St Peter's Institute of Pharmaceutical Sciences

Course : Bachelor of Pharmacy

Subject : Pharmaceutical Organic Chemistry I

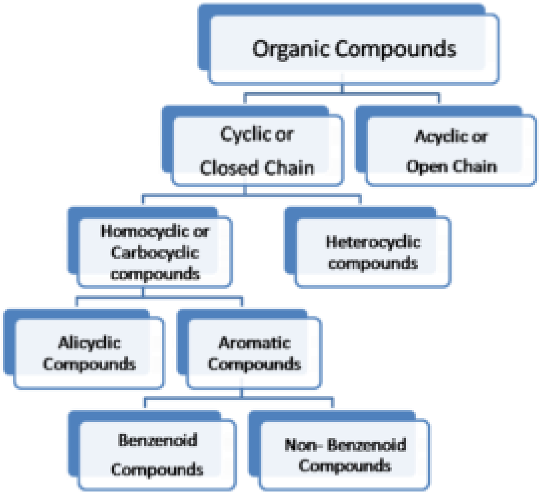
Subject Code:BP202T

Classification of Organic Compounds

Depending upon the arrangement of carbon atoms in their structure, organic compounds are broadly categorized into

- Acyclic or Open Chain compounds
- Cyclic or Closed Chain compounds

The following diagram will give you a clear idea about the classification of organic compounds:



Acyclic or Open Chain Compounds

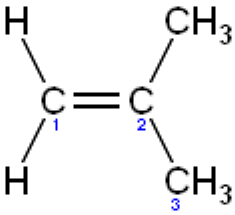
The carbon atoms are present in the form of an open chain.This chain may either be a straight chain or a branched chain. These were initially known as Aliphatic compounds because the compounds of this class were derived from either animal or vegetable fats

- Straight Chain Compounds: The carbon skeleton is in the form of a straight chain. Examples:

n-Propane $CH_3-CH_2-CH_3$

Propene $CH_2=CH-CH_3$

- Branched Chain Compounds: The carbon skeleton is in the form of a branched chain.



Examples: Isobutylene

Cyclic or Closed Chain Compounds

They are marked by the presence of one or more closed chains or ring of atoms in their structure. Depending on whether there is a presence of any other atom apart from carbon in the constitution of the ring, they are further classified as:

- Homocyclic or Carbocyclic Compounds
- Heterocyclic Compounds

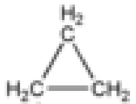
Homocyclic or Carbocyclic Compounds

The rings in these compounds are entirely made up of carbon atoms. No other atom is present in the ring skeleton.These can be further divided into two sub-classes:

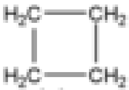
- Alicyclic Compounds
- Aromatic Compounds

Alicyclic Compounds

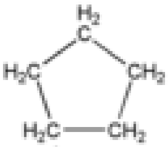
Their name is attributed to their resemblance to Aliphatic compounds in their properties. The examples of this category include cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc.



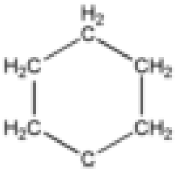
cyclopropane



cyclobutane



cyclopentane

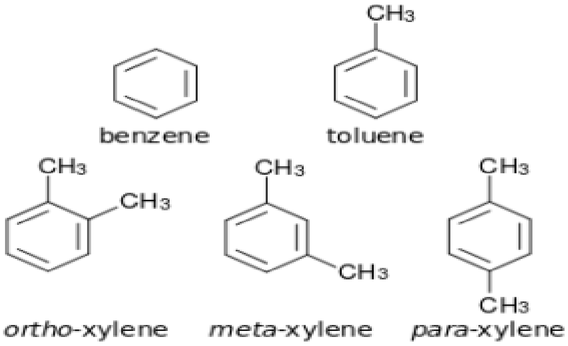


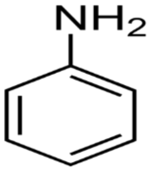
cyclohexane

Aromatic Compounds

These are cyclic unsaturated compounds. They derive their name from the Greek word *Aroma* which means “fragrant smell” since most of these compounds bear a pleasant smell. These are further classified into two types:

- **Benzenoid Aromatic Compounds:** They are characterized by the presence of one or more fused or isolated benzene rings as well as their derivatives in their structure. Depending upon the number of benzene rings that are fused together in their structure, they can be further classified as Monocyclic, Bicyclic, Tricyclic.
- **Non-Benzenoid aromatic Compounds:** They are characterized by the presence of a single benzene ring to which other groups are attached.

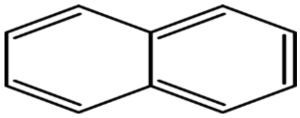




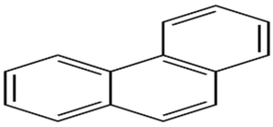
Aniline

Bicyclic and Tricyclic Compounds

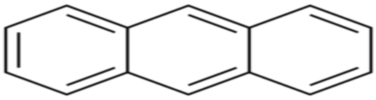
These are characterized by the presence of two or more rings in their structure.Examples include Naphthalene, Phenanthrene as well as Anthracene.



Naphthalene



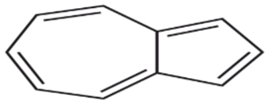
Phenanthrene



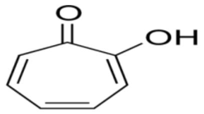
Anthracene

Non-Benzenoid Aromatic Compounds

Aromatic compounds that contain other highly unsaturated rings in place of the benzene ring are called non-benzenoid aromatic compounds. Examples include



Azulene



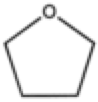
Tropolone

Heterocyclic Compounds

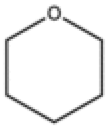
When one or more heteroatoms such as oxygen, nitrogen, sulphur, boron, silicon etc, are present in the ring such compounds are known as heterocyclic compounds.

- **Alicyclic heterocyclic compounds**: Aliphatic heterocyclic compounds that contain one or more heteroatoms in their rings are called alicyclic heterocyclic compounds.

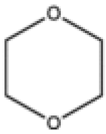
Tetrahydrofuran



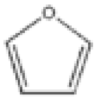
Tetrahydropyran



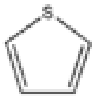
1,4 dioxane



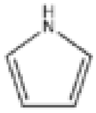
- **Aromatic heterocyclic compounds** Aromatic heterocyclic compounds that contain one or more heteroatoms in their ring skeleton are called aromatic heterocyclic compounds.



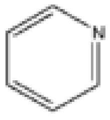
furan



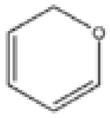
thiophene



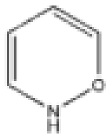
pyrrole



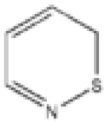
pyridine



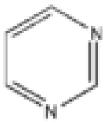
pyran



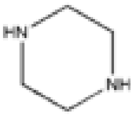
oxazine



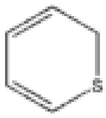
thiazine



pyrimidine



piperazine



thiine

Naming Organic Compounds

The increasingly large number of organic compounds identified with each passing day, together with the fact that many of these compounds are isomers of other compounds, requires that a systematic nomenclature system be developed. Just as each distinct compound has a unique molecular structure which can be designated by a structural formula, each compound must be given a characteristic and unique name.

As organic chemistry grew and developed, many compounds were given trivial names, which are now commonly used and recognized. Some examples are:

Name	Methane	Butane	Acetone	Toluene	Acetylene	Ethyl Alcohol
Formula	CH_4	C_4H_{10}	CH_3COCH_3	$CH_3C_6H_5$	C_2H_2	C_2H_5OH

Such **common names** often have their origin in the history of the science and the natural sources of specific compounds, but the relationship of these names to each other is arbitrary, and no rational or systematic principles underly their assignments.

The IUPAC Systematic Approach to Nomenclature

A rational nomenclature system should do at least two things. First, it should indicate how the carbon atoms of a given compound are bonded together in a characteristic lattice of chains and rings. Second, it should identify and locate any functional groups present in the compound. Since hydrogen is such a common component of organic compounds, its amount and locations can be assumed from the tetravalency of carbon, and need not be specified in most cases.

The IUPAC nomenclature system is a set of logical rules devised and used by organic chemists to circumvent problems caused by arbitrary nomenclature. Knowing these rules and given a structural formula, one should be able to write a unique name for every distinct compound. Likewise, given a IUPAC name, one should be able to write a structural formula. In general, an IUPAC name will have three essential features:

- A root or base indicating a major chain or ring of carbon atoms found in the molecular structure.
- A suffix or other element(s) designating functional groups that may be present in the compound.
- Names of substituent groups, other than hydrogen, that complete the molecular structure.

As an introduction to the IUPAC nomenclature system, we shall first consider compounds that have no specific functional groups. Such compounds are composed only of carbon and hydrogen atoms bonded together by sigma bonds (all carbons are sp^3 hybridized).

Alkanes

Hydrocarbons having no double or triple bond functional groups are classified as **alkanes** or **cycloalkanes**, depending on whether the carbon atoms of the molecule are arranged only in chains or also in rings. Although these hydrocarbons have no functional groups, they constitute the framework on which functional groups are located in other classes of compounds, and provide an ideal starting point for studying and naming organic compounds. The alkanes and cycloalkanes are also members of a larger class of compounds referred to as **aliphatic**. Simply put, aliphatic compounds are compounds that do not incorporate any aromatic rings in their molecular structure.

The following table lists the IUPAC names assigned to simple continuous-chain alkanes from C-1 to C-10. A common **"ane"** suffix identifies these compounds as alkanes. Longer chain alkanes are well known, and their names may be found in many reference and text books. The names **methane** through **decane** should be memorized, since they constitute the root of many IUPAC names. Fortunately, common numerical prefixes are used in naming chains of five or more carbon atoms.

Examples of Simple Unbranched Alkanes

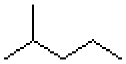
Name	Molecular Formula	Structural Formula	Isomers		Name	Molecular Formula	Structural Formula	Isomers
meth**ane**	CH_4	CH_4	1		hex**ane**	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
eth**ane**	C_2H_6	CH_3CH_3	1		hept**ane**	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
prop**ane**	C_3H_8	$CH_3CH_2CH_3$	1		oct**ane**	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
but**ane**	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2		non**ane**	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
pent**ane**	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3		dec**ane**	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

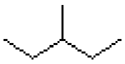
Some important behavior trends and terminologies:

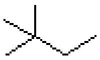
(i) The formulas and structures of these alkanes increase uniformly by a CH_2 increment.
(ii) A uniform variation of this kind in a series of compounds is called **homologous**.
(iii) These formulas all fit the $\mathbf{C_nH_{2n+2}}$ rule. This is also the highest possible H/C ratio for a stable hydrocarbon.
(iv) Since the H/C ratio in these compounds is at a maximum, we call them **saturated** (with hydrogen).

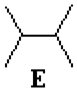
Beginning with butane (C_4H_{10}), and becoming more numerous with larger alkanes, we note the existence of alkane isomers. For example, there are five C_6H_{14} isomers, shown below as abbreviated line formulas (**A** through **E**):


A


B


C


D


E

Although these distinct compounds all have the same molecular formula, only one (**A**) can be called hexane. How then are we to name the others?

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

Group	CH_3–	C_2H_5–	$CH_3CH_2CH_2$–	$(CH_3)_2CH$–	$CH_3CH_2CH_2CH_2$–	$(CH_3)_2CHCH_2$–	$CH_3CH_2CH(CH_3)$–	$(CH_3)_3C$–	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	*sec*-Butyl	*tert*-Butyl	Alkyl

IUPAC Rules for Alkane Nomenclature

1. Find and name the longest continuous carbon chain.
2. Identify and name groups attached to this chain.
3. Number the chain consecutively, starting at the end nearest a substituent group.
4. Designate the location of each substituent group by an appropriate number and name.
5. Assemble the name, listing groups in alphabetical order using the full name (e.g. cyclopropyl before isobutyl). The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizin

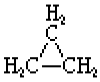
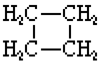
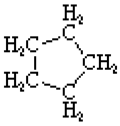
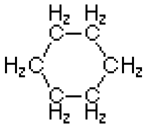
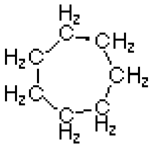
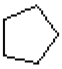
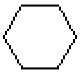
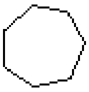
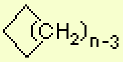
Halogen substituents are easily accommodated, using the names: fluoro (F-), chloro (Cl-), bromo (Br-) and iodo (I-). For example, $(CH_3)_2CHCH_2CH_2Br$ would be named 1-bromo-3-methylbutane. If the halogen is bonded to a simple alkyl group an alternative "alkyl halide" name may be used. Thus, C_2H_5Cl may be named chloroethane (no locator number is needed for a two carbon chain) or ethyl chloride. Halogenated alkyl substituents such as bromomethyl, $BrCH_2$–, and trichloromethyl, CCl_3–, may be listed and are alphabetized according to their full names.

Cycloalkanes

Cycloalkanes have one or more rings of carbon atoms. The simplest examples of this class consist of a single, unsubstituted carbon ring, and these form a homologous series similar to the unbranched alkanes. The IUPAC names of the first five members of this series are given in the following table. The last (yellow shaded) column gives the general formula for a cycloalkane of any size. If a simple unbranched alkane is converted to a cycloalkane two hydrogen atoms, one from each end of the chain, must be lost. Hence the general formula for a cycloalkane composed of **n** carbons is **C_nH_{2n}**. Although a cycloalkane has two fewer hydrogens than the equivalent alkane, each carbon is bonded to four other atoms so such compounds are still considered to be **saturated** with hydrogen.

Examples of Simple Cycloalkanes

Name	**Cyclopropane**	**Cyclobutane**	**Cyclopentane**	**Cyclohexane**	**Cycloheptane**	**Cycloalkane**
Molecular Formula	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}	C_nH_{2n}

Structural Formula						$(CH_2)_n$
Line Formula						

Substituted cycloalkanes are named in a fashion very similar to that used for naming branched alkanes. The chief difference in the rules and procedures occurs in the numbering system. Since all the carbons of a ring are equivalent (a ring has no ends like a chain does), the numbering starts at a substituted ring atom.

IUPAC Rules for Cycloalkane Nomenclature

1. For a monosubstituted cycloalkane the ring supplies the root name (table above) and the substituent group is named as usual. A location number is unnecessary.
2. If the alkyl substituent is large and/or complex, the ring may be named as a substituent group on an alkane.
3. If two different substituents are present on the ring, they are listed in alphabetical order, and the first cited substituent is assigned to carbon #1. The numbering of ring carbons then continues in a direction (clockwise or counter-clockwise) that affords the second substituent the lower possible location number.
4. If several substituents are present on the ring, they are listed in alphabetical order. Location numbers are assigned to the substituents so that one of them is at carbon #1 and the other locations have the lowest possible numbers, counting in either a clockwise or counter-clockwise direction.
5. The name is assembled, listing groups in alphabetical order and giving each group (if there are two or more) a location number. The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing.

For examples of how these rules are used in naming substituted cycloalkanes .

Small rings, such as three and four membered rings, have significant angle strain resulting from the distortion of the sp^3 carbon bond angles from the ideal 109.5° to 60° and 90° respectively. This angle strain often enhances the chemical reactivity of such compounds, leading to ring cleavage products. It is also important to recognize that, with the exception of cyclopropane, cycloalkyl rings are not planar (flat). The three dimensional shapes assumed by the common rings (especially cyclohexane and larger rings) are described and discussed in the Conformational Analysis Section.

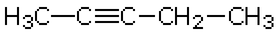
Hydrocarbons having more than one ring are common, and are referred to as **bicyclic** (two rings), **tricyclic** (three rings) and in general, **polycyclic** compounds. The molecular formulas of such compounds have H/C ratios that decrease with the number of rings. In general, for a hydrocarbon composed of **n carbon atoms** associated with **m rings** the formula is: $C_nH_{(2n + 2 - 2m)}$. The structural relationship of rings in a polycyclic compound can vary. They may be separate and independent, or they may share one or two common atoms. Some examples of these possible arrangements are shown in the following table.

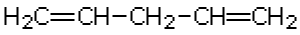
Alkenes and Alkynes

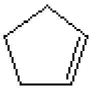
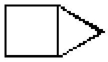
Alkenes and alkynes are hydrocarbons which respectively have **carbon-carbon double bond** and **carbon-carbon triple bond** functional groups. The molecular formulas of these **unsaturated** hydrocarbons reflect the multiple bonding of the functional groups:

Alkane	R–CH$_2$–CH$_2$–R	C_nH_{2n+2}	This is the maximum H/C ratio for a given number of carbon atoms.
Alkene	R–CH=CH–R	C_nH_{2n}	Each double bond reduces the number of hydrogen atoms by 2.
Alkyne	R–C≡C–R	C_nH_{2n-2}	Each triple bond reduces the number of hydrogen atoms by 4.

As noted earlier in the Analysis of Molecular Formulas section, the molecular formula of a hydrocarbon provides information about the possible structural types it may represent. For example, consider compounds having the formula C_5H_8. The formula of the five-carbon alkane pentane is C_5H_{12} so the difference in hydrogen content is 4. This difference suggests such compounds may have a triple bond, two double bonds, a ring plus a double bond, or two rings. Some examples are shown here, and there are at least fourteen others!





IUPAC Rules for Alkene and Cycloalkene Nomenclature

1. The **ene** suffix (ending) indicates an alkene or cycloalkene.
2. The longest chain chosen for the root name must include both carbon atoms of the double bond.
3. The root chain must be numbered from the end nearest a double bond carbon atom. If the double bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.
4. The smaller of the two numbers designating the carbon atoms of the double bond is used as the double bond locator. If more than one double bond is present the compound is named as a diene, triene or equivalent prefix indicating the number of double bonds, and each double bond is assigned a locator number.
5. In cycloalkenes the double bond carbons are assigned ring locations #1 and #2. Which of the two is #1 may be determined by the nearest substituent rule.
6. Substituent groups containing double bonds are:
    $H_2C=CH–$ Vinyl group
    $H_2C=CH–CH_2–$ Allyl group

IUPAC Rules for Alkyne Nomenclature

1. The **yne** suffix (ending) indicates an alkyne or cycloalkyne.
2. The longest chain chosen for the root name must include both carbon atoms of the triple bond.
3. The root chain must be numbered from the end nearest a triple bond carbon atom. If the triple bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.
4. The smaller of the two numbers designating the carbon atoms of the triple bond is used as the triple bond locator.
5. If several multiple bonds are present, each must be assigned a locator number. Double bonds precede triple bond

in the IUPAC name, but the chain is numbered from the end nearest a multiple bond, regardless of its nature.

6. Because the triple bond is linear, it can only be accommodated in rings larger than ten carbons. In simple cycloalkynes the triple bond carbons are assigned ring locations #1 and #2. Which of the two is #1 may be determined by the nearest substituent rule.

7. Substituent groups containing triple bonds are:

$HC\equiv C-$ Ethynyl group
$HC\equiv C-CH_2-$ Propargyl group

References:

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- Textbook of Organic Chemistry by B.S. Bahl & Arun Bahl.
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- Practical Organic Chemistry by Mann and Saunders.
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