LECTURE 1
CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry is the study of the chemistry of the element carbon. What is it about carbon that makes this one element the focus of an entire branch of chemistry? Carbon atoms, unlike most other elements, form stable bonds to each other as well as to a wide variety of other elements. Carbon containing compounds consist of chains and rings of carbon atoms – bonding in ways that form an endless variety of molecules. At this time, chemists have identified and/or synthesized more than ten million carbon-based compounds, and they add thousands of new organic molecules to this list every month.

Representation of structural formulas.

Organic chemists use a variety of ways to write structural formulas. The most common types of representation are the complete structural formula (Lewis structure).

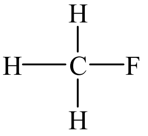
When we write Lewis structures (electron-dot formulas) we assemble the molecule or ion from the constituent atoms showing only the valence electrons (i.e., the electrons of the outermost shell). By having the atoms share or transfer electrons, we try to give each atom the electronic configuration of a noble gas. For example, we give hydrogen atoms two electrons because by doing so we give them the structure of helium. We give carbon, nitrogen, oxygen, and fluorine atoms eight electrons because by doing this we give them the electronic configuration of neon. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Carbon, for example, is in Group IVA and it has four valence electrons; fluorine, in Group VIIA has seven; hydrogen in Group IA, has one.

Write the Lewis structure of CH_3F.

1. We find the total number of valence electrons of all the atoms;

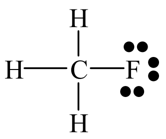
$$\underset{C}{\underset{\uparrow}{4}} + \underset{H_3}{\underset{\uparrow}{3(}} 1) + \underset{F}{\underset{\uparrow}{7}} = 14$$

2. We use pairs of electrons to form bonds between all atoms that are bonded to each other. We represent these bonding pairs with lines. Forexample this requires four pairs of electrons (8 of our 14 valence electrons).



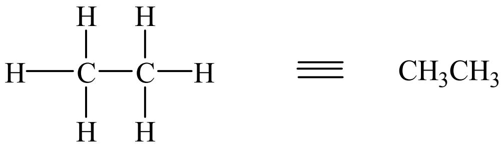
$$\begin{array}{ccc} & H & \\ & | & \\ H — & C & — F \\ & | & \\ & H & \end{array}$$

3. We then add the remaining electrons in pairs so as to give each hydrogen 2 electrons (a duet) and every other atom 8 electrons (an octet). In our example, we assign the remaining 6 valence electrons to the fluorine atom in three nonbonding pairs.



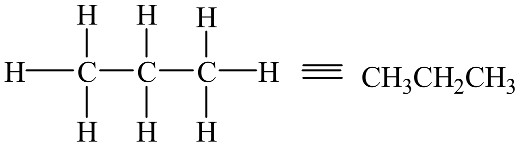
If the structure is an ion, we add or subtract electrons to give it the proper charge.

Although Lewis structural formulas are useful, they occupy a lot of space and are time-consuming to write. As a result, chemists have devised several ways of condensing them. One way to condense these structures is to use condensed structural formulas. In condense these structures is to use condensed structural formulas. In condensed structural formulas carbon-hydrogen and carbon-carbon bonds are implied instead of shown explicitly. For example, the condensed structural formula of ethane is written as follows:



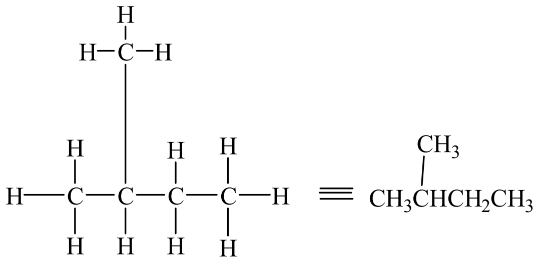
$\equiv CH_3CH_3$

Each carbon atom in ethane is bonded to three hydrogen atoms, so this is simply represented by writing CH_3. The three C–H bonds aren't shown, nor is the C–C bond. Instead we simply place the two CH_3 groups next to each other. In a similar way, a carbon atom bonded to two hydrogen atoms is written as CH_2, while a carbon atom bonded to a single hydrogen atom is written as CH, as illustrated in the following examples.



$\equiv CH_3CH_2CH_3$

Condensed structural formulas

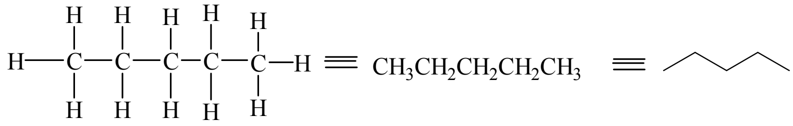


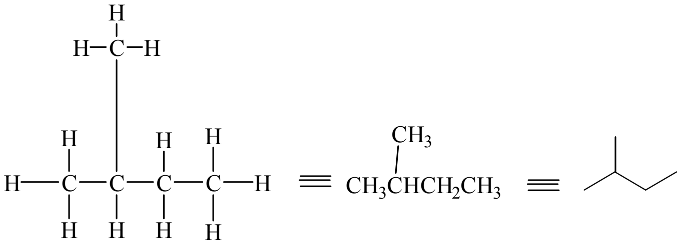
$\equiv CH_3\overset{CH_3}{C}HCH_2CH_3$

2-Methylbutane

Sometimes a C–C bond is included in the condensed structural formula for clarity. An example is the vertical C–C bond in the condensed formula of 2-methylbutane.

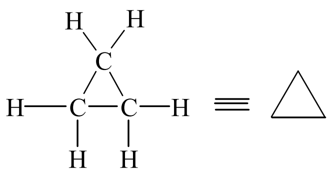
Finally the most drastic simplification is to write structural formulas in which nether carbon nor hydrogen atoms are shown explicitly. The following are examples of these structures, which are called line or skeletal structures.

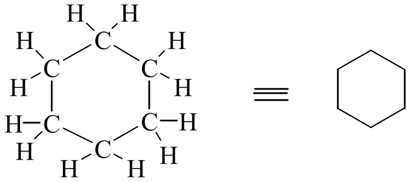




In line structures, a carbon atom is assumed to be at the end of each line and at the intersection of any two, three, or four lines. The correct number of hydrogen atoms is assumed to be bonded to each carbon atom to complete its valence of four.

Line or skeletal structures are particularly useful for writing the structures of cycloalkanes. For example:





FUNCTIONAL GROUPS

One great advantage of the structural theory is that it enables us to classify the vast number of organic compounds into a relatively small number of families based on their structures (Table 1.2). The molecules of compounds in a particular family are cheracterized by the presence of a certain arrangement of atoms called a **functional group (**Table 1.1). A functional group is the part of a molecule where most of its chemical reactions occur. It is the part that effectively determines the compound's chemical properties (and many of its physical properties as well). The functional group of an alkene, for example, is its carbon — carbon double bond. Most of the chemical reactions of alkenes are the chemical reactions of the carbon — carbon double bond.

The functional group of an alkyne is its carbon-carbon triple bond. Alkanes do not have a functional group. Their molecules have carbon — carbon single bonds and carbon-hydrogen bonds, but these bonds are present in molecules of almost all organic molecules, and C — C and C — H bonds are, in general, much less reactive than common functional groups.

Functional Group	**Compound Type**	**Functional Group**	**Compound Type**

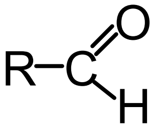
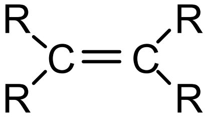
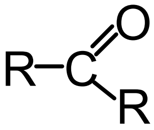
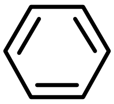
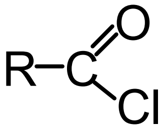
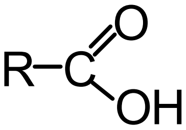
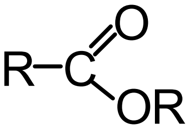
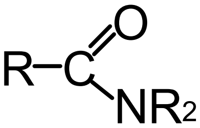
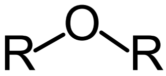
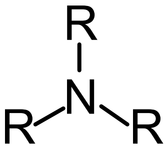
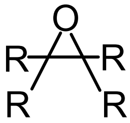
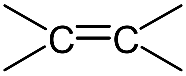
$R-H$	alkane		aldehyde
	alkene		ketone
	aromatic ring		acid chloride
$R-C\equiv C-R$	alkyne		carboxylic acid
$R-X$	alkyl halide		ester
$R-OH$	alcohol		amide
	ether	$R-C\equiv N$	nitrile
	amine		
$R-NO_2$	nitro compound		
	epoxide		

Table 1.1 Some common functional groups

Family	Specific example	IUPAC name	Common name	General formula	Functional group
Alkane	H_3C-CH_3	Ethane	Ethane	RH	C—H and C—C bonds
Alkene	$H_2C=CH_2$	Ethene	Ethylene	$RCH=CH_2$ $RCH=CHR$ $R_2H=CHR$ $R_2H=CR_2$	

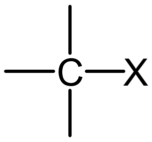
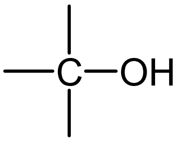
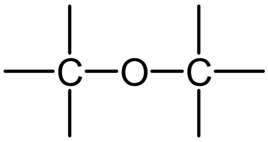
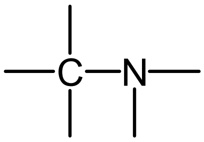
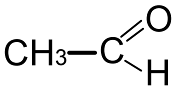
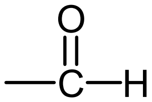
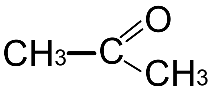
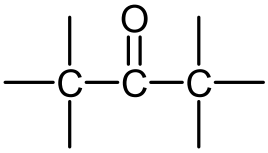
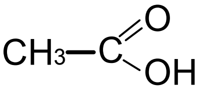
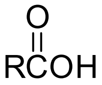
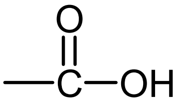
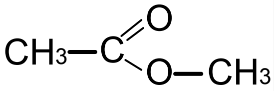
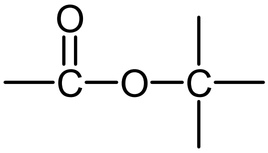
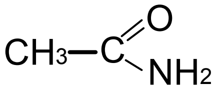
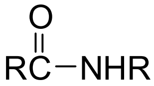
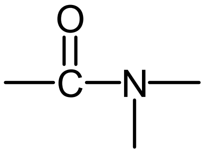
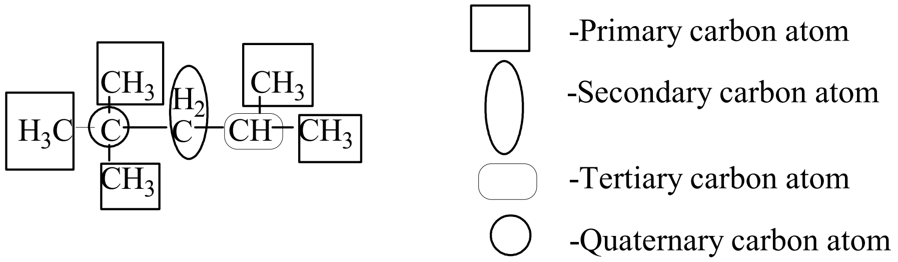
Alkyne	$HC\equiv CH$	Ethyne	Acetylene	$RC\equiv CH$ $RC\equiv CR$	$-C\equiv C-$
Arene		Benzene	Benzene	ArH	Aromatic ring
Haloalkane	CH_3-CH_2-Cl	Chloroethane	Ethyl chloride	RX	 $-\overset{\vert}{\underset{\vert}{C}}-X$
Alcohol	CH_3-CH_2-OH	Ethenol	Ethyl alcohol	ROH	 $-\overset{\vert}{\underset{\vert}{C}}-OH$
Ether	CH_3-O-CH_3	Methoxymethane	Dimethyl ether	ROR	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$
Amine	CH_3-NH_2	Methanamide	Methylamine	RNH_2 R_2NH R_3N	 $-\overset{\vert}{\underset{\vert}{C}}-\underset{\vert}{N}-$
Aldehyde		Ethanal	Acetaldehyde	 $R\overset{O}{\overset{\Vert}{C}}H$	 $-\overset{O}{\overset{\Vert}{C}}-H$
Ketone		Propanone	Acetone	 $R\overset{O}{\overset{\Vert}{C}}R$	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
Carboxylic acid		Ethanoic acid	Acetic acid	 $R\overset{O}{\overset{\Vert}{C}}OH$	 $-\overset{O}{\overset{\Vert}{C}}-OH$
Ester		Methyl-ethanoate	Methyl acetate	 $R\overset{O}{\overset{\Vert}{C}}OR$	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$
Amide		Ethanamide	Acetamide	 $R\overset{O}{\overset{\Vert}{C}}-NHR$	 $-\overset{O}{\overset{\Vert}{C}}-\underset{\vert}{N}-$

Table 1.2 Important families of organic compounds

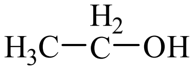
CLASSIFICATION OF CARBON ATOMS.

A carbon atom is classified according to the number of other carbon atoms bonded to it. There are four possibilities, designated **primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).** A **primary** carbon atom is bonded to only one carbon atom, a **secondary** carbon atom is bonded to two carbon atoms, a **tertiary** carbon atom to three, and **quaternary** carbon atom to four. Examples of these four kinds of carbon atoms are found in 2,2,4-trimethylpentane.

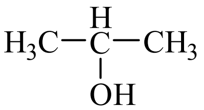


This designation is also the basic of the classification of alcols. The hydroxy group of a primary alcohols is bonded to a primary sp^3 hybrid carbon atom, the hydroxy group of a secondary alcohol is bonded to a secondary sp^3 hybrid carbon atom and the hydroxy group of a tertiary alcohol is bonded to a tertiary sp^3 hybrid carbon atom.

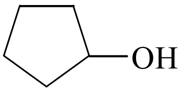
Examples:


$H_3C-\overset{H_2}{C}-OH$

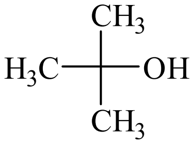
primary alcohol


$H_3C-\underset{OH}{\overset{H}{C}}-CH_3$

;



secondary alcohols

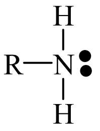

$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$

tertiary alcohol

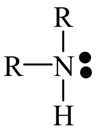
Amines are organic derivates in which one, two or all three hydrogens of ammonia are replaced by alkyl or aryl groups. Amines are classified as primary (1°), secondary (2°) or tertiary (3°).

Primary amines have one organic group bonded to nitrogen, secondary amines have two organic groups, while tertiary amines have three.

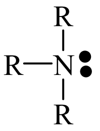
Examples:

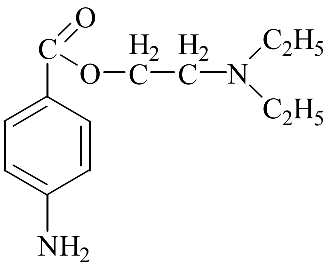

$R-\underset{H}{\overset{H}{N}}:$

primary amine


$R-\underset{H}{\overset{R}{N}}:$

secondary amine

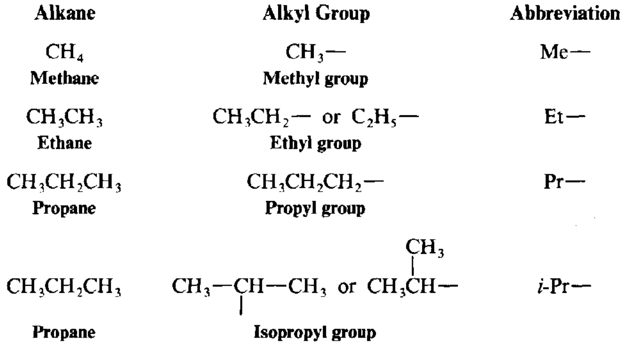

$R-\underset{R}{\overset{R}{N}}:$



tertiary amines

ALKYL GROUPS AND THE SYMBOL R

Alkyl groups are the groups that we identify for purposes of naming compounds. They are groups that would be obtained by removing a hydrogen atom from an alkane:

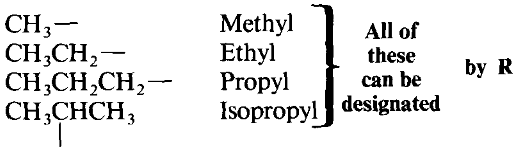


Alkane	Alkyl Group	Abbreviation
CH_4 Methane	CH_3- Methyl group	Me—
CH_3CH_3 Ethane	CH_3CH_2- or C_2H_5- Ethyl group	Et—
$CH_3CH_2CH_3$ Propane	$CH_3CH_2CH_2-$ Propyl group	Pr—
$CH_3CH_2CH_3$ Propane	$CH_3-\underset{\vert}{C}H-CH_3$ or $CH_3\overset{CH_3}{\overset{\vert}{C}}H-$ Isopropyl group	*i*-Pr—

Figure 1.1 Alkyl groups.

While only one alkyl group can be derived from methane and ethane (the **methyl and ethyl** groups, respectively), two groups can be derived from propane. Removal of a hydrogen from one of the end carbon atoms gives a group that is called the **propyl** group; removal of a hydrogen from the middle carbon atom gives a group that is **called the isopropyl** group. The names and structures of these groups are used so frequently in organic chemistry that you should learn them now.

We can simplify much of our future discussion if, at this point, we introduce a symbol that is widely used in designating general structures of organic molecules: The symbol **R.** ***R is used as a general symbol to represent any alkyl group.*** **For example, R** might be a methyl group, an ethyl group, a propyl group, or an isopropyl group.



Thus, the general formula for an alkane is R — H.

IUPAC NOMENCLATURE

The development of a formal system for naming organic compounds did not come about until near the end of the nineteenth century. Prior to that time many organic compounds had already been discovered. The names given these compounds sometimes reflected a source of the compound. Acetic acid, for example, can be obtained from vinegar; it got its name from the Latin word for vinegar, *acetum.* Formic acid can be obtained from some ants; it got its name from the Latin word for ants, *formicae.* Ethanol (or ethyl alcohol) was at one time called grain alcohol because it was obtained by the fermentation of grains.

These older names for organic compounds are now called "common" or "trivial" names. Many of these names are still widely used by chemists, biochemists, and in commerce. (Many are even written into laws.) For this reason it is still necessary to learn the common names for some of the common compounds. We shall point out these common names as we go along, and we shall use them occasionally. Most of the time, however, the names that we shall use will be those called IUPAC names.

The formal system of nomenclature used today is one proposed by the International Union of Pure and Applied Chemistry (IUPAC). This system was first developed in 1892 and has been revised at irregular intervals to keep it up to date. Underlying the IUPAC system of nomenclature for organic compounds is a fundamental principle: ***Each diferent compound should have u diferent name.*** Thus, through a systematic set of rules, the IUPAC system provides different names for the more than 7 million known organic compounds, and names can be devised for any one of millions of other compounds yet to be synthesized. In addition, the IUPAC system is simple enough to allow any chemist familiar with the rules (or with the rules at hand) to write the name for any compound that might be encountered. In the same way, one is also able to derive the structure of a given compound from its IUPAC name.

The IUPAC system for naming alkanes is not difficult to learn, and the principles involved are used in naming compounds in other families as well. For these reasons we begin our study of the IUPAC system with the rules for naming alkanes.

The names for several of the unbranched alkanes are listed in Table 1.3. The ending for all of the names of alkanes *is -ane.* The stems of the names of most of the alkanes (above C4) are of Greek and Latin origin. Learning the stems is like learning to count in organic chemistry. Thus, one, two, three, four, five, becomes meth-, eth-, prop-, but-, pent- .

NAME	NUMBER OF CARBON ATOMS	STRUCTURE	NAME	NUMBER OF CARBON ATOMS	STRUCTURE
Methane	1	CH_4	Heptadecane	17	$CH_3(CH_2)_{15}CH_3$
Ethane	2	CH_3CH_3	Octadecane	18	$CH_3(CH_2)_{16}CH_3$
Propane	3	$CH_3CH_2CH_3$	Nonadecane	19	$CH_3(CH_2)_{17}CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$	Eicosane	20	$CH_3(CH_2)_{18}CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$	Heneicosane	21	$CH_3(CH_2)_{19}CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$	Docosane	22	$CH_3(CH_2)_{20}CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$	Tricosane	23	$CH_3(CH_2)_{21}CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$	Triacontane	30	$CH_3(CH_2)_{28}CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$	Hentriacontane	31	$CH_3(CH_2)_{29}CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$	Tetracontane	40	$CH_3(CH_2)_{38}CH_3$
Undecane	11	$CH_3(CH_2)_9CH_3$	Pentacontane	50	$CH_3(CH_2)_{48}CH_3$
Dodecane	12	$CH_3(CH_2)_{10}CH_3$	Hexacontane	60	$CH_3(CH_2)_{58}CH_3$
Tridecane	13	$CH_3(CH_2)_{11}CH_3$	Heptacontane	70	$CH_3(CH_2)_{68}CH_3$
Tetradecane	14	$CH_3(CH_2)_{12}CH_3$	Octacontane	80	$CH_3(CH_2)_{78}CH_3$
Pentadecane	15	$CH_3(CH_2)_{13}CH_3$	Nonacontane	90	$CH_3(CH_2)_{88}CH_3$
Hexadecane	16	$CH_3(CH_2)_{14}CH_3$	Hectane	100	$CH_3(CH_2)_{98}CH_3$

Table 1.3 The unbranched alkanes

IUPAC NOMENCLATURE OF ALKANES

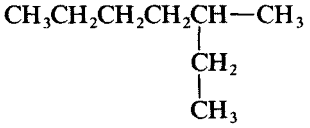
Alkanes are named according to the following rules:

1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane.

We designate the following compound, for example, as a *hexane* because the longest continuous chain contains six carbon atoms.

$$\mathrm{CH_3CH_2CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3}$$

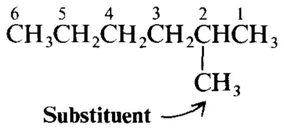
The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a *heptane* because the longest chain contains seven carbon atoms.



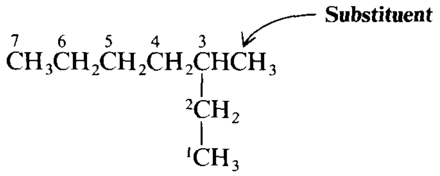
$$\mathrm{CH_3CH_2CH_2CH_2\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{CH_2}}{|}}{C}H{-}CH_3}$$

2. Number the longest chain beginning with the end of the chain nearer the substituent.

Applying this rule, we number the two alkanes that we illustrated previously in the following way.

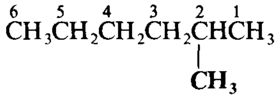


$$\mathrm{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}H_3}$$



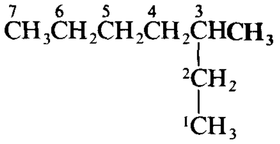
$$\mathrm{\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\underset{\underset{\underset{\underset{\displaystyle {}^{1}CH_3}{|}}{{}^{2}CH_2}}{|}}{\overset{3}{C}}HCH_3}$$

3. Use the numbers obtained by application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers are separated from words by a hyphen. Our two examples are 2-methylhexane and 3-methylheptane, respectively.



$$\mathrm{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}H_3}$$

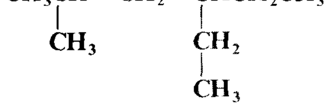
2-Methylhexane



$$\mathrm{\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\underset{\underset{\underset{\underset{\displaystyle {}^{1}CH_3}{|}}{{}^{2}CH_2}}{|}}{\overset{3}{C}}HCH_3}$$

3-Methylheptane

4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-ethyl-2-methylhexane.

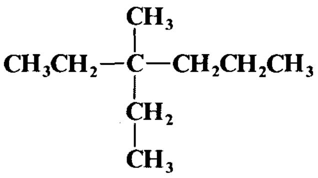


$$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{CH_2}}{|}}{C}HCH_2CH_3}$$

4-Ethyl-2-methylhexane

The substituent groups should be listed *alphabetically* (t.e., ethyl before methyl). In deciding on alphabetical order disregard multiplying prefixes such as "di" and "tri."

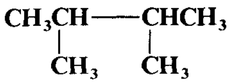
5. **When two substituents are present on the same carbon atom, use that number twice.**



$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_2CH_3$$

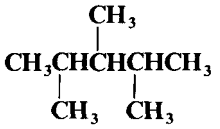
3-Ethyl-3-methylhexane

6. When two or more substituents are identical, indicate this by the use of the prefixes di-, tri-, tetra-, and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.



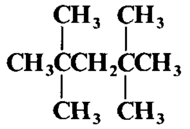
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_3$$

2,3-Dimethylbutane



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\overset{\displaystyle CH_3}{\overset{|}{CH}}\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_3$$

2,3,4-Trimethylpentane

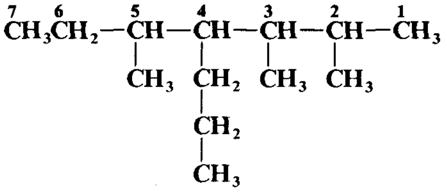


$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_3$$

2,2,4,4-Tetramethylpentane

Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

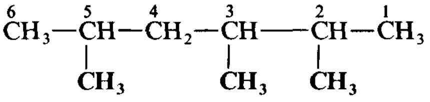
7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



$$\overset{7}{C}H_3\overset{6}{C}H_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}H}}-\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{\overset{4}{C}H}}-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$$

2,3,5-Trimethyl-4-propylheptane
(four substituents)
(*not* 4-*sec*-butyl-2,3-dimethylheptane)
(three substituents)

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.

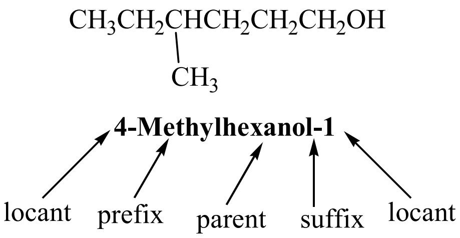


$$\overset{6}{C}H_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}H}}-\overset{4}{C}H_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$$

2,3,5-Trimethylhexane
(*not* 2,4,5-trimethylhexane)

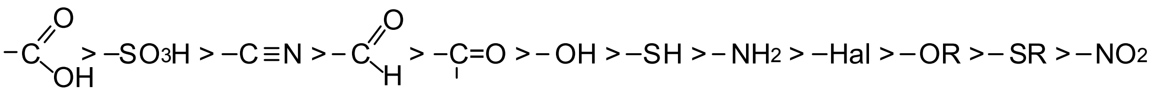
PRINCIPLES IUPAC NOMENCLATURE OF ORGANIC COMPOUNDS

In what is called IUPAC substitutive nomenclature a name may have as many as four reatures: locants, prefixes, parent compounds, and one suffix. Consider the following compounds as an illustration without, for the moment, being concerned as to how the name arises.



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_2OH$$

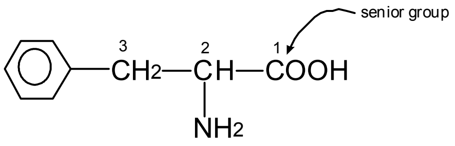
The locant 4-tells that the substituent methyl group, named as a prefix, is attached to the parent compound at C-4. The parent compound contains six carbon atoms and no multiple bonds, hence the parent name hexane, and it is an alcohol, therefore it has the suffix –ol. The locant 1-, tells that C-1 bears the hydroxyl group. In general, numbering of the chain always begins at the end nearer the group named as a suffix (senior group, figure 1.2).



prefix	carboxy-	sulfo-	——	oxo-	oxo-	hydroxy-	mercapto-	amino-	halo-	alkoxy-	alkylthio-	nitro-
suffix	-oic acid	-sulfonic acid	-nitrile	-al	-one	-ol	-thiol	-amine	——	——	——	——

Figure 1.2 Groups seniority range

The name of senior group make suffix, the other groups make prefix which must be added alphabetically to parent chain name.



2-amino-3-phenylpropanoic acid

Figure 1.3 Example of IUPAC naming