

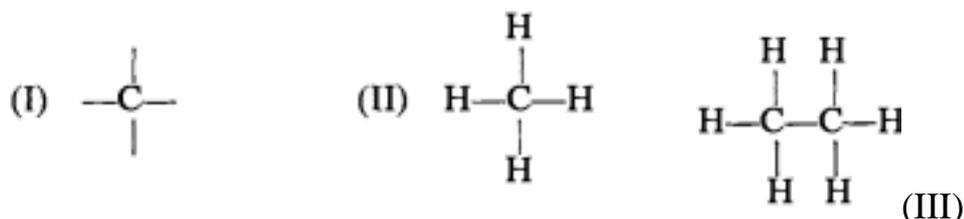
Chemistry of those substances which are closely related to the metabolism of living organisms is, in general, much more complex than the chemistry of inorganic substances. A distinction was made between organic and inorganic chemistry in the early history of chemistry, the former being restricted to the study of the various chemical products obtainable from living sources.

It was believed that these substances differed fundamentally from the compounds of inorganic chemistry by the possession of some "vital principle". In 1828 Wöhler showed that this was not true when he obtained a typical organic substance (urea) from an inorganic source (ammonium cyanate).

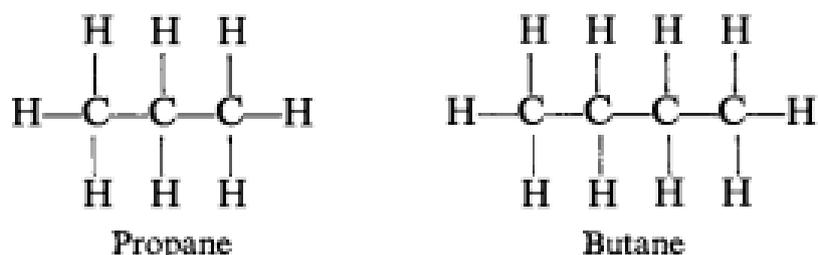
THE CONSTITUTIONAL FORMULAE OF ORGANIC COMPOUNDS

Owing to the complexity of the molecules of organic compounds, molecular formulae are inadequate representations of their chemical behaviour. The arrangements of the atoms within the molecules are as important as the total numbers of the various atomic species present and it is necessary to set out the arrangements if the whole chemical behaviour is to be understood.

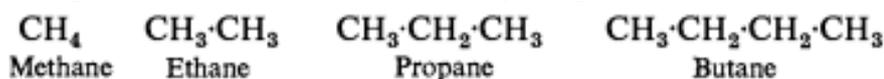
Graphic formulae reveal how each atom is chemically united, each univalent bond between the atoms being represented by a stroke on the paper. Thus the quadrivalent carbon atom with four equal covalencies, and the simplest hydrocarbon (methane) are represented thus (I and II). The next hydrocarbon (ethane) has the molecular formula C_2H_6 and the only arrangement of the atoms in the ethane molecule which is consistent with quadrivalent carbon atom and the univalent hydrogen atom is represented by formula (III).



The higher members of the paraffin series are formed by linkage of carbon to carbon (propane C_3H_8 and butane C_4H_{10})



These formulae reveal that chains of carbon atoms can be built up by the bonding of carbon to carbon and such chains are important in most organic compounds. This fact enables the writing of the graphic formulae to be simplified by writing the atoms attached to each carbon atom immediately after its symbol (C) and representing the carbon-carbon bond by a point (·) instead of a stroke.



Formulae of this type which show, in adequate detail, the arrangement of the different atoms in the molecule are called **constitutional formulae** or **structural formulae**.

HOMOLOGOUS SERIES: FUNCTIONAL GROUPS

The molecular formulae of the above four hydrocarbons differ from one another in the lengths of the carbon chains; each differs from its neighbours by CH_2 . These hydrocarbons constitute an example of a **homologous series**, which is defined as: **a series of organic compounds possessing similar chemical properties, whose molecular formulae show a constant difference of CH_2 from member to member as the series is ascended.**

The study of organic chemistry is greatly simplified by the existence of homologous series of closely related and similar substances, each series being characterized by the presence of a particular reactive group of atoms (the functional group).

A functional group is a particular arrangement of atoms which confers its own characteristic chemical behaviour on all organic substances whose molecules contain the group.

When a compound contains more than one functional group in the molecule, it usually exhibits the properties of, and takes part in the reactions characteristic of, all the different functional groups present. It is prepared by suitable modifications of the general methods of preparation for the particular groups.

The derivatives formed by replacing hydrogen by other atoms or groups are named from the parent hydrocarbon, e.g.

1 atom of hydrogen replaced — ending *ane* becomes *yl*;

2 atoms of hydrogen replaced — ending *ane* becomes *ylene*.

For example:

CH_4 methane, CH_3 methyl, CH_2 methylene;

C_2H_6 ethane, $\text{CH}_3\cdot\text{CH}_2$ or C_2H_5 ethyl, C_2H_4 ethylene;

C_3H_8 propane, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2$ or C_3H_7 propyl, C_3H_6 propylene.

The term *alkyl* (abbreviated to *alk*) is used generally to represent any of the groupings methyl (Me), ethyl (Et), propyl (Pr), butyl (Bu), etc.

NOMENCLATURE OF ORGANIC COMPOUNDS

International Union of Pure and Applied Chemistry (IUPAC).

Alkanes. The saturated open-chain (acyclic) hydrocarbons ($\text{C}_n\text{H}_{2n+2}$) have names ending in -ane. The first four members have the trivial names methane (CH_4), ethane ($\text{CH}_3\text{-CH}_3$) or C_2H_6 , propane (C_3H_8), and butane (C_4H_{10}). For the remainder of the alkanes, the *first portion of the name is derived from the Greek prefix* (see Table

11.4) that cites the number of carbons in the alkane followed by **-ane** with elision of the terminal **-a** from the prefix, as shown in Table 1.1.

TABLE 1.1 Names of Straight-Chain Alkanes

n^*	Name	n^*	Name	n^*	Name	n^*	Name
1	Methane	11	Undecane‡	21	Henicosane	60	Hexacontane
2	Ethane	12	Dodecane	22	Docosane	70	Heptacontane
3	Propane	13	Tridecane	23	Tricosane	80	Octacontane
4	Butane	14	Tetradecane			90	Nonacontane
5	Pentane	15	Pentadecane	30	triacontane	100	Hectane
6	Hexane	16	Hexadecane	31	hentriacontane	110	Decahectane
7	Heptane	17	Heptadecane	32	dotriacontane	120	Icosahectane
8	Octane	18	Octadecane			121	Henicosahectane
9	Nonane†	19	Nonadecane	40	Tetracontane		
10	Decane	20	Icosane§	50	Pentacontane		

* n = total number of carbon atoms.

† Formerly called enneane.

‡ Formerly called hendecane.

§ Formerly called eicosane.

For branching compounds, **1) the parent structure is the longest continuous chain present in the compound.** Consider the compound to have been derived from this structure by replacement of hydrogen by various alkyl groups. **2) Arabic number prefixes indicate the carbon to which the alkyl group is attached.** **3) Start numbering at whichever end of the parent structure that results in the lowest-numbered locants.** **4) The arabic prefixes are listed in numerical sequence, separated from each other by commas and from the remainder of the name by a hyphen.**

5) If the same alkyl group occurs more than once as a side chain, this is indicated by the prefixes di-, tri-, tetra-, etc. Side chains are cited in alphabetical order (before insertion of any multiplying prefix). The name of a complex radical (side chain) is considered to begin with the first letter of its complete name.

6) Where names of complex radicals are composed of identical words, priority for citation is given to that radical which contains the lowest-numbered locant at the first cited point of difference in the radical.

7) If two or more side chains are in equivalent positions, the one to be assigned the lowest-numbered locant is that cited first in the name. The complete expression for the side chain may be enclosed in parentheses for clarity or the carbon atoms in side chains may be indicated by primed locants.

8) If hydrocarbon chains of equal length are competing for selection as the parent, the choice goes in descending order to

(1) the chain that has the greatest number of side chains,

(2) the chain whose side chains have the lowest-numbered locants,

(3) the chain having the greatest number of carbon atoms in the smaller side chains,

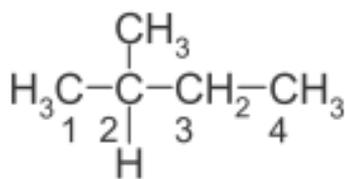
or (4) the chain having the least-branched side chains.

In general, organic compounds are given systematic names by using the order prefix–parent–suffix, where prefix indicates how many branching groups are present, parent indicates how many carbons are in the longest chain and suffix indicates the name of the family. Common names as well as systematic names are used for alkanes and their derivatives. However, it is advisable to use systematic names or the IUPAC (*International Union of Pure and Applied Chemistry*) nomenclature, which can be derived from a simple set of rules.

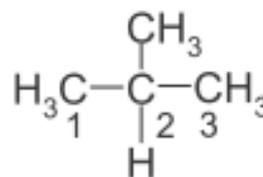
The IUPAC naming of the alkanes is based on a prefix indicating the number of carbon atoms in the chain (as shown below) followed by the suffix *-ane*. For example, if a chain contains three carbons the parent name is *propane*, if four carbons the parent name is *butane* and so on. The remaining parts of the structure are treated as substituents on the chain. Numbers are used to indicate the positions of the substituents on the parent carbon chain.

Prefix	Number of carbon atoms	Prefix	Number of carbon atoms
Meth-	1	Hept-	7
Eth-	2	Oct-	8
Prop-	3	Non-	9
But-	4	Dec-	10
Pent-	5	Undec-	11
Hex-	6	Dodec-	12

First, one has to identify and name the groups attached to the chain, and number the chain so that the substituent gets the lowest possible number. For example, one of the isomers of pentane is 2-methylbutane, where the parent chain is a four-carbon butane chain, and is numbered starting from the end nearer the substituent group (methyl group). Therefore, the methyl group is indicated as being attached to carbon atom number 2.



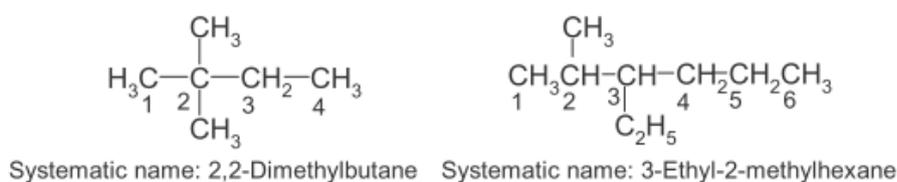
Systematic name: 2-Methylbutane



Systematic name: 2-Methylpropane
Common name: Isobutane

Similarly, *isobutane* is the common name of one of the structural isomers of C_4H_{10} (butane). The longest continuous chain of carbons consists of three atoms in length, so the systematic name is based on propane. Finally, since a methyl group appears on the second carbon, the correct name is 2-methylpropane.

When more than one substituent is present, the location of each substituent should be designated by an appropriate name and number. The presence of two or more identical substituents is indicated by the prefixes di-, tri-, tetra- and so on, and the position of each substituent is indicated by a number in the prefix. A number and a word are separated by a hyphen, and numbers are separated by comma. For example, in 2,2-dimethylbutane, both methyl groups are attached to carbon atom 2 of a butane chain. The names of the substituents are arranged in alphabetical order, not numerical order, e.g. 3-ethyl-2-methylhexane, *not* 2-methyl-3-ethylhexane.



These trivial names may be used for the unsubstituted hydrocarbons only:

Isobutane $(\text{CH}_3)_2\text{CHCH}_3$

Neopentane $(\text{CH}_3)_4\text{C}$

Isopentane $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$

Isohexane $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$

Univalent radicals derived from saturated unbranched alkanes by removal of hydrogen from a terminal carbon atom are named by adding **-yl** in place of **-ane** to the stem name.

Thus the alkane ethane becomes the radical ethyl. These exceptions are permitted for unsubstituted radicals only:

Isopropyl $(\text{CH}_3)_2\text{CH}-$

Isopentyl $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2-$

Isobutyl $(\text{CH}_3)_2\text{CHCH}_2-$

Neopentyl $(\text{CH}_3)_3\text{CCH}_2-$

sec-Butyl $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-$

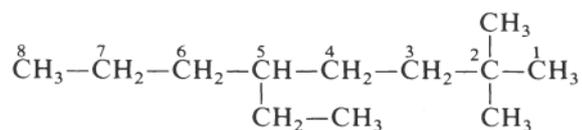
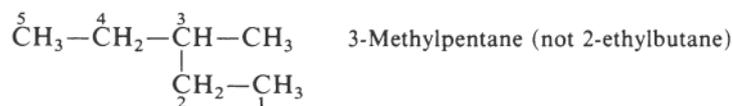
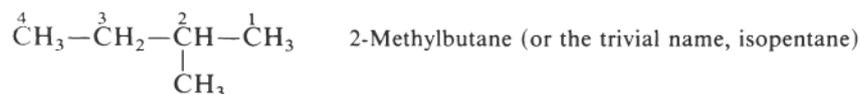
tert-Pentyl $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2-$

tert-Butyl $(\text{CH}_3)_3\text{C}-$

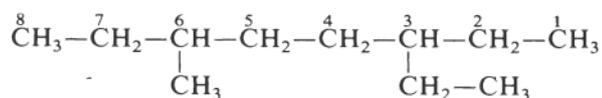
Isohexyl $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2-$

Note the usage of the prefixes *iso-*, *neo-*, *sec-*, and *tert-*, and note when italics are employed. Italicized prefixes are never involved in alphabetization, except among themselves; thus *sec*-butyl would precede isobutyl, isohexyl would precede isopropyl, and *sec*-butyl would precede *tert*-butyl.

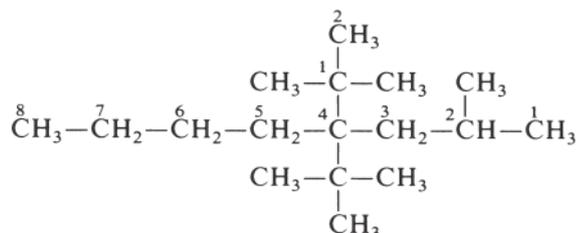
Examples of alkane nomenclature are



5-Ethyl-2,2-dimethyloctane (note cited order)



3-Ethyl-6-methyloctane (note locants reversed)



4,4-Bis(1,1-dimethylethyl)-2-methyloctane

4,4-Bis-1',1'-dimethylethyl-2-methyloctane

4,4-Bis(*tert*-butyl)-2-methyloctane

Bivalent radicals derived from saturated unbranched alkanes by removal of two hydrogen atoms are named as follows: (1) If both free bonds are on the same carbon atom, the ending -ane of the hydrocarbon is replaced with -ylidene. However, for the first member of the alkanes it is methylene rather than methylidene. Isopropylidene, *sec*-butylidene, and neopentylidene may be used for the unsubstituted group only. (2) If the two free bonds are on different carbon atoms, the straight-chain group terminating in these two carbon atoms is named by citing the number of methylene groups comprising the chain. Other carbon groups are named as substituents. Ethylene is used rather than dimethylene for the first member of the series, and propylene is retained for $\text{CH}_3 - \text{CH} - \text{CH}_2 -$ (but trimethylene is $-\text{CH}_2 - \text{CH}_2 -$).

Trivalent groups derived by the removal of three hydrogen atoms from the same carbon are named by replacing the ending -ane of the parent hydrocarbon with -ylidyne.

Alkenes and Alkynes. Each name of the corresponding saturated hydrocarbon is converted to the corresponding alkene by changing the ending -ane to -ene. For alkynes the ending is -yne. With more than one double (or triple) bond, the endings are -adiene, -atriene, etc. (or -adiyne, -atriyne, etc.). The position of the double (or triple) bond in the parent chain is indicated by a locant obtained by numbering from the end of the chain nearest the double (or triple) bond; thus $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ is 1-butene and $\text{CH}_3\text{C}\equiv\text{CCH}_3$ is 2-butyne.

For multiple unsaturated bonds, the chain is so numbered as to give the lowest possible locants to the unsaturated bonds. When there is a choice in numbering, the double

bonds are given the lowest locants, and the alkene is cited before the alkyne where both occur in the name. Examples:

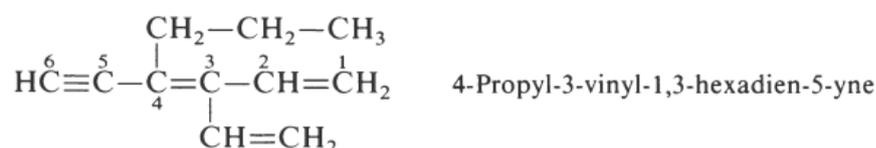


Unsaturated branched acyclic hydrocarbons are named as derivatives of the chain that contains the maximum number of double and/or triple bonds. When a choice exists, priority goes in sequence to (1) the chain with the greatest number of carbon atoms and (2) the chain containing the maximum number of double bonds.

These nonsystematic names are retained:



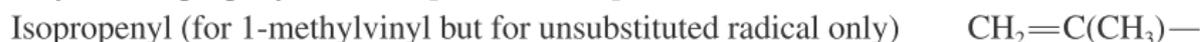
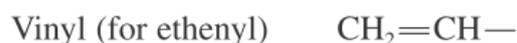
An example of nomenclature for alkenes and alkynes is



Univalent radicals have the endings -enyl, -ynyl, -dienyl, -diynyl, etc. When necessary, the positions of the double and triple bonds are indicated by locants, with the carbon atom with the free valence numbered as 1. Examples:



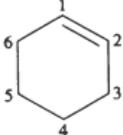
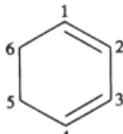
These names are retained:



Should there be a choice for the fundamental straight chain of a radical, that chain is selected which contains (1) the maximum number of double and triple bonds, (2) the largest number of carbon atoms, and (3) the largest number of double bonds. These are in descending priority.

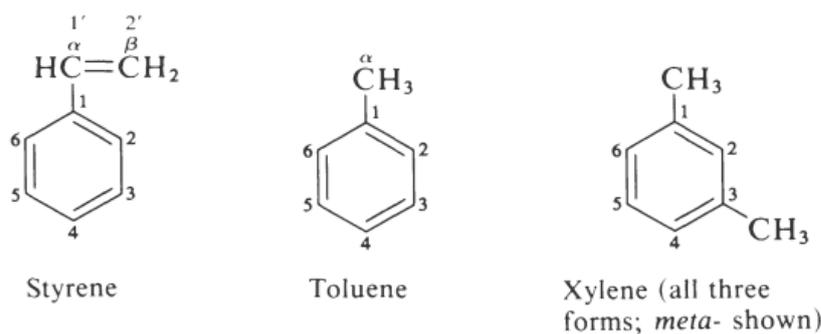
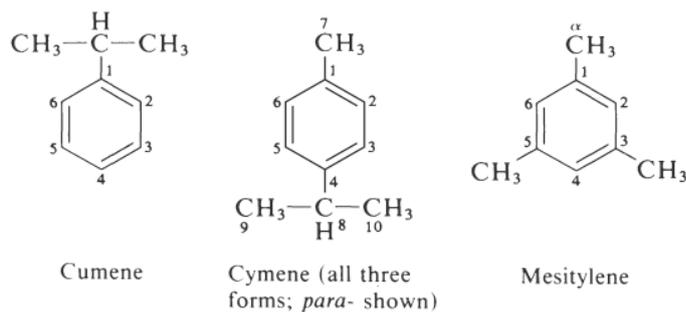
Bivalent radicals derived from unbranched alkenes, alkadienes, and alkynes by removing a hydrogen atom from each of the terminal carbon atoms are named by replacing the endings -ene, -diene, and -yne by -enylene, -dienylene, and -ynylene, respectively. Positions of double and triple bonds are indicated by numbers when necessary. The name *vinylene* instead of ethenylene is retained for $-\text{CH}=\text{CH}-$.

Monocyclic Aliphatic Hydrocarbons. Monocyclic aliphatic hydrocarbons (with no side chains) are named by prefixing cyclo- to the name of the corresponding open-chain hydrocarbon having the same number of carbon atoms as the ring. Radicals are formed as with the alkanes, alkenes, and alkynes. Examples:

	Cyclohexane	Cyclohexyl- (for the radical)
	Cyclohexene	1-Cyclohexenyl- (for the radical with the free valence at carbon 1)
	1,3-Cyclohexadiene	Cyclohexadienyl- (the unsaturated carbons are given numbers as low as possible, numbering from the carbon atom with the free valence given the number 1)

For convenience, aliphatic rings are often represented by simple geometric figures: a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon (as illustrated) for cyclohexane, etc. It is understood that two hydrogen atoms are located at each corner of the figure unless some other group is indicated for one or both.

Monocyclic Aromatic Compounds. Except for six retained names, all monocyclic substituted aromatic hydrocarbons are named systematically as derivatives of benzene. Moreover, if the substituent introduced into a compound with a retained trivial name is identical with one already present in that compound, the compound is named as a derivative of benzene. These names are retained:



The position of substituents is indicated by numbers, with the lowest locant possible given to substituents. When a name is based on a recognized trivial name, priority for lowest-numbered locants is given to substituents implied by the trivial name. When only two substituents are present on a benzene ring, their position may be indicated by *o*- (*ortho*-), *m*- (*meta*-), and *p*- (*para*-) (and alphabetized in the order given) used in place of 1,2-, 1,3-, and 1,4-, respectively.

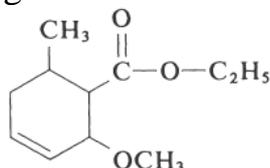
Radicals derived from monocyclic substituted aromatic hydrocarbons and having the free valence at a ring atom (numbered 1) are named phenyl (for benzene as parent, since benzyl is used for the radical $C_6H_5CH_2-$), cumenyl, mesityl, tolyl, and xylyl. All other radicals are named as substituted phenyl radicals. For radicals having a single free valence in the side chain, these trivial names are retained:

Benzyl $C_6H_5CH_2-$
 Benzhydryl (alternative to
 diphenylmethyl) $(C_6H_5)_2CH-$
 Cinnamyl $C_6H_5CH=CH-CH_2-$

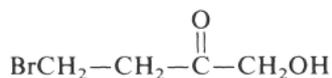
Phenethyl $C_6H_5CH_2CH_2-$
 Styryl $C_6H_5CH=CH-$
 Trityl $(C_6H_5)_3C-$

Substitutive Nomenclature. The first step is to determine the kind of characteristic (**functional**) group for use as the principal group of the parent compound. A *characteristic group is a recognized combination of atoms that confers characteristic chemical properties on the molecule in which it occurs*. Carbon-to-carbon unsaturation and heteroatoms in rings are considered nonfunctional for nomenclature purposes. *Substitution means the replacement of one or more hydrogen atoms in a given compound by some other kind of atom or group of atoms, functional or nonfunctional*. In substitutive nomenclature, *each substituent is cited as either a prefix or a suffix to the name of the parent (or substituting radical) to which it is attached*; the latter is denoted the parent compound (or parent group if a radical).

In Table 1.2 are listed the general classes of compounds in descending order of preference for citation as suffixes, that is, as the parent or characteristic compound. When oxygen is replaced by sulfur, selenium, or tellurium, the priority for these elements is in the descending order listed. The higher valence states of each element are listed before considering the successive lower valence states. Derivative groups have priority for citation as principal group after the respective parents of their general class.



Structure 1



Structure 2

Structure 1 contains an ester group and an ether group. Since the ester group has higher priority, the name is ethyl 2-methoxy-6-methyl-3-cyclohexene-1-carboxylate. Structure 2 contains a carbonyl group, an hydroxy group, and a bromo group. The latter is never a suffix. Between the other two, the carbonyl group has higher priority, the parent has **-one** as suffix, and the name is 4-bromo-1-hydroxy-2-butanone.

Classification of carbon substitution

A carbon atom is classified as primary (1), secondary (2), tertiary (3) and quaternary (4) depending on the number of carbon atoms bonded to it.

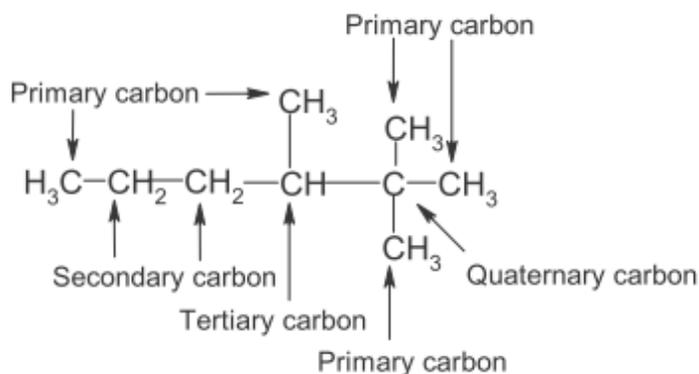


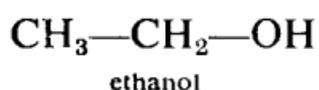
Table 1.2. Characteristic Groups for Substitutive Nomenclature

NAME OF CLASS	GENERAL FORMULA	FUNCTIONAL GROUP		IUPAC	
		FORMULA	NAME	PREFIX	SUFFIX
Carboxylic acids	RCOOH	$-(C)OOH^*$	Carboxyl	-----	-oic acid
		-COOH		Carboxy-	
Sulfonic acids	R-SO ₃ H	-SO ₃ H	Sulfonate	Sulfo-	- sulfo acid
Esters	R-COO-R	$-(C)OOR^*$	Carbalkoxy	-----	-oate
Amides	R-CONH ₂	-CONH ₂	Amide	Carbamyl-	-amide
Nitriles	R-C≡N	$-(C)≡N^*$	Nitrile	-----	-nitrile
		-CN		Cyano-	-----
Aldehydes	$R-\overset{\text{O}}{\parallel}{C}-H$	$-(C)\overset{\text{O}}{\parallel}{C}-H$	Carbonyl	Formyl-	-al
Ketones	R-CO-R	>C=O		Oxo or keto-	-one
Alcohols	R-OH	-OH	Hydroxyl	Hydroxy-	-ol
Thioalcohols	R-SH	-SH	Thiol	Mercapto-	-thiol
Amines	R-NH ₂	-NH ₂	Amino	Amino-	-amine
Nitro compound	R-NO ₂	-NO ₂	Nitro	Nitro-	-----
Ethers	R-O-R	-OR	Alkoxy	Alkoxy-	-----
Halogen derivatives	R-Hal	-Hal(-F,-Cl, -Br, -I)	Halogens	Fluoro-, chloro-, bromo-, iodo-	-----

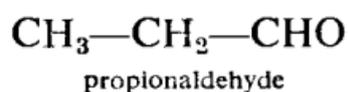
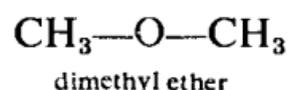
FUNCTIONAL GROUP ISOMERISM

Here the functional group present differs in the different isomers, making them readily distinguishable by chemical (and generally by physical) properties.

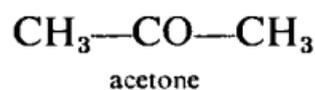
E.g.



and



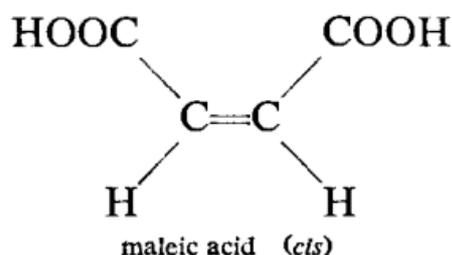
and



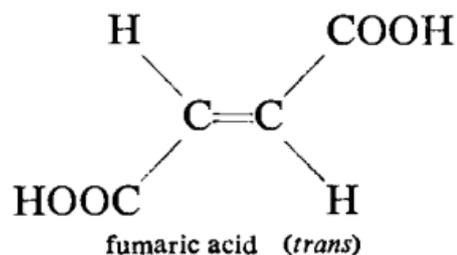
II. SPATIAL OR STEREOISOMERISM

GEOMETRICAL ISOMERISM

When carbon atoms are linked by double bonds, free rotation is prevented; thus any pair of groups may be on the same side or on opposite sides of the double bond, giving rise to *cis* or *trans* isomers respectively. Here the physical properties are very different, and this has led in some cases to quite different names being given to the two isomers, even though some of the chemical properties are similar.

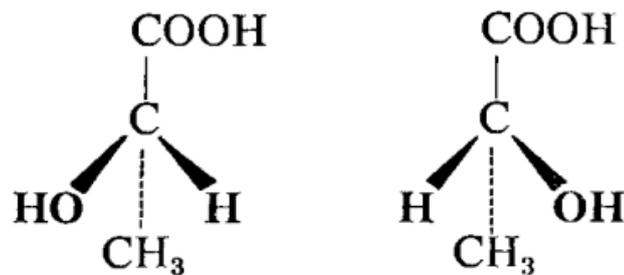


and



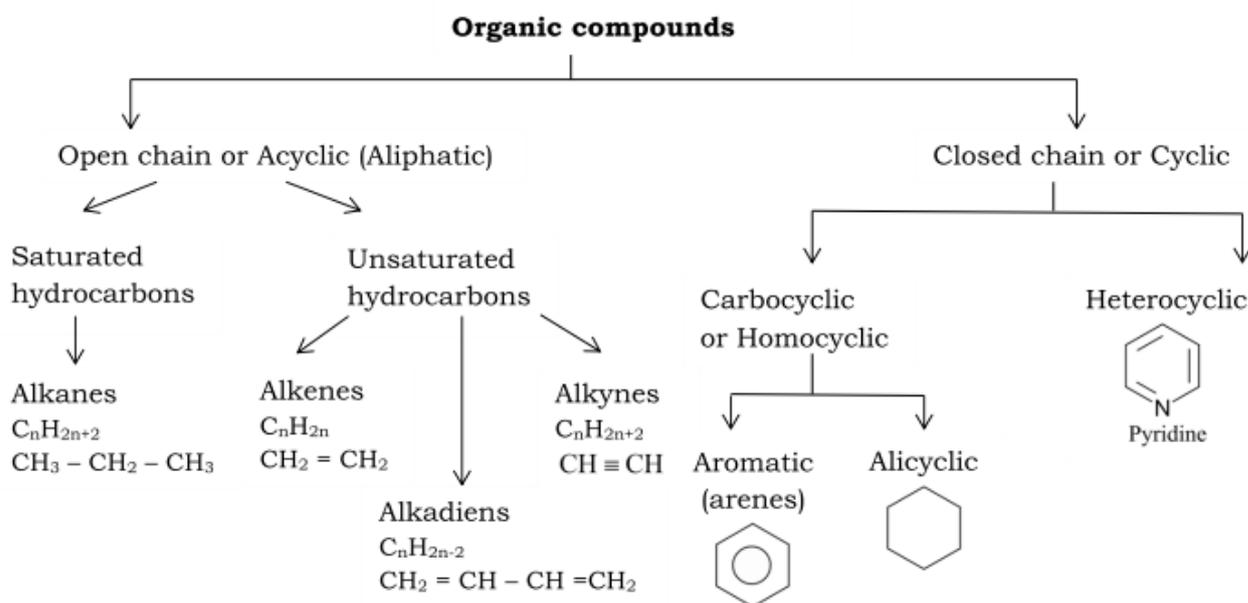
OPTICAL ISOMERISM

If a molecule is asymmetric, and the mirror image is not superimposable on the original, *enantiomorphs* or optical isomers are obtained. These differ in that one, the dextrorotatory or (+) isomer rotates a beam of plane polarized light to the right, whilst the other, the laevorotatory or (−), rotates it the same amount to the left. Their chemical properties are identical but their rates of reaction with other optical isomers may differ. Four different groups linked to one so-called “asymmetric” carbon atom give rise to molecules which can exist as optical isomers, since each bond is directed to one corner of a regular tetrahedron.



(+) and (-) isomers of lactic acid

According to the structure of chain of carbon atoms the organic compounds are divided into:



Acyclic compounds (or aliphatic) are organic chemicals having open chains of carbon atoms, branched or unbranched. For example:

CH₃ - CH₂ - CH₃ unbranched
propane

CH₂ = CH - CH₂ - CH₃
butene - 1
(but - 1- ene)

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$$
 branched
2 - methylpropane

$$\begin{array}{c} \text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 3 - methylbutene - 1

Exercises

- 1). Define and write notes on the following terms: (a) Optical isomers, (b) Racemic mixture, (c) Geometrical isomers.
- 2) An organic compound, containing only carbon, hydrogen and oxygen, on complete combustion gave the following data: 0.116 g gave 0.264 g carbon dioxide and 0.108 g water. A further 0.210 g gave 81.1 ml of vapour at S.T.P. Calculate the molecular formula of the compound and write structural formulae for the possible isomers.
- 3) Write the structural formulae of the compounds which are produced by the replacement of one or two atoms in a molecule of ethane by bromine.