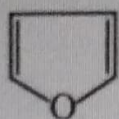
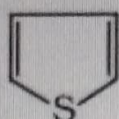


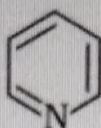
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into *families* or *homologous series*.

12.4.1 Functional Group

The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group ($-\text{OH}$), aldehyde group ($-\text{CHO}$) and carboxylic acid group ($-\text{COOH}$) etc.

12.4.2 Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called *homologues*. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-\text{CH}_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanolic acids, amines etc.

It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

12.5: NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named

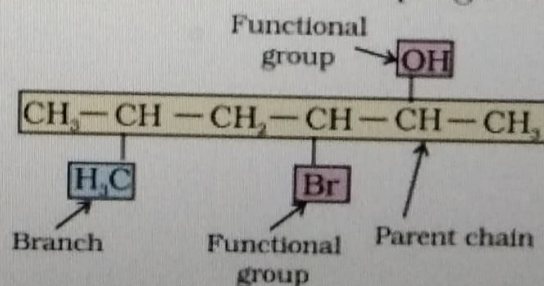
so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are considered as *trivial* or *common names*. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 12.1.

Table 12.1 Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_3$	<i>n</i> -Butane
$(\text{H}_3\text{C})_2\text{CHCH}_3$	Isobutane
$(\text{H}_3\text{C})_4\text{C}$	Neopentane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{OH}$	<i>n</i> -Propyl alcohol
HCHO	Formaldehyde
$(\text{H}_3\text{C})_2\text{CO}$	Acetone
CHCl_3	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$\text{C}_6\text{H}_5\text{OCH}_3$	Anisole
$\text{C}_6\text{H}_5\text{NH}_2$	Aniline
$\text{C}_6\text{H}_5\text{COCH}_3$	Acetophenone
$\text{CH}_3\text{OCH}_2\text{CH}_3$	Ethyl methyl ether

12.5.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.



By further using *prefixes* and *suffixes*, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is *alkane*. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

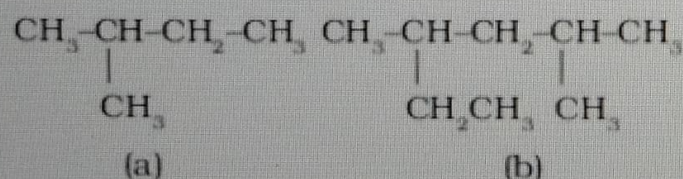
12.5.2 IUPAC Nomenclature of Alkanes

Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10} , where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 12.2. The alkanes in Table 12.2 differ from each other by merely the number of $-\text{CH}_2$ groups in the chain. They are homologues of alkane series.

Table 12.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$\text{C}_{10}\text{H}_{22}$
Pentane	C_5H_{12}	Icosane	$\text{C}_{20}\text{H}_{42}$
Hexane	C_6H_{14}	Triacotane	$\text{C}_{30}\text{H}_{62}$

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:

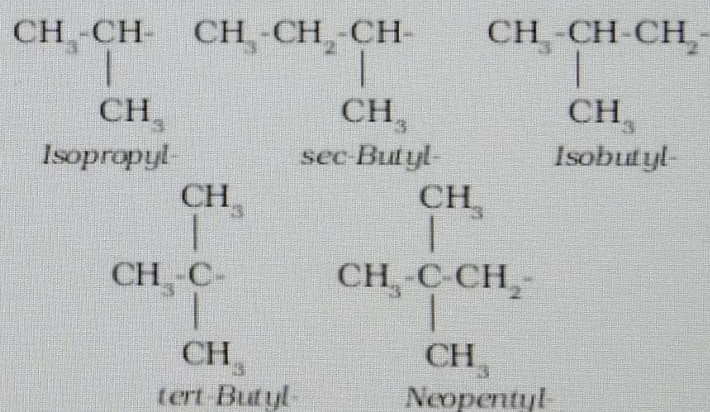


In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH_4 becomes $-\text{CH}_3$ and is called *methyl group*. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 12.3.

Table 12.3 Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-\text{CH}_3$	Methyl
C_2H_6	Ethane	$-\text{CH}_2\text{CH}_3$	Ethyl
C_3H_8	Propane	$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
C_4H_{10}	Butane	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\text{C}_{10}\text{H}_{22}$	Decane	$-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$	Decyl

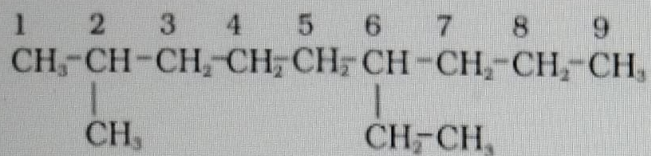
Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.



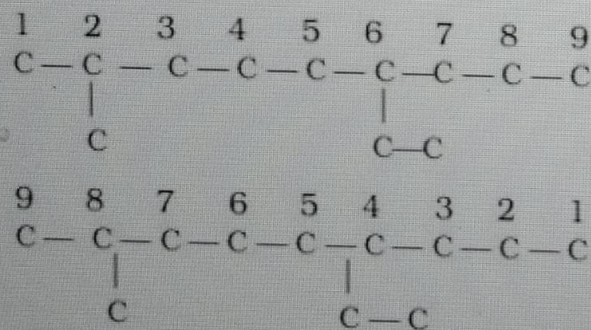
Common branched groups have specific trivial names. For example, the propyl groups can either be *n*-propyl group or isopropyl group. The branched butyl groups are called *sec*-butyl, *isobutyl* and *tert*-butyl group. We also encounter the structural unit, $-\text{CH}_2\text{C}(\text{CH}_3)_3$, which is called neopentyl group.

Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the **longest carbon chain in the molecule is identified**. In the example (I) given below, the longest chain has nine carbons and it is considered as the *parent* or *root* chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.



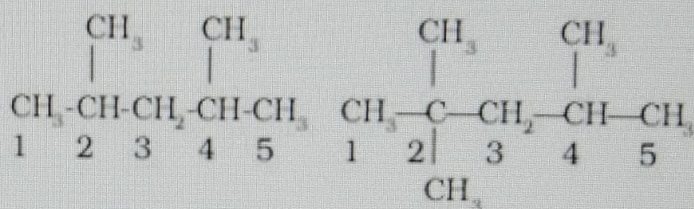
2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.** Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).



3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are

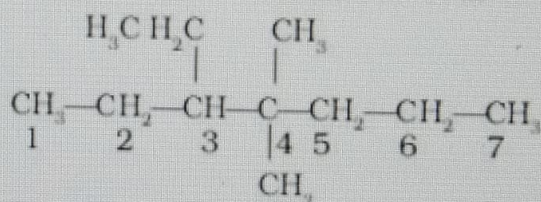
separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:



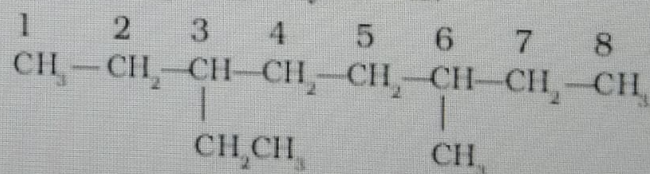
2,4-Dimethylpentane

2,2,4-Trimethylpentane

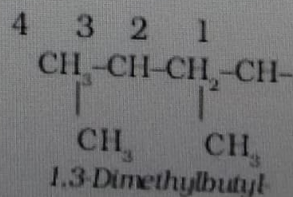


3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the **lower number is given to the one coming first in the alphabetical listing**. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.

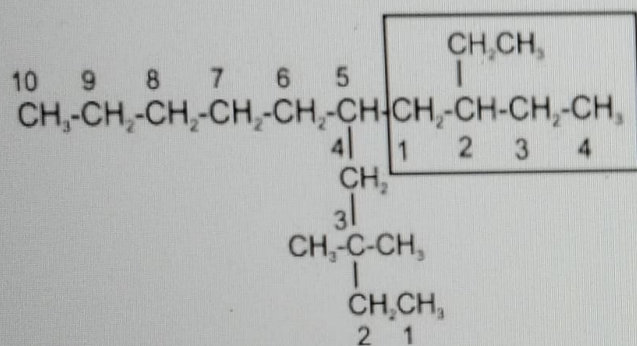


6. The branched alkyl groups can be named by following the above mentioned procedures. However, the **carbon atom of the branch that attaches to the root alkane** is numbered 1 as exemplified below.

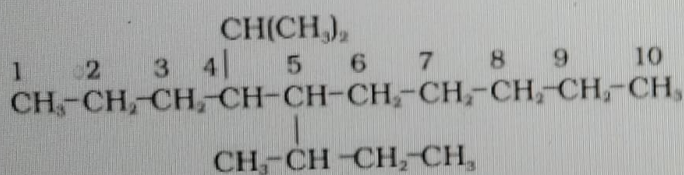


The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' **in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name.** The use of *iso* and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multi-substituted compounds, the following rules may also be remembered:

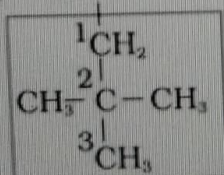
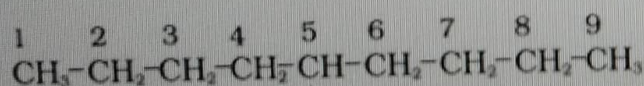
- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.



5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

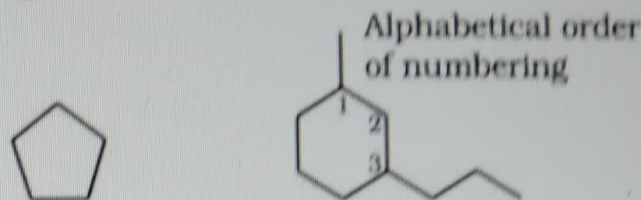


5-sec-Butyl-4-isopropyldecane

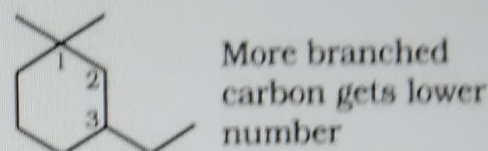


5-(2,2-Dimethylpropyl)nonane

Cyclic Compounds: A saturated monocyclic compound is named by prefixing '*cyclo*' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.



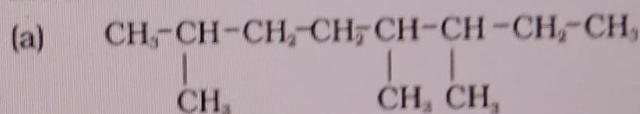
Cyclopentane 1-Methyl-3-propylcyclohexane



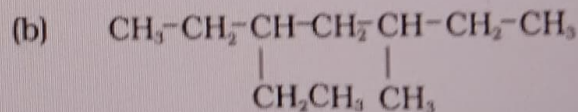
3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Problem 12.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.



2,5,6-Trimethyloctane
[and not 3,4,7-Trimethyloctane]



3-Ethyl-5-methylheptane
[and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

12.5.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of

chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, and $(\text{CH}_3)_2\text{CHOH}$ — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 12.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. **The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.** By using the suffix as given in Table 12.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is:**

$-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{COOR}$ (R=alkyl group), COCl , $-\text{CONH}_2$, $-\text{CN}$, $-\text{HC}=\text{O}$, $>\text{C}=\text{O}$, $-\text{OH}$, $-\text{NH}_2$, $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$.

The $-\text{R}$, C_6H_5- , halogens (F, Cl, Br, I), $-\text{NO}_2$, alkoxy ($-\text{OR}$) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group.

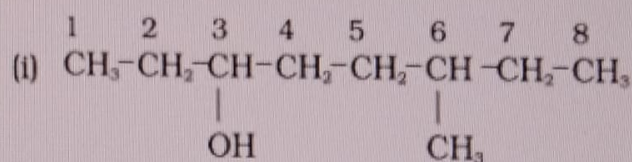
For example, $\text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{COCH}_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan-7-ol. Similarly, $\text{BrCH}_2\text{CH}=\text{CH}_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class

suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$ is named as ethane-1,2-diol. However, the ending -ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ is named as buta-1,3-diene.

Problem 12.8

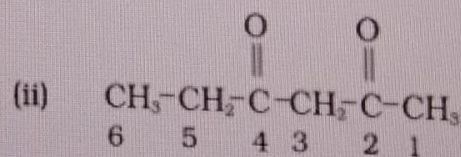
Write the IUPAC names of the compounds i-iv from their given structures.



Solution

- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

Hence, the systematic name of this compound is 6-Methyloctan-3-ol.



Solution

The functional group present is ketone ($>\text{C}=\text{O}$), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

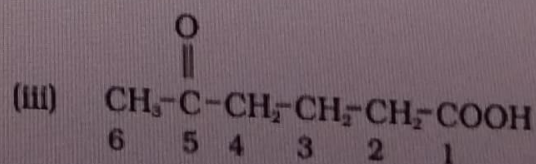

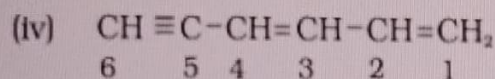


Table 12.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Alkenes	$>\text{C}=\text{C}<$	-	-ene	But-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
Alkynes	$-\text{C}\equiv\text{C}-$	-	-yne	But-1-yne, $\text{CH}\equiv\text{CCH}_2\text{CH}_3$
Arenes	-	-	-	Benzene, 
Halides	$-\text{X}$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)	halo-	-	1-Bromobutane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$
Alcohols	$-\text{OH}$	hydroxy-	-ol	Butan-2-ol, $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
Aldehydes	$-\text{CHO}$	formyl, or oxo	-al	Butanal, $\text{CH}_3(\text{CH}_2)_2\text{CHO}$
Ketones	$>\text{C}=\text{O}$	oxo-	-one	Butan-2-one, $\text{CH}_3\text{CH}_2\text{COCH}_3$
Nitriles	$-\text{C}\equiv\text{N}$	cyano	nitrile	Pentanenitrile, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$
Ethers	$-\text{R}-\text{O}-\text{R}-$	alkoxy-	-	Ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
Carboxylic acids	$-\text{COOH}$	carboxy	-oic acid	Butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$
Carboxylate ions	$-\text{COO}^-$	-	-oate	Sodium butanoate, $\text{CH}_3(\text{CH}_2)_2\text{CO}_2^- \text{Na}^+$
Esters	$-\text{COOR}$	alkoxycarbonyl	-oate	Methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$
Acyl halides	$-\text{COX}$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)	halocarbonyl	-oyl halide	Butanoyl chloride, $\text{CH}_3(\text{CH}_2)_2\text{COCl}$
Amines	$-\text{NH}_2$, $>\text{NH}$, $>\text{N}-$	amino-	-amine	Butan-2-amine, $\text{CH}_3\text{CHNH}_2\text{CH}_2\text{CH}_3$
Amides	$-\text{CONH}_2$, $-\text{CONHR}$, $-\text{CONR}_2$	-carbamoyl	-amide	Butanamide, $\text{CH}_3(\text{CH}_2)_2\text{CONH}_2$
Nitro compounds	$-\text{NO}_2$	nitro	-	1-Nitrobutane, $\text{CH}_3(\text{CH}_2)_3\text{NO}_2$
Sulphonic acids	$-\text{SO}_3\text{H}$	sulpho	sulphonic acid	Methylsulphonic acid $\text{CH}_3\text{SO}_3\text{H}$

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of -COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

**Solution**

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

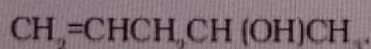
Problem 12.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3-Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal.

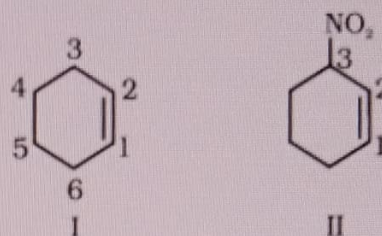
Solution

(i) 'hexane' indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$.

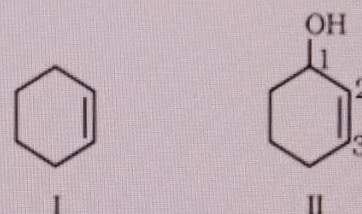
(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is



(iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO_2 is prefixed functional group therefore double bond gets preference over $-\text{NO}_2$ group:



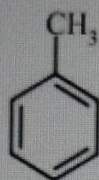
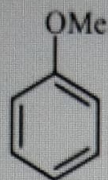
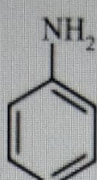
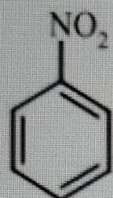
(iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II):



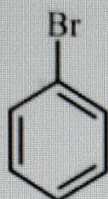
(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$. Carbon atom of -CHO group is included while numbering the carbon chain.

12.5.4 Nomenclature of Substituted Benzene Compounds

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.

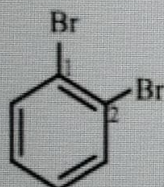
Methylbenzene
(Toluene)Methoxybenzene
(Anisole)Aminobenzene
(Aniline)

Nitrobenzene

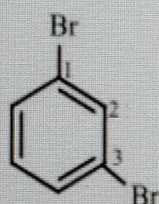


Bromobenzene

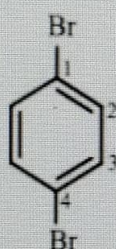
If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound (b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



(a)

1,2-Dibromo-
benzene

(b)

1,3-Dibromo-
benzene

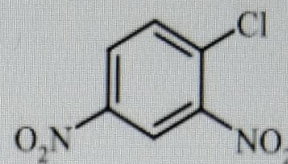
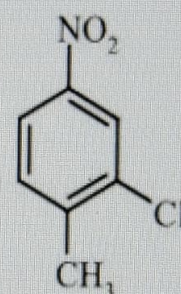
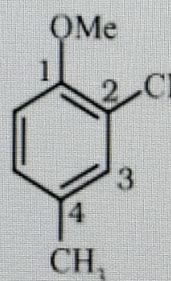
(c)

1,4-Dibromo-
benzene

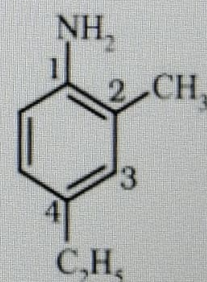
In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2; 1,3 and 1,4 respectively. Thus, 1,3-dibromobenzene (b) is named as *m*-dibromobenzene (*meta* is abbreviated as *m*-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as *ortho* (or just *o*-) and *para* (or just *p*-) dibromobenzene, respectively.

For tri- or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

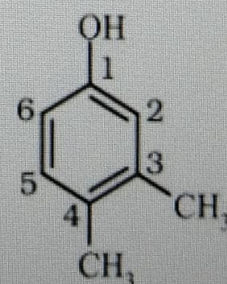
Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.

1-Chloro-2,4-dinitrobenzene
(not 4-chloro,1,3-dinitrobenzene)2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)

2-Chloro-4-methylanisole



4-Ethyl-2-methylaniline



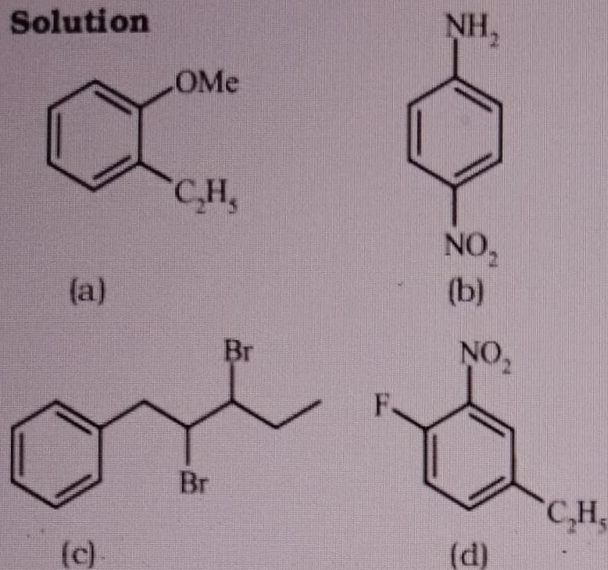
3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* (C_6H_5 ·, also abbreviated as Ph).

Problem 12.10

Write the structural formula of:

- (a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
 (c) 2,3 - Dibromo -1 - phenylpentane,
 (d) 4-Ethyl-1-fluoro-2-nitrobenzene.

Solution**12.6 ISOMERISM**

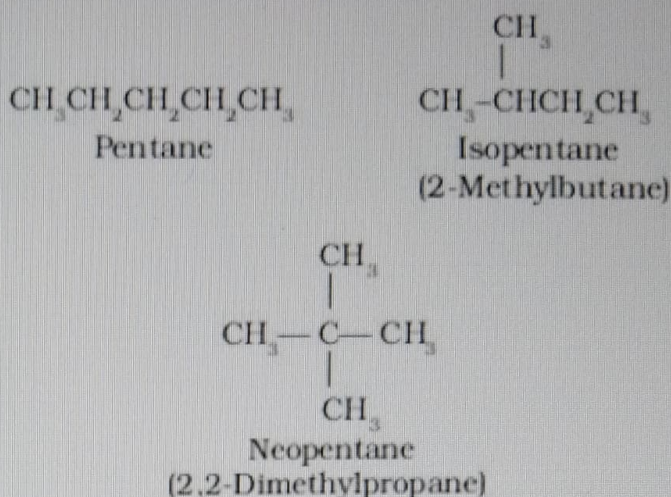
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

12.6.1 Structural Isomerism

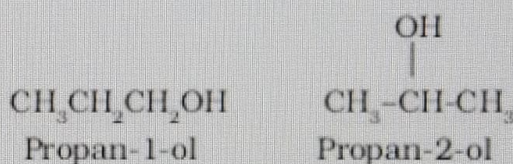
Compounds having the same molecular formula but different structures (manner in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

(i) Chain isomerism: When two or more compounds have similar molecular formula but

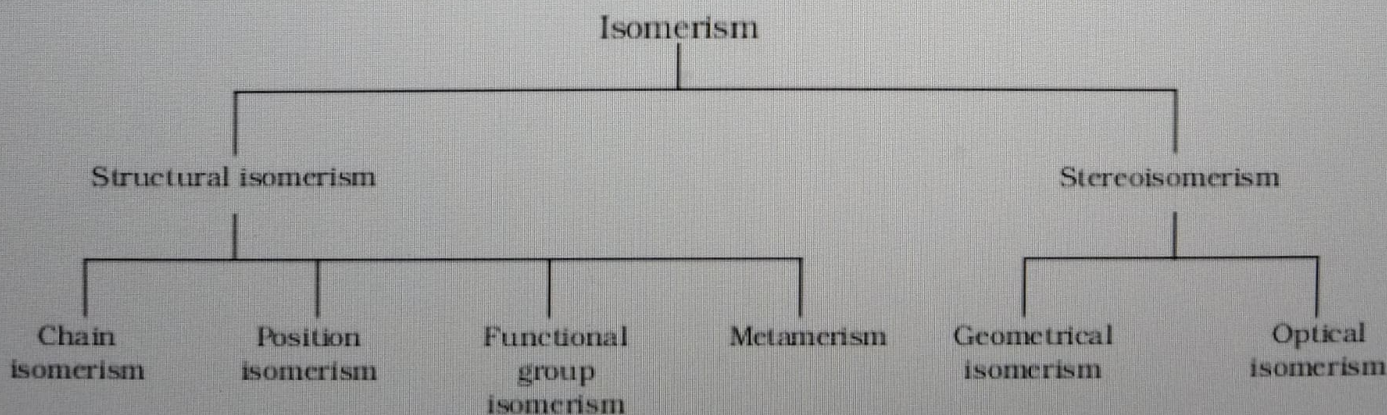
different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C₅H₁₂ represents three compounds:

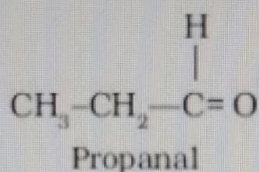
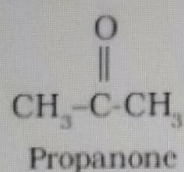


(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C₃H₈O represents two alcohols:



(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C₃H₆O represents an aldehyde and a ketone:





(iv) **Metamerism:** It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $\text{C}_4\text{H}_{10}\text{O}$ represents methoxypropane ($\text{CH}_3\text{OC}_3\text{H}_7$) and ethoxyethane ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$).

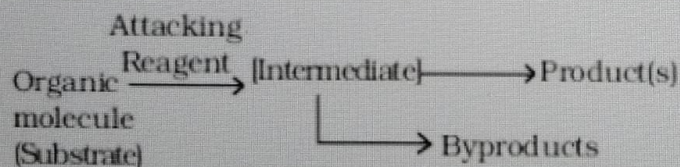
12.6.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and *optical isomerism*.

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s).

The general reaction is depicted as follows :



Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate*.

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps in

understanding the reactivity of organic compounds and in planning strategy for their synthesis.

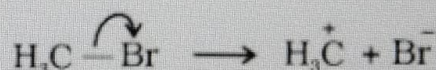
In the following sections, we shall learn some of the principles that explain how these reactions take place.

12.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) **heterolytic cleavage**, or by (ii) **homolytic cleavage**.

In **heterolytic cleavage**, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\overset{+}{\text{C}}\text{H}_3$ and Br^- as shown below.



A species having a carbon atom possessing sextet of electrons and a positive charge is called a **carbocation** (earlier called *carbonium ion*). The $\overset{+}{\text{C}}\text{H}_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $\text{CH}_3\overset{+}{\text{C}}\text{H}_2$ (ethyl cation, a primary carbocation), $(\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$ (isopropyl cation, a secondary carbocation), and $(\text{CH}_3)_3\overset{+}{\text{C}}$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 12.7.5 and 12.7.9. The observed order of carbocation stability is: $\overset{+}{\text{C}}\text{H}_3 < \text{CH}_3\overset{+}{\text{C}}\text{H}_2 < (\text{CH}_3)_2\overset{+}{\text{C}}\text{H} < (\text{CH}_3)_3\overset{+}{\text{C}}$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $\overset{+}{\text{C}}\text{H}_3$ may be considered as being derived from the overlap of three equivalent $\text{C}(sp^2)$ hybridised orbitals