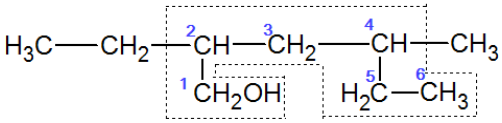
(....Contd.) ORGANIC CHEMISTRY : BASIC PRINCIPLES AND TECNIQUES

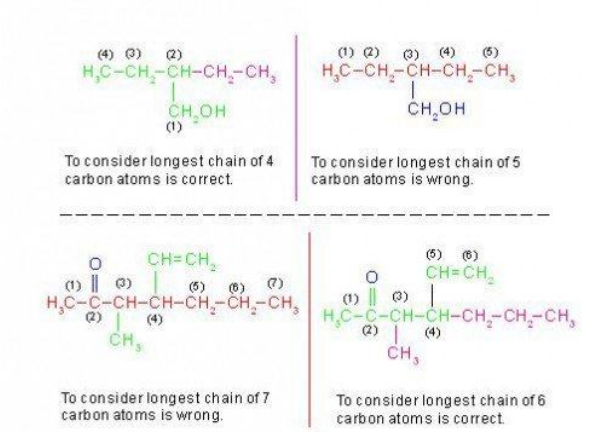
Kumud Bala

Rules for IUPAC nomenclature of compounds containing one functional group, multiple bonds and substituent :- While naming organic compounds containing one functional group, double and triple bonds, and substituents, the following additional rules are observed.

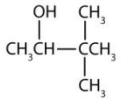
1. **Parent chain**:- Select the longest possible chain of carbon atoms containing the functional group and the maximum number of multiple bonds as the parent chain without caring whether it also denotes the longest possible carbon chain or not . For example, in below shown compound, the parent chain containing the functional group has six carbon atoms while the longest possible carbon chain has seven carbon atoms.



Parent chain contains six rather than seven carbon atoms

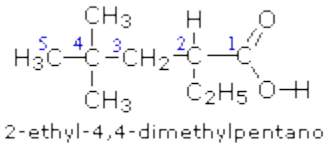


2. **Lowest locant rule for the functional group: -** Number the parent chain in such a way that the functional group gets the lowest possible number followed by the double and triple bonds even if it violates the lowest set of locants rule. For example

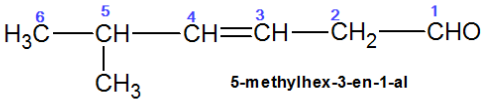


has set of locant= 4,4 not 2,2 name of the compound is 4,4-dimethy-2-butanol

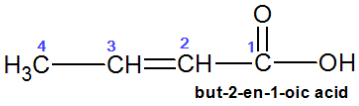
3. **Numbering the chain terminating functional groups:-** when a chain terminating functional groups such as –CHO, -COOH, -COOR, -$CONH_2$, -COCl , -C≡N ,etc. is present, it is always given number 1 and number 1 is usually omitted from the final name of the compound when there is no ambiguity . For example



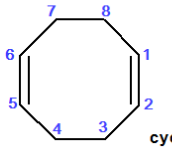
2-ethyl-4,4-dimethylpentanoic acid



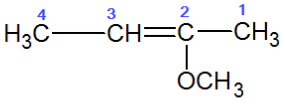
5-methylhex-3-en-1-al



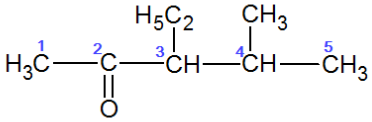
but-2-en-1-oic acid



cycloocta-1,5-diene



2-methoxybut-2-ene



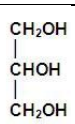
3-ethyl-4-methylpentan-2-one

However, in the following examples, the numerical locant 1 is always included when another numerical locant appears in the same name.

$CH_3CH_2CH(Br)COOC_2H_5$	Ethyl 2-bromobutan-1-oate
CH_3-CH=CH-CH_2OH	But-2-en-1-ol
CH_3C≡C-CH_2-CH=O	Pent-3-yn-1-al

If a compound contains two or more like groups the numerical prefixes di, tri, tetra , etc. are used and terminal ‘e’ from the primary suffix is retained (not dropped) while writing the IUPAC name. For example :-

NC-CH=CH-CN	But-2-ene-1,4-dinitrile
OHC-CH=CH-CHO	But-2-ene-1,4-dial
HOOC-COOH	Ethane-1,2-dioic acid

HOOC-CH=CH-COOH	But-2-ene-1,4-dioic acid
$H_5C_2OOC-CH_2-CH_2-COOC_2H_5$	Diethylbutane-1,4 –dioate
$HOCH_2CH_2OH$	Ethane-1,2-diol
	Propane-1,2,3-triol

Rules for IUPAC Nomenclature of polyfunctional compound:- Organic compounds which contain two or more functional groups are called polyfunctional compounds. Their IUPAC names are obtain as follow:

Principal functional group:- When an organic compound contains two or more different functional groups, one of the functional group is selected as the principal functional group while all other groups (also called the secondary functional group) are treated as substituents . The choice of the principal functional group is made on the basis of the following order of preference.

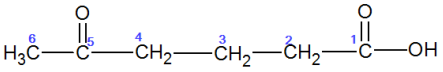
Amine salts > Carboxylic acids > Sulphonic acid > Anhydrides > esters >acid chlorides > acid amides >nitrile > aldehydes > ketones > alcohols > phenols >thiols > amines > ethers > alkenes > alkynes. All the remaining functional groups such as halo(fluoro, chloro, bromo , iodo) , nitroso (-NO) , nitro ($-NO_2$) , and alkoxy (-OR) , -R (alkyl), C_6H_5- etc. are always treated as substituent groups. It may be noted that while writing the names of the polyfunctional compounds, the principal functional group is indicated by adding the secondary suffix to the word root while the secondary functional groups are indicated by adding suitable prefixes to the word root . The prefixes for secondary functional groups are listed below:

SECONDARY FUNCTIONAL GROUP	PREFIX	SECONDARY FUNCTIONAL GROUP	PREFIX
-X (F, Cl , Br, I)	Halo	-CHO	Forml
-OH	Hydroxy	>C=O	Keto
-SH	Sulphanyl or marcapto	-COOH	Carboxy
-OR	Alkoxy	-COOR	Alkoxycarbonyl
$-NH_2$	Amino	-COCl	Halocarbonyl
-NHR	Alkylamino	-CN	Cyano
$-NR_2$	Dialkylamino	$-CONH_2$	Carbamoyl or carboxami
			do

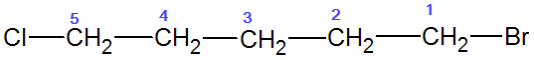
Selecting the principal chain:- While selecting the principal chain present in a polyfunctional compound care should be taken that it must contain the principal functional group and the maximum number of secondary functional groups and multiple bonds if any.

Numbering the principal chain:- The principal chain present in a polyfunctional compound must be numbered in such a way that the principal functional group gets the lowest possible number followed by double bond , triple bond and the substituents i.e. Principal functional group > double bond > triple bond >substituent

Alphabetical order:- The prefixes for the secondary functional groups and other substituents should be placed in alphabetical order before the word root. If, however, two groups of the same preference occupy identical position from either end of the parent chain, the lower number must be given to the group whose prefix comes first in the alphabetical order. For example:-



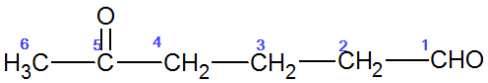
5-ketohexan-1-oic acid
or
5-oxohexan-1-oic acid



1-bromo-5-chloropentane (correct)

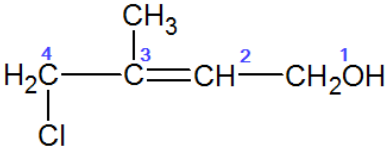
1-chloro-5-bromopentane (wrong)

-COOH is principal functional group , wWhile >C=O is the substituent group



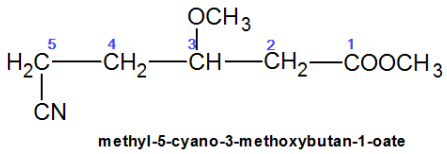
5-ketohexan-1-al
or
5-oxohexan-1-al

-CHO is the principal functional group and >C=O is the substituent group



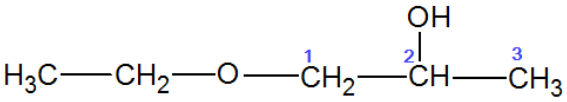
4-chloro-3-methylbut-2-en-1-ol

-OH is the principal functional group and –Cl ,$-CH_3$ are substituents.



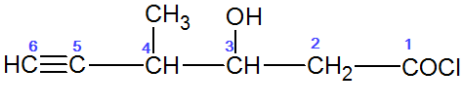
methyl-5-cyano-3-methoxybutan-1-oate

-$COOCH_3$ is the principal functional group and $-OCH_3$ and –CN are the substituent groups



1-ethoxypropan-2-ol

-OH is the principal functional group and $-O-CH_2-CH_3$ is substituent group

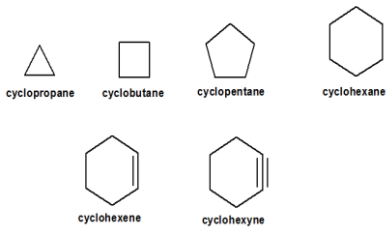


3-hydroxy-4-methylhex-5-yn-1-oylchloride

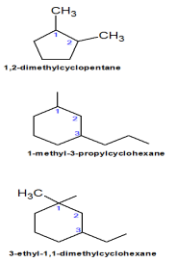
-COCl is the principal functional group. –OH and $-CH_3$ are substituents

Rules for naming alicyclic compound:- the following rules are generally used

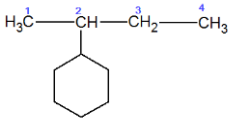
1. The names alicyclic compound are obtained by adding prefix 'cyclo' to the name of the corresponding straight chain hydrocarbon (alkane, alkene or alkyne) .

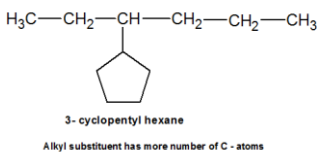


2. If two or more alkyl groups or other substituent groups are present in the ring, their positions are indicated by Arabic numerals ,i.e., 1,2,3,4,….. etc. While numbering the carbon atoms of the ring, the substituent which comes first in the alphabetical order is given the lowest number provided it does not violate the lowest sum rule. For example:-

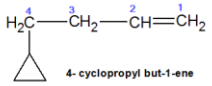


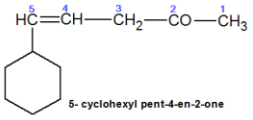
3. (a) If the ring contains more or equal number of carbon atoms than the alkyl group attached to it , it is named as a derivative of cycloalkane and alkyl group is treated as a substituent group, otherwise it is named as a derivative of alkane and the cycloalkyl group is considered as a substituent group. For example:-

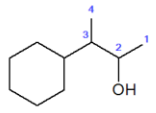




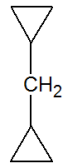
(b) If the side chain contains a multiple bond or a functional group, the alicyclic ring is treated as the substituent irrespective of the size of the ring. For example,

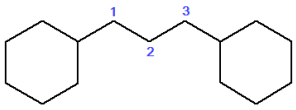




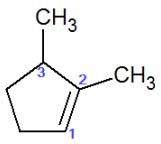


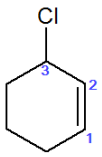
(c) If more than one alicyclic ring is attached to a single chain, the compound is named as a derivatives of alkane irrespective of the number of carbon atoms in the ring or the chain. For example





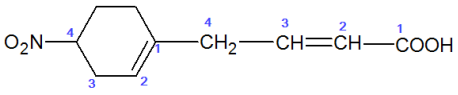
4. If a multiple (double or triple) bond and some other substituent are present in the ring, the number is done in such a way that the multiple bond gets the lowest number. For example:-





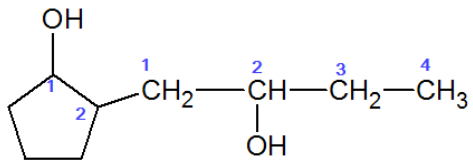
5. If the ring contains a multiple bond and the side chain contains a functional group, then the ring is treated as the substituent and the compound is named as a derivative of the side chain. For example

6. If the ring as well as the side chain contain functional group, the compound is named as a derivative of the side chain or the alicyclic ring according as the side chain or the ring contains the principal functional group. For example



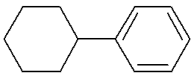
4-(4-nitrocyclohex-1-enyl)but-2-en-1-oic acid

If , the alicyclic ring and the side chain contain the same functional group, the compound is named as a derivative of the side chain of the ring according as the side chain or the ring contains higher number of carbon atoms. for example :-



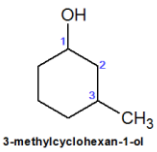
2-(2-hydroxybut-1- yl)cyclopentan-1-ol

7. If a compound contains an alicyclic ring directly linked to the benzene ring, it is named as a derivatives of benzene, i.e., the compound having lowest state of hydrogenation. For example:-

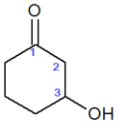


cyclohexyl benzene

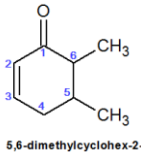
8. If some functional group along with other substituent groups are present in the ring, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring in such a way that the functional group gets the lowest number. For example



3-methylcyclohexan-1-ol



3-hydroxycyclohexan-1-one

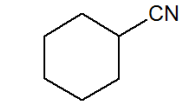


5,6-dimethylcyclohex-2-en-1-one

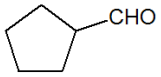
9. If an alicyclic ring is directly attached to a carbon containing functional group, the carbon atoms of the functional group is not included in the parent name of the alicylic system. Therefore ,for such systems, the following prefixes and suffixes for the functional groups are commonly used.

FUNCTIONAL GROUP	PREFIX	SUFFIX
-CHO	Formyl	Carbaldehyde
-COOH	Carboxy	Carboxylic acid
-COX (X=F,Cl,Br, I)	Halocarbonyl	Carbonyl halide
-COOR	Alkoxy carbonyl or Carbalkoxy	Alkyl Carboxylate
$-CONH_2$	Carbamoyl	Carboxamide
-CN	Cyano	Carbonitrile

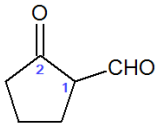
For example:-



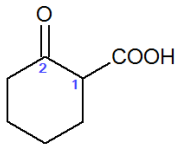
cyclohexanecarbonitrile



cyclopentanecarbaldehyde



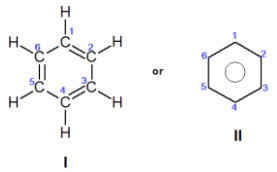
2-oxocyclopentanecarbaldehyde



2-oxo-hexane-1-carboxylic acid

Nomenclature of Simple Aromatic Compounds:- Aromatic compounds contain one or more isolated or fused benzene rings. An aromatic compound consists of two parts: (i) Nucleus and (ii) Side chain

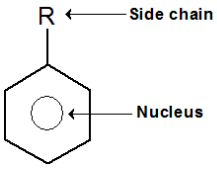
(i) Nucleus : The most ideal aromatic compound is benzene . It is represented by a hexagon of six carbon atoms with three alternate single and double bonds. This is called the nucleus.



I or II

A circle inside the cyclohexane ring represents six completely delocalized π- electrons or three conjugated double bonds.

(ii) Side chain: The alkyl group or any other aliphatic group containing at least one carbon atom which is attached to the benzene ring is called side chain.

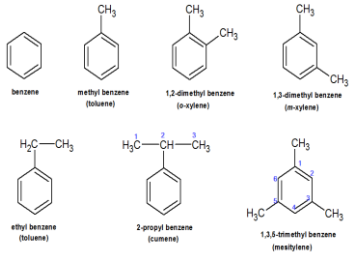


Each family of aromatic compounds consists of the following two type of compounds with quite different chemical properties. (1) Nuclear substituted (2) Side chain substituted

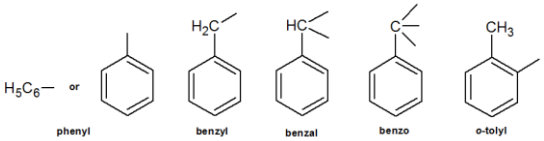
1. **Nuclear substituted**- In these compounds the functional group is directly attached to the benzene ring. Most of these compounds are better known by their common names. In the IUPAC system they are named as derivative of benzene. However , many of their common names have also been adopted by the IUPAC system. The positions of the substituents in disubstituted benzene are indicated either by prefixes or by Arabic numerals such as o (ortho), for 1,2; m(meta) for 1,3 and p (para) for 1,4.

2. **Side chain substituted-** those in which the functional group is present in the side chain of the benzene ring. Both in the common and IUPAC systems, these are usually named as phenyl derivatives of the corresponding aliphatic compounds(except arenes which are named as derivatives of the benzene in the IUPAC system). The position of the substituents on the side chain including the benzene ring are indicated by Greek letters i.e., α,β,γ …. In the common system, and by Arabic numerals, i.e. 1,2,3….etc. in the IUPAC system. However , many of these compounds are better known by their common names. The IUPAC and common names(given in brackets) of a few important members of each family are given below.

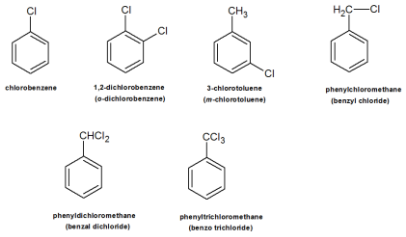
Aromatic hydrocarbons : Hydrocarbons which contain both aliphatic and aromatic units are called arenes.



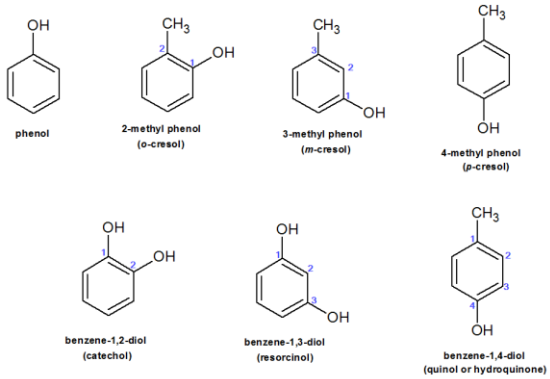
Aryl groups



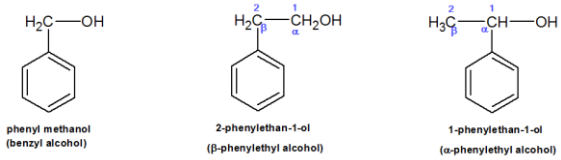
Halogen derivatives



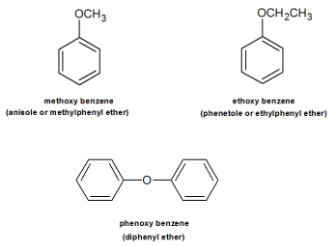
Hydroxy derivatives. The nuclear hydroxy derivatives are called phenols while the side chain substituted hydroxyl derivatives are called aromatic alcohols.



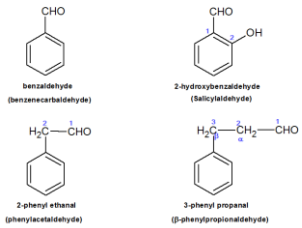
Aromatic alcohols



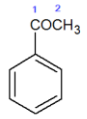
Aromatic ethers.



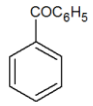
Aldehydes



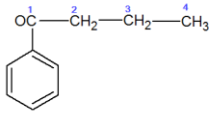
Ketones.



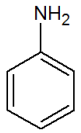
1-phenyl ethan-1-one
(acetophenone or
methyl phenyl ketone)



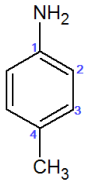
diphenyl methanone
(benzophenone or
diphenyl ketone)



1-phenyl butan-1-one
(butyrophenone)

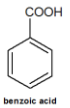


benzenamine
(aniline)



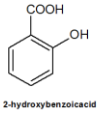
4-methylbenzenamine
(*p*-toluidine)

Carboxylic acids.

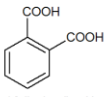


benzoic acid
(benzenecarboxylic acid)

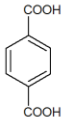
2-methylbenzoicacid
(o-toluic acid)



2-hydroxybenzoicacid
(Salicylic acid)



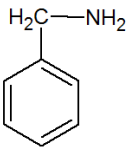
benzene-1,2-dicarboxylic acid
(phthalic acid)



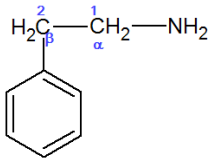
benzene-1,4-dicarboxylic acid
(terephthalic acid)

Aralkyl amines.

Amines. Aryl amines



phenylmethanamine
(benzylamine)

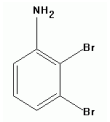


2-phenyl ethanamine
(β-phenylethanamine)

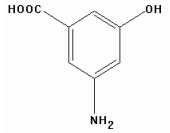
—00—

ASSIGNMENT

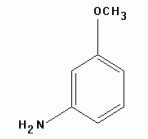
1. IUPAC name of $CH_3CH{=}CHCOOC_2H_5$ is
   (a) Ethylbut-1-enoate (b) Ethylbut-2-enoate
   (c) Ethylprop-2-enoate (d) none of these
2. What is the name of this compound



   (a) 2,3-dibromoaniline (b) 1,2-dibromoaniline
   (c) 1,2-dibromophenylamine (d) none of these
3. What is the name of the given compound



   (a) 5-amino-3-hydroxybenzoic acid
   (b) 3-amino-5-hydroxybenzoic acid
   (c) 1-hydroxybenzoic acid
   (d) none of these
4. The IUPAC name of C_6H_5COCl is
   (a) Chlorobenzyl ketone (b) benzene chloro ketone
   (c) benzenecarbonyl chloride (d) chlorophenyl ketone
5. Give the name of the compound given below



   (a) 3-methoxybenzenamine (b) 3-aminoanisole
   (c) 3-methoxyaniline (d) 4-aminoanisole

Answers to the Assignment: 1. (b) 2. (a) 3. (c) 4. (a) 5. (b)