridized *nitrogen*. The classifications are **methyl** (nitrogen atom is singly bonded to one carbon), **primary** (nitrogen atom bonded is singly bonded to one carbon), **secondary** (nitrogen atom bonded is singly bonded to two carbons), **tertiary** (nitrogen atom is singly bonded to three carbons) and **quaternary** (nitrogen atom is singly bonded to four carbons). Notice that the quaternary amine has a plus charge and exists with a counterion.

primary amine   secondary amine   tertiary amine   quatenary amine
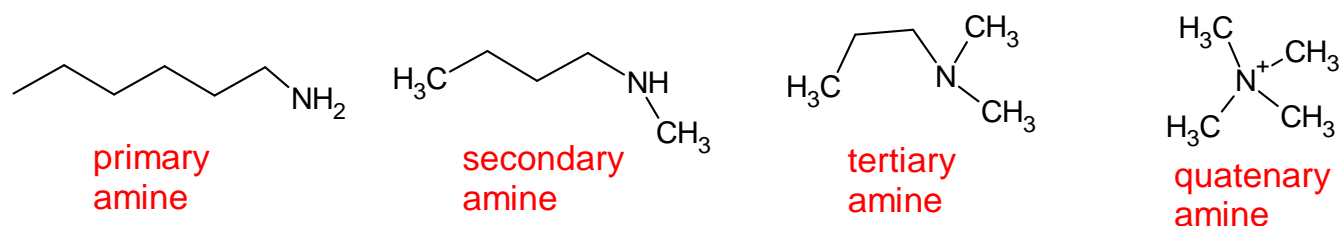
Primary amines can be reduced to alkenes using the Hoffman elimination reaction. This reaction occurs in three steps. The first step of the overall reaction is the reaction of the amine with excess Iodomethane. The second step is the reaction of the product from the step 1 with Ag_2O in water and the final step is the addition of heat.


1) Excess CH3-I
2) Ag_2O in H_2O
3) Heat
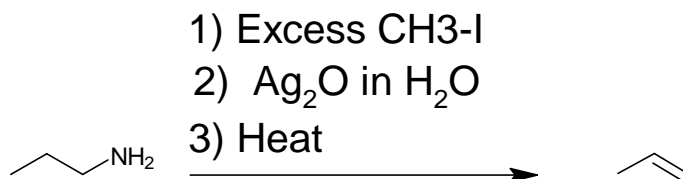
1.13 Aldehydes

Aldehydes have the general formula C_nH_{2n+2}. CHO (where CHO indicates the aldehyde functional group). Aldehydes contain a carbonyl group (C=O), where both the carbon of the carbonyl group and the oxygen of the carbonyl group are sp^2 hybridized. The carbon of a carbonyl group is called the carbonyl carbon, and the oxygen it is doubly bonded to is called the carbonyl oxygen. The IUPAC rules for naming aldehydes are as follows:

1. Find the longest continuous chain of carbons that contains the aldehyde group to determine the parent name of the compound. The suffix for alcohols is (-**al**)
2. Aldehydes will always have the carbonyl group located at the ends of the compound. Count the carbons in the direction that gives the carbonyl carbon the lowest possible number (1).
3. Assemble the name, listing and numbering all substituent groups in alphabetical order.
4. When attached to ring structures, the suffix carbaldehyde is added to the ring's name.

Below are several examples of aldehydes named using the IUPAC system of naming organic compounds.
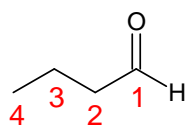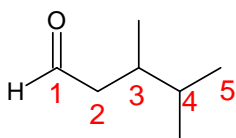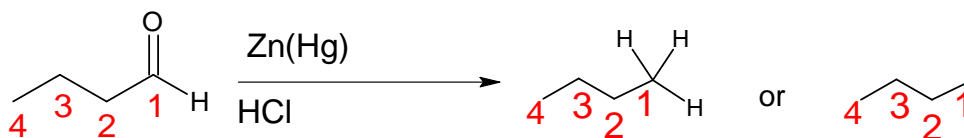

butanal   3,4-dimethylpentanal   cyclohexanecarbaldehyde
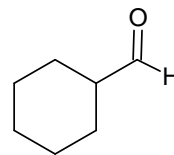
Aldehydes can be converted to alkanes using the Clemmensen reaction. In the Clemmensen reaction an aldehyde is reacted with a Zn/Hg amalgam in the presence of concentrated hydrochloric acid. The product is an alkane where the carbonyl oxygen has been replaced by two hydrogens.


1.14 Ketones

Ketones have the general formula $C_nH_{2n}O$. As with aldehydes, ketones possess a carbonyl group however, the carbonyl carbon is bonded to carbons on both sides. The IUPAC rules for naming ketones are as follows:
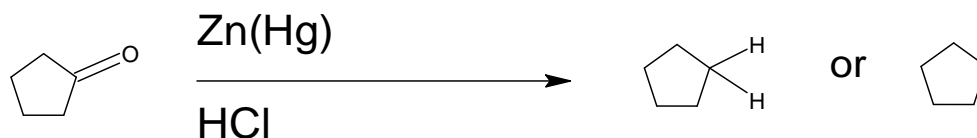
1. Find the longest continuous chain of carbons that contains the ketone group to determine the parent name of the compound. The suffix for ketones is (-**one**)

2. Count the carbons in the direction that gives the carbonyl carbon of the ketone the lowest possible number.
3. Assemble the name, listing and numbering all substituent groups in alphabetical order.
4. If more than one hydroxyl group is present in the compound, then the numerical prefixes should be used to indicate the number. The prefix is inserted on the suffix (ol) For instance 2 hydroxyl groups = (dione)
5. When attached to ring structures the suffix (-**one**) is added to the name of the ring.

Below are several examples of ketones named using the IUPAC system of naming organic compounds.

2-pentanone   3-ethyl-2-hexanone   2-chlorocyclopentanone   cyclohexane-1,3-dione
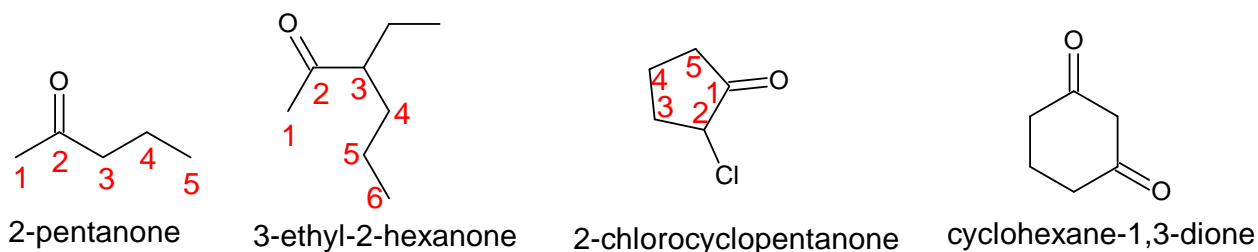
Ketones can also be converted to alkanes using the Clemmensen reaction similarly to ketones. In the Clemmensen reaction a ketone is reacted with a Zn/Hg amalgam in the presence of concentrated hydrochloric acid. The product is an alkane where the carbonyl oxygen has been replaced by two hydrogens.

1.15 Carboxylic acids

Carboxylic acids have the general formula C_nH_{2n+1} (COOH). Carboxylic acids contain a carboxyl group (COOH). The carboxyl group contains a carbonyl carbon doubly bonded to an oxygen and singly bonded to the oxygen of a hydroxy group. The IUPAC rules for naming carboxylic acids are as follows:

1. Find the longest continuous chain of carbons that contains the carboxyl group to determine the parent name of the compound. The suffix for carboxylic acids is (-**oic acid**)
2. Carboxylic acids will always have the carboxyl group located at the ends of the compound. Count the carbons in the direction that gives the carbonyl carbon of the carboxyl group the lowest possible number (1).
3. Assemble the name, listing and numbering all substituent groups in alphabetical order.
4. When attached to ring structures the suffix carboxylic acid is added to the name of the ring.

5. If more than one carboxyl group is present in the compound, then numeric prefixes should be used to indicate the number. The prefix is inserted on the suffix (oic acid) For instance 2 carboxyl groups = (dioic acid)

Below are several examples of carboxylic acids named using the IUPAC system of naming organic compounds.

butanoic acid   2,2-dimethylpentanoic acid   cycloheptanecarboxylic acid   propanedioic acid
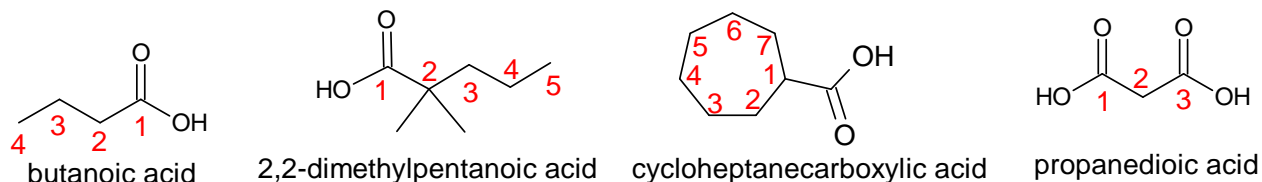
Carboxylic reactions: Carboxylic acids can be reduced to alkanes by reacting them with a strong base NaOH (sodium hydroxide) and CaO (calcium oxide). This mixture is commonly referred to as soda ash. In addition to alkane formation CO_2 is also produced as a side product. Notice that the resulting alkane contains one fewer carbon than the original carboxylic acid.

$$\xrightarrow[\text{high temperature}]{\text{NaOH, CaO}}$$

+ CO_2
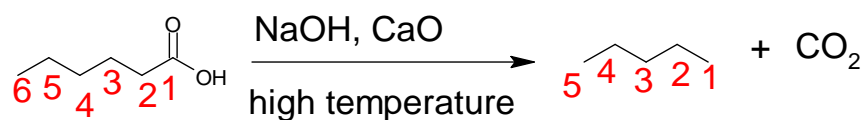
1.16 Aromatic Hydrocarbons

Arenes are aromatic cyclic hydrocarbons that consist of alternating single and double bonds. All carbons in the ring of an aromatic hydrocarbon are sp^2 hybridized. Compounds that are classified as aromatic consist of one or more benzene rings. Benzene, discovered by scientist Michael Faraday, has a molecular formula of C_6H_6 and is a 6-carbon flat cyclic structure with alternating double bonds and six pi electrons. Aromatic compounds were originally named due to their sweet aroma. For example, benzene has a sweet and strong odor. However, benzene and other aromatic compounds are toxic chemicals. Below is the structure of benzene as proposed by scientist August Kekule Friedrich. Notice that benzene can be represented with either of the following alternating double bonds (A or B). is, however,most often represented by a six-member ring with a circle in the middle. This circle represents the pi electrons of benzene being delocalized around the entire ring.

A   B

or

Kekule Structure of Benzene
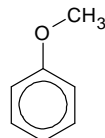
Delocalized electrons around ring
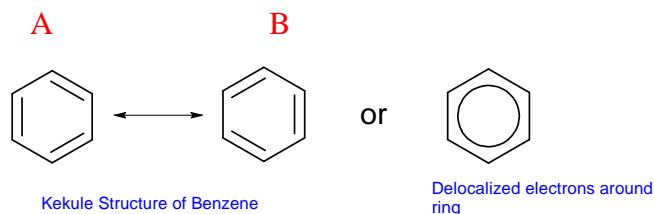
The naming of aromatic hydrocarbons can often be confusing due to the continuous use of common names. This text will focus on naming benzene using IUPAC rules. However, there are a few common names that the IUPAC approves of. Below are the structures of several benzene derivatives and their common names.
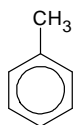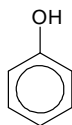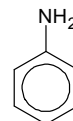
Toluene   Phenol   Anilsole   Aniline

The IUPAC rules for naming benzene derivatives are as follows:

1. Monosubstitued benzene derivatives have the parent name (**benzene**). Any group attached to the benzene ring is named as a substituent.
2. If more than one substiuent is attached to the benzene ring, designate the location of each substituent relative to the parent chain (Benzene) by number.
3. Assemble the name, numbering each substituent group and placing it in alphabetical order.
4. The benzene ring is considered the parent name if it contains more carbons than any of the alkyl substituent(s). If any alkyl group contains more carbons than the benzene ring (7 or more) then it is given the parent name and the benzene ring structure is named as a substituent **(phenyl).**

Below are several examples of benzene derivatives named using the IUPAC system of naming organic compounds.
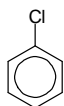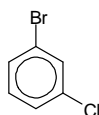
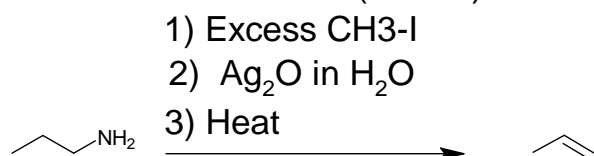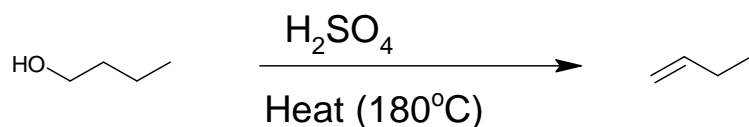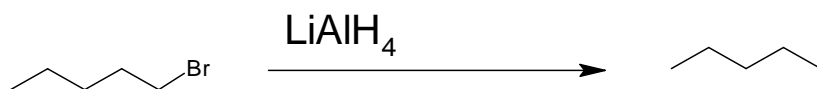chlorobenzene   1-bromo-3-chlorobenzene   propylbenzene   2-phenylnonane
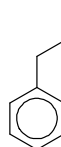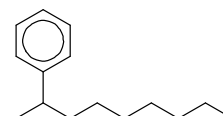
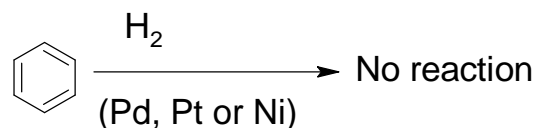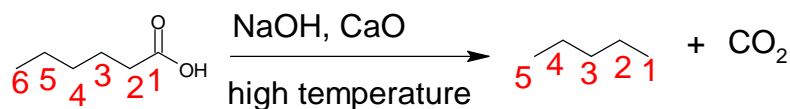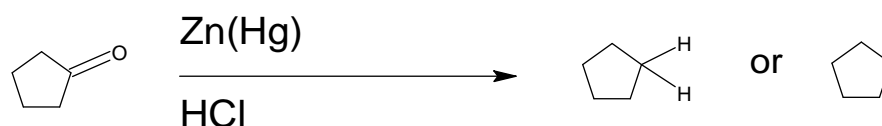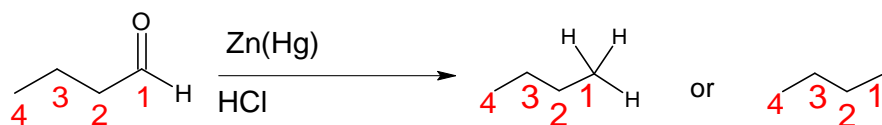 Although benzene has double bonds in a ring, benzene does not react similarly to cycloalkenes. The difference in reactivity is due to the pi electron delocalization around the ring which makes benzene very stable. Reacting benzene with H_2 in the presence of a transitions metal catalyst (Ni, Pt, Pd) under normal conditions does not result in cycloalkane formation. Instead, we must use a reaction with much harsher conditions to achieve unsaturation of the ring (removal of double bonds). Reacting benzene reacted with 3 equivalents of H_2 (one for each double bond) and Rhodium or Nickel at 1000 psi and 150 °C, results in the loss of all three double bonds of the benzene ring and addition of three hydrogen atoms. When drawing the line angle product of this reaction we simply remove the three alternating double bonds.

$$\text{benzene} \xrightarrow[\text{(Pd, Pt or Ni)}]{H_2} \text{No reaction}$$

$$\text{benzene} \xrightarrow[\text{(Rh or Ni)}]{3H_2 \ 1000 \text{ psi, } 150^{\circ}C} \text{cyclohexane}$$

Review

Essential reactions:
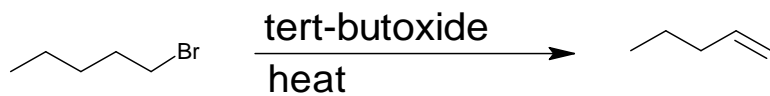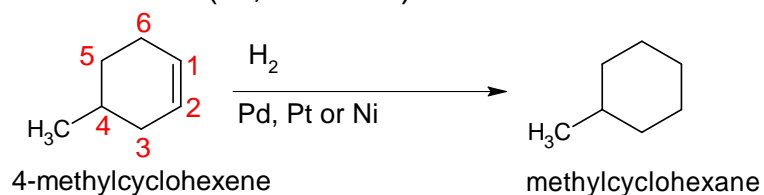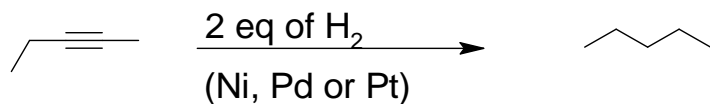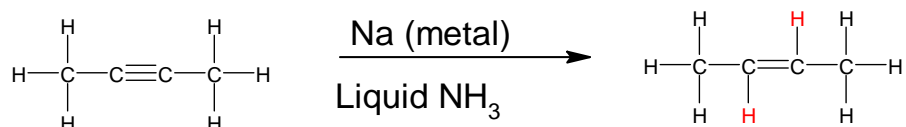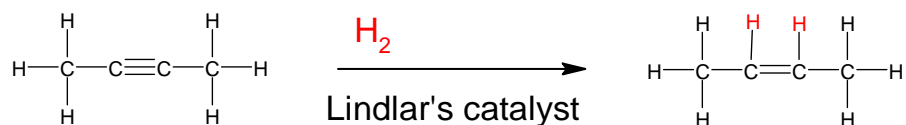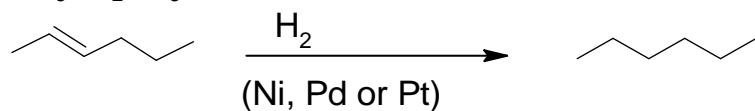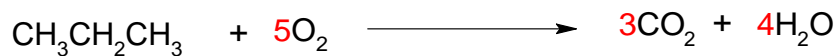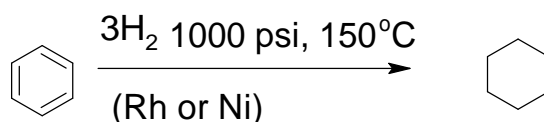
$$CH_3CH_2CH_3 \ + \ 5O_2 \longrightarrow 3CO_2 \ + \ 4H_2O$$

$$\text{hexene} \xrightarrow[\text{(Ni, Pd or Pt)}]{H_2} \text{hexane}$$

$$\xrightarrow[\text{Lindlar's catalyst}]{H_2} \text{cis-alkene}$$

$$\xrightarrow[\text{Liquid } NH_3]{\text{Na (metal)}} \text{trans-alkene}$$

$$\xrightarrow[\text{(Ni, Pd or Pt)}]{2 \text{ eq of } H_2} \text{pentane}$$

$$\text{4-methylcyclohexene} \xrightarrow[\text{Pd, Pt or Ni}]{H_2} \text{methylcyclohexane}$$

$$\xrightarrow[\text{heat}]{\text{tert-butoxide}}$$

$$\xrightarrow{\text{LiAlH}_4}$$

$$HO\text{-butanol} \xrightarrow[\text{Heat } (180^{\circ}C)]{H_2SO_4}$$

1) Excess CH3-I
2) Ag_2O in H_2O
3) Heat

$$\text{NH}_2 \longrightarrow$$

Zn(Hg) / HCl reactions, NaOH/CaO decarboxylation, and H₂ hydrogenation reaction schemes

Essential Vocabulary

IUPAC, functional group, constitutional isomers, line angle (zigzag) structures, aliphatic hydrocarbons, alicyclic hydrocarbons, saturated, unsaturated, parent chain, substituent, combustion reaction, aromatic hydrocarbon.
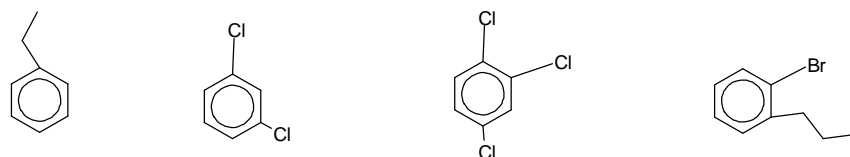
Problems:

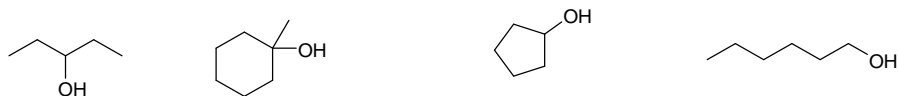1) Give the IUPAC name for the following aliphatic hydrocarbons
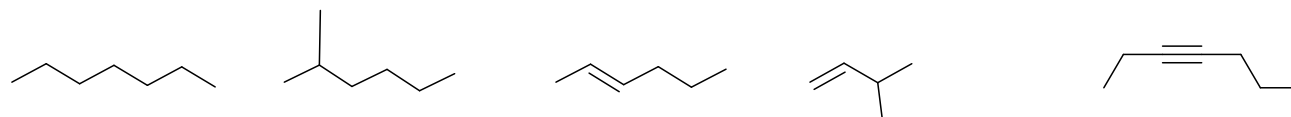
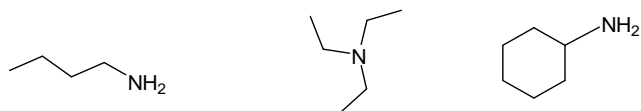2) Give the IUPAC name for the following alicyclic hydrocarbons
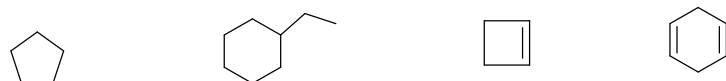
3) Give the IUPAC name for the following aromatic hydrocarbons
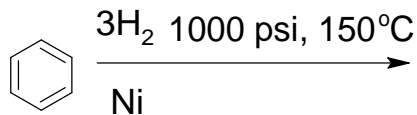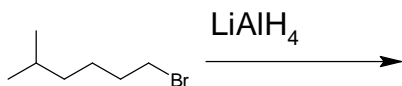

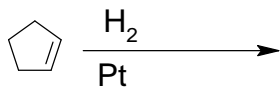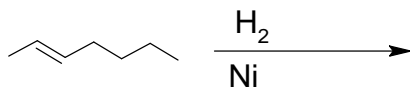4) Classify the following as 1°,2°, 3° or 4° alcohols

5) Classify the following as 1°,2°, 3° or 4° amines

6) Circle and identify the functional groups in the following molecules

7) Draw the products of the following reactions

$$\xrightarrow[\text{Ni}]{H_2}$$

$$\xrightarrow[\text{Pt}]{H_2}$$

$$\xrightarrow{\text{LiAlH}_4}$$

$$\xrightarrow[\text{Ni}]{3H_2 \ 1000 \text{ psi}, \ 150°C}$$

Summary: The field of organic chemistry is fascinating and affects everything in our lives. Organic chemistry is based on carbon-based compounds which make up the entire world. Understanding organic chemistry through its structures, language and nomenclature is of paramount importance.

PHET Build a Molecule Lab

https://phet.colorado.edu/en/simulations/build-a-molecule/activities
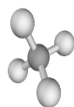
Build the following molecules using the PHET build a molecule simulation. Copy the image and post it to the lab.

Example: Methane   Methanol   Methylamine

PHET Simulation

Butane   2-methylpropane   propylamine

Ethylene   1-chloro-2-fluoropropane   1-propene(prop-1-ene)

2-butanone (butan-2-one)