HISTORICAL INTRODUCTION

It was observed that initially compounds were found from two sources living organism and non living matter. The compounds which were derived from living organism were called as organic compounds while those from non living matter were named as inorganic compounds. Berzilius thought that organic compounds were produced from their element by laws different from those governing the formation of inorganic compounds. This led him to the belief that organic compounds are formed under the influence of a vital force and they couldn't be prepared artificially. This myth continued till Wohler converted inorganic compound ammonium cyanate found from non living matters into urea an organic compound.

heat NH₄CNO ammonium cyanate

NH,CONH,

urea

The myth of vital force theory was completely ended with the synthesis of acetic acid from its elements by Kolbe in 1845, and the synthesis of methane by Berthelot in 1856

Since then millions of compounds have been produced in laboratory. Basically organic compounds are made of essentially carbon and other elements like Hydrogen, Oxygen, Nitrogen Phosphorus, Sulphur etc..

SOME IMPORTANT DEFINITIONS

- Catenation: The property of atoms of an element (i) to link with one another forming chains of identical atoms is called catenation.
- (ii) Homologous series : Homologous series may be defined as a series of similarly constituted compounds in which the members possess the same functional group, have similar chemical characteristics and have a regular gradation in their physical properties. The two consecutive members differ in their molecular formula by CH₂.
- (iii) Isomerism : Compounds which have the same molecular formula but differ in physical and chemical properties are called isomers and the phenomena is called isomerism.

Isomerism can be broadly classified into two categories

2. Stereoisomerism 1. Structural Isomerism

CLASSIFICATION OF ORGANIC COMPOUNDS

If we look at the vast number of organic compounds, two things will strike our mind-the skeleton is either open or closed. Based on this, organic compounds are classified as acyclic (open-chain) or cyclic (closed-chain)

Organic Chemistry – Some Basic Principles and Techniques



ORGANIC COMPOUNDS AND FUNCTIONAL GROUPS

Number of known organic compounds is much more than inorganic compounds but, it has been possible to group them into classes or families based on their structural features. This has given organic chemistry a logical and systematic shape.

In these compounds, there are a number of atoms or groups which show constancy of properties. Such groups are called functional groups. Examples of functional groups are :

1. Alkanes

These are open-chain aliphatic compounds which have no functional groups. These are

represented by the general formula, $C_n H_{2n+2}$

where n = 1, 2, 3,

The names of the alkanes for $n = 1, 2, \dots, 10$ must be committed to memory since all of organic nomenclature is related directly or indirectly to the name of alkane $C_n H_{2n+2}$

11 211 2		
$n = 1$ means CH_4	—	Methane
$n = 2 \text{ means } C_2 H_6$	_	Ethane
$n = 3 \text{ means } C_3 H_8$	-	Propane
$n = 4 \text{ means } C_4 H_{10}$	-	Butane
$n = 5$ means $C_5 H_{12}$	_	Pentane
$n = 6$ means $C_6 H_{14}$	_	Hexane
$n = 7$ means $C_7 H_{16}$	-	Heptane
$n = 8$ means $C_8 H_{18}$	_	Octane
$n = 9$ means $C_9 H_{20}$	_	Nonane
$n = 10$ means $C_{10}H_{22}$	_	Decane

2. **Alkyl Groups**

When we remove a hydrogen from alkane, we get an alkyl group :

General formula $C_nH_{2n+2} \xrightarrow{-H} C_nH_{2n+1}$ alkane $\xrightarrow{-ane}{+yl}$ alkyl $\underset{+yl}{\text{methane}} \xrightarrow{-ane} \\ \text{methyl}$ e.g. $CH_4 \xrightarrow{-H} - CH_3$ propane <u>____</u>+vl → propyl e.g. $C_3H_8 \xrightarrow{-H} - C_3H_7$

3. Alkenes

Alkenes are open chain hydrocarbons and having carbon–carbon double bonds, C = C. They have the general formula $C_n H_{2n}$ where $n = 2, 3, 4 \dots$ etc. and are also called alkylenes or olefins. The first three members are commonly named by their common names

$$H_2 = CH_2$$
 $CH_3 - CH = CH_2$
ethylene propylene

 CH_3 |CH₃ – C = CH₂ $CH_3 - CH_2 - CH = CH_2$ Isobutylene

butylene

Alkenyl Groups

Like alkyl groups (alkane - H), there are three commonly encountered alkenyl groups which are given common names.

e.g.

4.

5. Alkynes

Unsaturated aliphatic hydrocarbons containing a carbon-carbon triple bond are called alkynes. In the common system, they are called acetylenes, after the name of the first member of this family. i.e. acetylene

General formula C_nH_{2n-2}

where n = 2, 3, 4... etc.

Common Names Acetylene and its alkyl derivatives.

IUPAC names

Alkane - ane + yne = Alkyne

The position of the triple bond on the parent chain is designated by lowest possible arabic numerals

The common IUPAC names of a few simple alkynes are given below.

 $n = 2 \longrightarrow CH \equiv CH$ Acetylene

 $n = 3 \longrightarrow CH_3 - C \equiv CH$ Methyl acetylene

$$n = 4 \longrightarrow CH_3 - CH_2 - C \equiv CH$$

Ethylacetylene

$$n = 6 \longrightarrow CH_3 - C \equiv C - CH$$

Methyl isopropyl acetylene

6. Alkynyl Groups

 $HC \equiv CH \longrightarrow HC \equiv C -$ (-e + yl = Ethynyl) $H_{3}C - C \equiv CH \longrightarrow H_{3}C - C \equiv C -$ (-e + yl = propynyl)

7. Functional group and Residue

The characteristic group of atom which decided the physical and chemical properties of an organic molecule is called functional group.

Functional group is that portion of molecule which is highly reactive and takes part in chemical reactions. Rest of the molecule is called Residue.

e.g. $CH_3CH_2CH_2CH_2 - COOH$

Residue Functional

Group

	Class of functional groups	Name		
1.	R – COOH	Carboxylic acid		
2.	$R - SO_3H$	Sulfonic acid		
3.	R-C-O-C-R O O	Anhydride		
4.	R – COOR	Ester		
5.	R – C – X O	Acid halide		
6.	$\begin{array}{c} R-C-NH_{\scriptscriptstyle 2} \\ \\ O \end{array}$	Amide		
7.	R-C N	Alkane nitrile		
8.	R – C – H II O	Aldehyde		
9.	R – C – R 0	Ketone		
10.	R – OH	Alcohol		
11.	R – SH	Thiol		
12.	$R - NH_2$	Amine		

Examples of Compound containing different functional groups

(1) -COOH group

(i) HCOOH	Formic acid
(ii) CH ₃ COOH	Acetic acid
(iii) $CH_3 - CH_2 - COOH$	Propionic acid

(2) $-SO_3H$ group

(i) CH ₃ SO ₃ H	Methane sulfonic acid
(ii) CH ₃ CH ₂ SO ₃ H	Ethane sulfonic acid
(iii) $CH_3 - CH_2 - C$	SO ₃ H

Propane sulfonic acid

$(10) - \textbf{OH}\, \textbf{group}$

(i) $CH_3 - OH$ Methyl alcohol (ii) $CH_3 - CH - CH_3$ Isopropyl alcohol OH

(iii) $CH_3 - CH_2 - CH_2 - OH$ n-Propylalcohol

(11) – SH group

(i) $CH_3 - SH$ Methane thiol (ii) $CH_3 - CH_2 - SH$ Ethane thiol (iii) $CH_3 - CH_2 - CH_2 - SH$ Propane thiol

$(12) - \mathbf{NH}_2$ group

(i) $CH_3 - NH_2$ Methylamine or Aminomethane (ii) $CH_3 - CH_2 - NH - CH_3$ Ethyl methyl amine or N-Methylaminoethane (iii) $(CH_3)_3N$ Trimethylamine or N N-Dimethyl

Trimethylamine or N, N-Dimethyl aminomethane

SOME COMMON NAMES OF HYDROCARBON ALKYL GROUPS

1 Iso Alkyl group

 CH_3 A compound having $-CH - CH_3$ group is called iso alkyl group

e.g.

Iso propyl

$$CH_3 - CH - CH_2 - CH_3$$

|
 CH_3
Iso pentane

Note: Iso alkyl group name can be used in IUPAC Nomenclature and its first letter 'I' is consider for alphabetical seniority

e.g.

$$\begin{array}{c} \overset{1}{C}H_{3} - \overset{2}{C}H - \overset{3}{C}H - \overset{4}{C}H_{2} - \overset{5}{C}H_{2} - \overset{6}{C}H_{3} \\ | & | \\ CH_{3} CH - CH_{3} \\ | \\ CH_{3} \end{array}$$

3-Isopropyl-2-methylhexane

2. Neo Alkyl group

Compound having
$$\begin{pmatrix} CH_3 \\ I \\ CH_3 - C - CH_2 - \\ I \\ CH_3 \end{pmatrix}$$
 group is called

neo alkyl group.

$$CH_3$$

|
e.g. $CH_3 - C - CH_2 - |$
 CH_3

Neopentyl

$$\begin{array}{c} \mathsf{CH}_3\\ \mathsf{I}\\ \mathsf{CH}_3-\mathsf{C}-\mathsf{CH}_3\\ \mathsf{I}\\ \mathsf{CH}_3\end{array}$$

Neopentane

$$CH_3 \\ | \\ CH_3 - C - CH_2 - CH_3 \\ | \\ CH_3$$

Neohexane

TYPES OF CARBON AND HYDROGEN ATOMS IN ALKANES

The carbon atoms in an alkane molecule may be classified into four types as primary (1°) , secondary (2°) , tertiary (3°) and quaternary (4°) as follows

 A carbon atom attached to one another (or no other) carbon atom is called a primary carbon atom and is designated as 1° carbon

e.g. (i)
$$\overset{1^{\circ}}{C}H_{3} - \overset{1^{\circ}}{C}H_{3}$$

(ii) $\overset{1^{\circ}}{C}H_{3} - CH_{2} - \overset{1^{\circ}}{C}H_{3}$

 (ii) A carbon atom attached to two other carbon atoms is called a secondary carbon atom and is designated as 2° carbon

e.g. (i)
$$CH_3 - \overset{2^{\circ}}{C}H_2 - CH_3$$

(ii) $CH_3 - \overset{2^{\circ}}{C}H_2 - \overset{2^{\circ}}{C}H_2 - CH_3$

 (iii) A carbon atom attached to three other carbon atoms is called a tertiary carbon atom and is designated as 3° carbon.

e.g. (i)
$$CH_3 = CH_3$$

 $| H_3 = CH_3 - CH_3$

$$\begin{array}{c} \mathsf{CH}_3 \\ \stackrel{|}{\underset{(ii)}{\mathsf{CH}}_3} - \stackrel{|}{\underset{3^\circ}{\mathsf{CH}}} \mathsf{H} - \mathsf{CH}_2 - \mathsf{CH}_3 \end{array}$$

 (iv) A carbon atom attached to four other carbon atoms is called a quaternary carbon atom and is designated as 4° carbon

e.g. (i)
$$\begin{array}{c} CH_{3} \\ | \\ CH_{3} - 4^{\circ}C - CH_{3} \\ | \\ CH_{3} \end{array}$$

(ii)
$$CH_3 = {}^{4^{\circ}}C - CH_2 - CH_3$$

 $| \\CH_2 - CH_3$

The hydrogen atoms attached to 1° , 2° and 3° carbon atoms are called primary (1°) secondary (2°) and tertiary (3°) hydrogen atoms. It may be noted here that there is nothing like quaternary hydrogen atom. Since a quarternary carbon does not carry any hydrogen.

Solved Examples

Ex.1 How many 1°, 2°, 3° and 4° carbon atoms are present in following molecule.

- **Sol.** 1° Carbon atoms = 6, 2° Carbon atoms = 2, 3° Carbon atoms = 2, 4° Carbon atom = 1
- **Note :** Primary, secondary, tertiary & quaternary carbon atoms in a molecule are denoted by the letters p, s, t and q respectively.

Ex.2 How many 1°, 2°, 3° and 4° carbon atoms are present in following molecule

$$\begin{array}{c} CH_{3} \\ | \\ CH_{3} - C - CH_{2} - CH - CH_{3} \\ | \\ | \\ CH_{3} \\ CH_{3} \\ \end{array}$$

Sol.
$$\overset{1^{\circ}}{C}H_{3}$$

 $\overset{1^{\circ}}{C}H_{3} - \overset{2^{\circ}}{C} - \overset{3^{\circ}}{C}H_{2} - \overset{1^{\circ}}{C}H_{-}\overset{1^{\circ}}{C}H_{3}$
 $\overset{1^{\circ}}{C}H_{3} - \overset{1^{\circ}}{C} - \overset{1^{\circ}}{C}H_{2} - \overset{1^{\circ}}{C}H_{-}\overset{1^{\circ}}{C}H_{3}$

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1° Carbon atoms = 5, 2° Carbon atom = 1, 3° Carbon atom = 1, 4° Carbon atom = 1

Discoverer

(Acc to name

of scientist)

NOMANCLATURE SYSTEM

The organic compounds are generally named in three systems :

- 1. Trivial name System (Common names)
- 2. Derived names system
- 3. IUPAC name system

Source

(Acc to source

from which they

TRIVIAL NAME SYSTEM

Based on their Property Acc (to their property)

were prepared) CH_{4} – Marshgas, **Oxalic acid** – oxalus Glucose RMgX Pentane Grignard's reagent (Marshy place) Glycerol Hexane Acetic acid – acetum, Urea – urine Glycol R,Zn Octane (vinegar) (Glycus = sweet)Frankland's reagent Formic acid – formica, Uric acid – urine (Red ants) Malic acid – pyrusmallus, Citric acid – citrus Note: Ethylene glycol is poisonons in nature.

Methyl alcohol – wood spirit

Common names of Saturated

Hydrocarbons : $-(C_nH_{2n+2})$

(1) According to trivial or common name system of nomenclature, unbranched alkanes are named according to the number of carbon atoms.

Alk - means number of carbon atoms.

- (2) As first three members of alkanes have no isomers, so their common names and IUPAC names are same. Chain isomerism starts from butane. All isomeric paraffines have same parent name. They are distinguished by the use of prefixes such as - n, iso, neo etc.
 - (a) **Prefix n :** It is used for unbranched and normal alkanes.
 - **Ex.** $CH_3 CH_2 CH_2 CH_3$ n butane $CH_3 - CH_2 - CH_3$ Propane [n is not used because it has no isomers]

(b) **Prefix iso :** It is used when one methyl group is attached to the second or second last C-atom of the continuous chain.

Ex.
$$CH_3 \rightarrow CH_3 \rightarrow CH_$$

Iso butane (consists 3° carbon)

(c) **Prefix neo :** When two methyl groups are attached to the second or second last C-atom of the continuous chain -

Ex.
$$CH_3 - C - CH_3$$

 $CH_3 - C - CH_3$
 CH_3

Neo - pentane (consists 4° C-atom)

Structure

(Acc to no

of carbon)

Note : Prefixes sec., tert. are not used in (b) Compounds Containing Carbon - Carbon triple hydrocarbons.

Exceptions

$$CH_{3} CH - CH_{3}$$
 Isopropyl

:

$$CH_3 = CH_3 CH_3$$

 $CH_3 = CH = CH_2 = CH_3 CH_3$ Isooctane

$$CH_{3} CH_{3} CH_{3}$$

$$CH_{3} - CH - CH - CH_{3}$$

$$CH_{3} CH_{3}$$
Isoheptane(Triptane)

Unsaturated Hydrocarbons :

(a) Compounds Containing Carbon - Carbon double bond:

These are called alkylene or olifins (General formula $C_n H_{2n}$), because their halogen derivatives are used for the manufacture of oil. (Olium - oil, fiant - making) Ethvlene

Ex.
$$CH_2 = CH_2$$
 Ethylene
 $CH_3 - CH = CH_2$ Propylene
 $CH_3 - CH_2 - CH = CH_2$ α -Butylene
 $CH_3 - CH = CH - CH_3$ β -Butylene
 $CH_3 - C = CH_2$
 $CH_3 - C = CH_2$
 CH_3 Isobutylene

Saturated Hydrocarbon Radical :

Ex. Alkane -HAlkyl (monovalent radical) -H Bivalent radical -H Trivalent radical **MonovalentRedicals:** Priority order: n, iso, neo > Sec., tert. > Active $C_2H_6 \rightarrow -C_2H_5$ Ethyl $CH_4 \rightarrow -CH_3$ Methyl \rightarrow (i) CH₃-CH₂-CH₂- $CH_3 - CH_2 - CH_3$ n-proppyl Propane \rightarrow (ii) CH₃-CH-CH₃ Iso-proppyl

bond : General Formula is $C_n H_{2n-2}$

There names are derived by replacing H-atoms of acetylene by alkyl group.

Ex.
$$CH \equiv CH$$
 Acetylene
 $CH_3 - C \equiv CH$ Methyl acetylene or Allylene
(as it is isomer of Allene
 $CH_2 = C = CH_2$)
 $CH_3 - C \equiv C - CH_3$ Dimethyl acetylene
or crotonylene

(1) Common Name of Hydrocarbon Derivatives :

Ex.
$$R - H \xrightarrow{-H} X$$

 $R - H \xrightarrow{-H} X$
Hydrocarbon Functional group
group or radical

(A) Common names of organic compounds depends on the basis of hydrocarbon radical.

Functional group	Prefix
-OH	Alcohol
$-NH_2$	Amine
-0-	Ether
—S—	Thio ether
—X	Halide
-CN	Cyanide
-N C	Iso cyanide
-CO-	Ketone



While writing IUPAC names of hydrocarbon radicals, numbering of C-atom is started from free bond-Catom.

Ex.
$$CH_3 - CH_2 - CH - CH_3$$

1 — methyl propyl

Polymethylene

Alkylidene From same carbon atom -From vicinal carbon atom -Alkylene

From terminal carbon atom -

Ex. $\begin{array}{c} CH_2 - CH_2 - CH_2 \\ | \\ C | \\ C | \\ C | \\ \end{array}$ Trimethylenedichloride

Trivalent:

Alkane $_-3H$, Trivalent (Alkylidyne)

Bivalent radicals -

Ex. $CH_4 \longrightarrow CH_2$ Methylidene (Methylene) $CH_3 \longrightarrow CH_3 \longrightarrow$ $CH_3 \longrightarrow CH_2 \longrightarrow CH_3 \longrightarrow$ (i) CH_3 — CH_2 —CH < Propylidene(ii) CH_3 — C_1 — CH_3 Iso-propylidene $CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - CH_3 - CH_2$ Propylene $CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2}$ Ethylene

Un

Unsaturated Hydrocarbon Radicals -
(a) Alkene
$$\xrightarrow{-H}$$
 Alkenyl
Ex. $CH_2 = CH_2 \longrightarrow CH_2 = CH -$
 $Ethenyl (vinyl)$
 $CH_3 - CH = CH_2 \longrightarrow$
(1) $CH_3 - CH = CH -$
(2) $CH_3 - \stackrel{1}{C} = CH_2$ Iso propenyl or
1-methyl ethenyl

 $(3) - CH_2 - CH = CH_2$ 2-Propenyl (Allyl)

(b) Alkyne $_-H_{\rightarrow}$ Alkynyl

Ex.

$$CH \equiv CH \longrightarrow CH \equiv C - Ethynyl$$

$$CH_{3}-C \equiv CH \longrightarrow CH_{3}-C \equiv C - 1 - Propynyl$$

$$-CH_{2}-C \equiv CH 2 - Propynyl (Propargyl)$$

Bivalent radical of ethylene :-

$$CH_{2} = CH_{2} \longrightarrow$$
(i) $CH_{2} = C \lt$ vinylidene radical
(ii) $\stackrel{i}{C}H = \stackrel{i}{C}H$ Acetylene radical
Trivalent radicals :-
 $CH_{3} \longrightarrow CH_{3}C \lt$ Ethylidyne

Aromatic Hydrocarbon Radical -



(B) Common names of Hydrocarbon derivatives.

Which don't depend on hydrocarbon radical

 $Prefix \rightarrow Number of carbon atoms$

Suffix \rightarrow Functional group

No. of Carbon	Prefix
atoms	
1	Form
2	Acet
3	Propion
4	Butyr
5	Valer

Note : Three Carbon with one double bond \rightarrow

 $\operatorname{Acryl}\left[C=C-C\right]$

Four carbon with one double bond \rightarrow

 $\operatorname{croton}\left[\mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{C}\right]$

Functional Group	Suffix
—СНО	aldehyde
—СООН	ic acid
—COOR	alkyl ate
CO CO ≻O	ic anhydride
-COCI	yl chloride
$-CONH_2$	amide
—CN	onitrile
-N C	oisonitrile

Functional group	Structure	Common name
—СНО	НСНО	Formaldehyde (Form –1C atom)
	CH ₃ CHO	Acetaldehyde (acet-2C atom)
	CH ₃ CH ₂ CHO	Propionaldehyde
	CH ₃ CH ₂ CH ₂ CHO	n - butyraldehyde
	CH ₃ CH ₃ -CH-CHO	Iso - butyraldehyde
	$CH_2 = CH - CHO$	Acrylaldehyde
	$CH_3 - CH = CH - CHO$	Crotonaldehyde
—СООН	$CH_3 - CH_2 - COOH$	Propionic acid
	$CH_2 = CH - COOH$	Acrylic acid
	CH_3 $H_3 - CH - CH_2COOH$	Isovaleric acid
—COOR	HCOOCH ₃	Methyl formate
	$CH_3 - CH - O - C - CH_3$ CH_3	Iso propyl acetate
	$CH_2 = CHCOO C_2H_5$	Ethyl acrylate
-co>o	CH ₃ -CO CH ₃ -CO	Acetic anhydride
	$CH_3 - CO CO CH_3CH_2 - CO O$	Acetic Propionic anhydride

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-COCI	CH ₃ CH ₂ COCl	Propionyl chloride
	HCOC1	Formyl chloride
-CONH ₂	HCONH ₂	Formamide
	CH ₃ CH ₂ CONH ₂	Propionamide
—CN	HCN	Formonitrile or Hydrogen cyanide
	CH ₃ CN	Acetonitrile or Methyl cyanide
—N≡C	$CH_3 - N \equiv C$	Acetoisonitrile
	$CH_3 - CH - N \equiv C$ $ CH_3$	Isobutyroisonitrile or Isopropylisocyanide

- Note.(1) If suffix isocyanide is used then carbon atom of -NC not counted.
 - (2) If suffix carbyl amine is used then Carbon atom of -NC not counted.
 - (3) If oisonitrile is used then Carbon atom of -NC counted.
- (2) **Derived Names :** In a homologous series the homologues are considered to be the derivative of the first homologue.

Exceptions - aldehydes and acids (second member)

$$\begin{array}{c} (H) \\ (H) - C - (H) \\ (H) \end{array} \qquad CH_3 - C - H \\ (H) \\ (H$$

Methane

Methyl methane

$$CH_3 - CH_3 - CH_3$$

Dimethyl methane

first homologue of alkane series encircled H atom will be replaced by any substituents/functional group Similarly : $CH_2 = CH_2 \rightarrow Ethylene$ is the first homolgue of the alkylene series.

Names derived from ethylene are -

 CH_3 -CH= CH_2 \rightarrow Methyl ethylene

 CH_3 -CH- CH_3 \rightarrow

Symm. dimethyl ethylene

$$\begin{array}{c} CH_{3}-C=CH_{2} \\ | \\ CH_{3} \end{array} \rightarrow$$

Unsym. dimethyl ethylene

 $CH_3 - CH_2 - CH = CH_2 \rightarrow$

Ethyl ethylene

 $CH \equiv CH \text{ (First homologue of alkyne series)} \rightarrow Acetylene$

$$CH_3 - C \equiv CH \rightarrow$$

Methyl acetylene or Allylene

 $CH_3 - C \equiv C - CH_3 \rightarrow$ Dimethyl acetylene or crotonylene

CH₃OH

Carbinol (First member of alcoholic series)

 $\begin{array}{cccc} CH_{3}-CH_{2}-OH \rightarrow & \text{Methyl carbinol} \\ CH_{3}-CH-OH & & \\ & CH_{3}-CH-OH & \\ & CH_{3}-CH-CH_{2}OH & \\ & CH_{3}-CH-CH_{2}OH & \\ & CH_{3}-CH_{2}CHO & \rightarrow & \text{Iso propyl carbinol} \\ \end{array}$ $\begin{array}{cccc} CH_{3}-CH_{2}CHO \rightarrow & \text{Methyl acetaldehyde} \\ CH_{3}-CH_{2}CHO \rightarrow & \text{Methyl acetaldehyde} \\ CH_{3}-CH-CHO \rightarrow & \text{Dimethyl acetaldehyde} \\ & CH_{3}-CH-CHO \rightarrow & \text{Dimethyl acetaldehyde} \\ \end{array}$

Organic Chemistry – Some Basic Principles and Techniques 2. Primary Suffix. A primary suffix is always added

IUPAC SYSTEM OF NOMENCLATURE

The basic criteria for naming a structure by IUPAC system is choice of a parent name or the basic carbon skeleton.

Nomenclature of alkanes is fundamental to naming whole class of organic compounds because it helps us to identify the basic carbon skeleton.

General rules for IUPAC nomenclature

The IUPAC system is the most rational and widely used system of nomenclature in organic chemistry. The most important feature of this system is that any given molecular structure has only one IUPAC name and any given IUPAC name denotes only one molecular structure.

The IUPAC name of any organic compound consists of five parts, i.e.,

- 1. Word root
- 2. Primary suffix
- 3. Secondary suffix
- 4. Primary prefix
- 5. Secondary prefix

Thus, a complete IUPAC name of an organic compound consists of the following parts :

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

1. Word root : It is the basic unit of the name. It denotes the number of carbon atoms present in the principal chain (the longest possible continuous chain of carbon atoms including the functional group and based upon the common names of alkanes) of the organic molecules.

Chain	Word root	Chain	Word root
length		length	
C ₁	Meth-	C ₇	Hept(a)-
C_2	Eth-	C ₈	Oct(a)-
C ₃	Prop(a)-	C9	Non(a)-
C_4	But(a)-	C ₁₀	Dec(a)-
C ₅	Pent(a)-	C ₁₁	Undec(a)-
C ₆	Hex(a)-	C ₁₂	Dodec(a)-

Primary Suffix. A primary suffix is always added to the word root to indicate whether the carbon chain is saturated or unsaturated. The three basic primary suffixes are given below :

Type of carbon chain	Primary suffix	General name
(a) Saturated	– ane	Alkane
(b) Unsaturated with one double bond	– ene	Alkene
(c) Unsaturated with one triple bond	– yne	Alkyne

If the parent carbon chain contains two, three or more double or triple bonds, numerical prefix such as di (for two), tri (for three), tetra (for four) etc. are added to the primary suffix. For example,

Type of carbon chain	Primary	General
	suffix	name
(a) Unsaturated with two double bonds	- diene	Alkadiene
(b) Unsaturated with two triple bonds	- diyne	Alkadiyne

3. Secondary suffix. A secondary suffix is then added to the primary suffix to indicate the nature of the functional group present in the organic compounds. Secondary suffix of some important functional groups are given below :

Class of organic compounds	Functional group	Secondary suffix
Alcohols	– OH	- ol
Aldehydes	– CHO	– al
Ketones	> C = O	- one
Carboxylic acids	– COOH	– oic acid
Acid amides	$-CONH_2$	– amide
Acid halide	– COX	– oyl halide
Esters	- COOR	alkanoate
Nitriles	- CN	- nitrile
Thioalcohols	– SH	- thiol
Amines	$-NH_2$	- amine

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming of organic compounds.

Organic compounds	Word root	Primary suffix	Secondary suffix	IUPAC name
CH₃CH₂OH	Eth	an(e)	ol	Ethanol
CH ₃ CH ₂ CH ₂ NH ₂	Prop	an(e)	amine	Propanamine
CH ₃ CH ₂ CH ₂ COOH	But	an(e)	oic acid	Butanoic acid
CH ₃ CH ₂ CN	Prop	an(e)	nitrile	Propanenitrile
CH ₂ = CHCHO	Prop	en(e)	al	Propenal
HC≡CCOOH	Prop	yn(e)	oic acid	Propynoic acid

4. Primary prefix. A primary prefix is used simply to distinguish cyclic from acyclic compounds.

For example, in case of carbocyclic compounds, (cyclic compounds containing only carbon atoms in the ring), a primary prefix, **cyclo** is used immediately before the word root. Thus.



If the prefix cyclo is not used, it simply indicates that the compound is acyclic or open chain.

5. Secondary prefix. In IUPAC system of nomenclature, certain groups are not considred as functional groups but are treated as substituents. These are called secondary prefixes and are added immediately before the word root (or the primary prefix in case of carbocyclic compounds) in alphabetical order to denote the side chains or substituent groups. The secondary prefixes for some groups which are always treated as substituent groups (regardless of the fact whether the organic compound is monofunctional or polyfunctional) are given below :

Substituent group	Secondary prefix	Substituent group	Secondary prefix
- F	Fluoro	$-OCH_3$ ($-OMe$)	Methoxy
- Cl	Chloro	$-OC_2H_5(-OEt)$	Ethoxy
– Br	Bromo	- R	Alkyl
- I	Iodo	- CH ₃ (- Me)	Methyl
$-NO_2$	Nitro	$-C_{2}H_{5}(-Et)$	Ethyl
– NO	Nitroso	- CH ₂ CH ₂ CH ₃ (n-Pr	n-Propyl
$-\overset{\oplus}{N}=N$	Diazo	$-CH(CH_3)_2(-iPr)$	Isopropyl
-OR	Alkoxy	$-C(CH_3)_3$ (t-But)	t-Butyl

Organic compounds	Secondary prefix	Word root	Primary suffix	IUPAC name
$CH_3CH_2 - Br$	Bromo	eth	ane	Bromoethane
$CH_3 - NO_2$	Nitro	meth	ane	Nitromethane
$C_2H_5 - OC_2H_5$	Ethoxy	eth	ane	Ethoxyethane

In case of carbocylic compounds, primary prefixes are also used.



Solved Examples

Ex.3 Write IUPAC name of following compound



Sol.



2-Iodo-3-methylcyclopentanesulfonic acid.

Here Secondary prefix

	=2-	Iodo – 3 – methyl
Primary prefix	=	cyclo
Word root	=	pent
Primary suffix	=	ane
Secondary suffix	=	sulfonic acid

Ex.4 Write the IUPAC name of following compound



Sol. 2–Isopropyl–5–methylcyclohexanol Here Secondary prefix

= 2 - Isopropyl - 5 - methyl

- Primary prefix = cyclo
- Word root = hex

Primary suffix = an(e)

Secondary suffix = ol

IUPAC Nomenclature of

Organic Chemistry – Some Basic Principles and Techniques

Branched / Complex Alkanes

(1) (a) Select the longest chain of carbon atoms in the molecule.

(b) Count the number of carbon atoms in that chain and name according to the following rules.

e.g.
$$CH_3$$

 CH_2
 $e.g. CH_3 = \begin{pmatrix} \dot{C} \\ - \\ \dot{C} \\ -$

Longest chain has 7 carbons.

 $\therefore It is a \frac{hept}{word root} + \frac{ane}{primary suffix}$

When chains of equal lengths are competing for selection, that chain is selected which has more number of substituents.

$$CH_{3} - H_{2}C + CH - CH_{3} - CH_{3}$$

$$CH_{3} - H_{2}C + CH_{2} - CH_{3} - CH_{3}$$

$$CH_{2} - CH_{2} - CH_{3} - CH_{3}$$

Here the chain shown is selected.

(2) Carbon atoms in the longest chain selected as above is numbered consecutively from one end to the other such that the substituents attached get the lowest number.

In the above example, according to this rule, the numbering will be done as :

$$CH_3$$

 $CH_3 - H_2C - CH_2 - CH_3$
 $CH_3 - CH_2 - CH_3$
 $CH_2 - CH_2 - CH_3$
 $CH_2 - CH_2 - CH_3$

By this numbering, locant (substituents) get the number 2, 3 and 4 compared to 4, 5 and 6 if numbering is done from other end.

(3) Each substituent, which, obviously, is an alkyl group is named according to number of carbon atoms present in it and it is prefixed by the number to which it is located in the main chain.

In the above example, substituents are as follow :

- \Rightarrow 2-methyl
 - $-C_2H_5$ (ethyl) group at carbon no. 3
- \Rightarrow 3-ethyl

 $-CH_2CH_2CH_3 (propyl) \text{ group at carbon no. 4}$ $\Rightarrow 4-propyl$

Hence, the above compound is named as :

3-Ethyl-2-methyl-4-propylheptane

(4) If the same substituent occurs more than once in the molecule, the prefix di (for two), tri (for three), etc. are used to indicate how many times it appears.

The above example can be written with a little modification as :

$$CH_{3}CH_{3}$$

$$CH_{3} - H_{2}C - \overset{I}{C} - \overset{I}{C}H - \overset{L}{C}H_{3}$$

$$e.g.$$

$$CH_{3} - H_{2}C - \overset{I}{C}H - \overset{L}{C}H_{2} - \overset{L}{C}H_{2} - \overset{L}{C}H_{2} - \overset{L}{C}H_{2} - \overset{L}{C}H_{2} - \overset{L}{C}H_{3}$$

Methyl at No. 2,3, Ethyl at no. 3, Propyl at no. 4 This will be named as :

3-Ethyl-2,3-dimethyl-4-propylheptane

(5) The name of the compound is composed in such a manner that each substituent with its number and name is written alphabetically just before the word root. Prefixes di, tri, tetra etc. are not considered in deciding alphabetical order.

 \therefore Ethyl will be written before methyl which will be written before propyl.

Note that in the above examples, this pattern has been compiled with.

* Also, as per convention,

(1) numbers are separated each other by commas(,).

(2) numbers are separated from words by hyphens and

(3) write the name of the compound as a single word (with no space between)

$$\begin{array}{c} H_{s}^{1}C - H_{C}^{2} - H_{C}^{3} - H_{C}^{4} - H_{z}^{5} - C_{H_{s}}^{6} \\ H_{s}^{1}C - H_{c}^{2} - H_{c}^{2} \\ C H_{s}^{1} - H_{z}^{1} \\ C H_{s}^{2} - C H_{s}^{3} \\ H_{c}^{1} \\ C H_{s}^{3} \end{array}$$

- 1. Primary suffix is ane as all are single bonds
- 2. Chain is numbered as shown
- 3. Root word is hex
- 4. Prefixes methyl appears twice

$$\therefore$$
 it is 2, 4-dimethyl and 3 - ethyl

- 5. While arranging in alphabetical order Replicators di, tri, tetra are not considered.
 - \therefore 3 Ethyl–2, 4–dimethylhexane

Solved Examples

Ex. 5 Write the IUPAC name of following compounds

(i)
$$\dot{C}H_3 - \dot{C}H_2 - \dot{C}H - \dot{C}H_3$$

 $\dot{C}H_3 - \dot{C}H_3 - \dot{C}H_3$
 $\dot{C}H_3 - \dot{C}H_3$

$$\dot{C}H_{3} - \dot{C}H_{2} - \dot{C}H_{3} \overset{1}{C}H - CH_{3} \overset{2}{C}H - CH_{3} \overset{3}{C}H_{2}$$

Ex.6 Write IUPAC name of the following compounds:-

(a)
$$CH_3 - CH_2 - CH_1 - CH_2 - CH_2 - CH_2 - CH_3$$

 $CH_3 \qquad CH_2 - CH_3$

(b)
$$CH_3 - CH_2 - CH_3$$

 $H_3 - CH_2 - CH_2 - CH_2 - CH_3$
 $CH_3 - CH_2 - CH_2 - CH_3$

Ans.(a) 5-Ethyl-3-methyloctane

(b) 4-Ethyl-2,2,6-trimethylheptane

(c) 3-Methylhexane

Organic Chemistry – Some Basic Principles and Techniques Solved Examples

IUPAC Nomenclature of Alkenes Functional group : -C=C-

 Select the longest chain containing carbon–carbon double bond. This need not be the longest chain in the compound as a whole. Parent name will be alkene corresponding to number of carbon atoms in the longest chain.

e.g.
$$CH_{3}CH_{2} + C - CH = CH_{2}$$

 $CH_{2} + C - CH = CH_{2}$
 $CH_{2} + C - CH = CH_{2}$
 $CH_{2} + C + CH_{2}$
 $CH_{3} + C + CH_{2}$

Longest chain is as shown above. It has 6 atoms \Rightarrow hexene = parent name

- (2) Carbon atoms in the longest chain is numbered so that doubly bonded carbon atom gets the lowest number. The position of double bond is indicated by the smaller of the numbers assigned to two carbon atoms of double bond.
 - \therefore The above example can be rewritten as,

$$CH_{3}CH_{2} - CH_{3}^{2} - CH_{2}^{3} - CH_{2}^{1} = CH_{2}^{1}$$

$$4CH_{2}^{1}$$

$$5CH_{2}^{1}$$

$$6CH_{3}^{1}$$

Position of double bond will be indicated as no. 1.

Hence, name will be,

3-Ethyl-3-methylhex-1-ene

e.g.

$$\overset{\mathsf{C}\mathsf{H}_3}{\overset{\mathsf{d}}{\mathsf{C}}\mathsf{H}_3} - \overset{\mathsf{C}\mathsf{H}_3}{\overset{\mathsf{d}}{\mathsf{C}}} - \overset{\mathsf{C}\mathsf{H}_3}{\overset{\mathsf{C}\mathsf{C}}{\mathsf{H}}} = \overset{\mathsf{C}\mathsf{H}}{\overset{\mathsf{C}\mathsf{C}}{\mathsf{H}}} - \overset{\mathsf{C}\mathsf{H}_3}{\overset{\mathsf{C}\mathsf{H}_3}{\mathsf{C}}}$$

2, 2, 5, 5-Tetramethylhex-3-ene

Ex.-7 Write the IUPAC name of the following compounds:-

(a)
$$CH_3 - CH_2 - CH_3 - CH = CH - CH_2 - CH_3$$

Ans. (a) 5-Methylhept-3-ene

(b) 5-Ethyl-2,6-dimethyl-4-(3-methylbutyl)

oct-2-ene

- **Ex.8** Draw the bond line structures of the following compounds.
 - (a) 2-Methylhept-3-ene
 - (b) 2, 6–Dimethylhepta–1, 5–diene



IUPAC Nomenclature of alkynes

 $(-C \equiv C - group)$

Numbering of longest chain is exactly same as that for naming alkenes.

e.g.
$$\begin{array}{l} CH_{3}C \equiv C - CH_{3} \\ But - 2 \text{-yne} \end{array}$$
$$\dot{C}H_{3} - \dot{C}H_{3} - \dot{C}H_{2} - \dot{C} \equiv \dot{C}H \\ CH_{3} \end{array}$$

4,4-Dimethylpent-1-yne

Solved Examples

Ex.9 Write the IUPAC name of the following compounds:-

(a)
$$CH_3 - CH_3 - C = C - CH_3$$



Ans. (a) 4-Methylpent-2-yne

(b) 4-Propylhept-2-yne

- **Ex.10** Write the IUPAC name of the following compounds:-
 - (a) $CH_3 C \equiv CCH(CH_3)_2$

(b)
$$H_3C - CH_2 - CH_2 - CH - CH - C = CH$$

 CH_3CH_3

Sol. (a) 4-Methyl-pent-2yne

(b) 3,4,4-Trimethylhex-1-yne

IUPAC nomenclature of hydrocarbons containing both double and triple bonds occuring only once

(i) Such hydrocarbon is named as alkenyne (not alkynene).

(ii) Numbering is done in a manner that double and triple bonds get the lowest possible number. If double bond and triple bond both have same number then double bond is given preference our triple bond.

$$HC \equiv C - CH, - CH = CH,$$

2

(wrong) 2 3 5

(numbering is done from alkyne)

1

(numbering is done from alkene)

Solved Examples

Ex.11 Write IUPAC name of the following compounds.

(a)
$$CH_3 - CH_2 - C \equiv C - CH - CH = CH_2$$

 CH_2
 CH_2
 $CH - CH_3$
 CH_3



Ans. (a) 3-(2-Methyl propyl)hept-1-en-4-yne (b) Oct-1-en-4-yne

Ex.12 Write IUPAC name of the following compounds.

(a)
$$HC \equiv CCH_2CH = CH_2$$



Ans. (a) Pent-1-en-4-yne

(b) Hepta-3,6-dien-1-yne

IUPAC Nomenclature of Alicyclic

Compounds





2. The numbering of the carbon atoms in the ring is done in such a way that the substituent which comes first in the alphabetical order is given the lowest possible number and it does not violate the lowest set of locants rule.

e.g.





1 - Ethyl - 3 - methylcyclohexane

2 - Ethyl - 1, 4 - dimethylcyclohexane



- 3 Ethyl 1, 1 dimethylcyclohexane
- 2 Bromo 1 chloro-3-iodocyclohexane

(3) When the ring contains more or equal number of carbon atoms than the alkyl group attached to it, then it is named as a derivative of cycloalkane and the alkyl group is treated as substituent



Propylcyclopropane



1, 3, 5 Trihexylcyclohexane



Cyclohexylcyclohexane

(4) The alkane chain contains greater number of carbon atoms than present in the ring, the compound is considered as the derivative of alkane and the ring is designated as substituent.

e.g. 2-Cyclopropylbutane $\mathsf{CH}_{\scriptscriptstyle 3}-\mathsf{CH}_{\scriptscriptstyle 2}-\mathsf{CH}-\mathsf{CH}_{\scriptscriptstyle 2}-\mathsf{CH}_{\scriptscriptstyle 2}-\mathsf{CH}_{\scriptscriptstyle 3}$

3-Cyclopentylhexane

(5) If ring has unsaturation and side chain is saturated then ring is selected as parent chain.

If side chain has unsaturation and ring is saturated then side chain is selected as parent chain.

If both have unsaturation the chain with maximum unsaturation has selected as parent chain.

If equal unsaturation then longest chain is selected as parent chain.

If unsaturation and number of carbon atoms both are equal then ring is selected as parent chain.





1 - Ethylcyclohex - 1 - ene



6-Ethyl-3, 3-dimethylcyclohex-1-ene



Methylenecyclohexane



3 - Cyclopropylprop - 1 - ene



1-(Hex-3-envl)cyclohex-1-ene

(6) If more than one alicyclic ring is attached to a single chain, the compound is named as a derivative of alkane and the ring is treated as a substituent group.

e.g.
$$CH_2$$

Dicyclopropylmethane



1 - Cyclohexyl - 4 - cyclopropylbutane

(7) If a multiple bond and some other substitutents are present in the ring, the numbering is done in such a way that the multiple bond gets the lowest number



3 – Nitrocyclohex – 1 – ene

(8) If a compound contains an alicyclic ring directly linked to the benzene ring. It is named as a derivative of benzene.

e.g.

e.g.



Cyclohexylbenzene



1-(2-Methylcyclohexyl)-4-nitrobenzene

(9) If functional group is present in cyclic compounds than the main chain is taken in which principal functional lie's, if the principal functional group is present in ring also then main chain will be taken for the maximum no. of carbon atoms.



1-Cyclohexylpropan-2-ol

(10) When chain terminating functional group is directly attached with ring then ring is taken as parent chain & special suffix used for functional group.

Functional Group	Suffix
СНО	Carbaldehyde
соон	Carboxylic Acid
сох	Carbonyl halide
COOR	Alkyl Carboxylate
CONH ₂	Carboxamide
CN	Carbonitrile



Cyclohexanecarbonitrile



Cyclohexanecarbaldehyde

Ethyl (2-oxo)cyclohexane - 1 - carboxylate

Solved Examples

Ex.13 Write the IUPAC name of following compound







4 - Cyclohexylbut - 3 - en - 2-one



1,5-Dimethylcyclopent-1-ene

Ex.14 The correct IUPAC name of following compound is



Sol. 2 - (2 - hydroxybutyl) cyclohexan - 1 - ol



1. Rules for non chain terminating functional groups

(1) **Parent chian :** Select the longest possible chain with maximum functional group and maximum unsaturation without caring whether it also denotes the longest possible chain or not.

e.g.
$$\overset{4}{\mathsf{CH}_3} - \overset{3}{\mathsf{CH}_2} - \overset{2}{\mathsf{CH}} - \mathsf{CH}_2 - \mathsf{CH}_3$$
$$\overset{1}{\overset{1}{\mathsf{CH}_2\mathsf{OH}}}$$

(Parent chain contains four rather than five carbon atoms)

(2) Lowest number for the functional group

Numbering is done from that side of the chain which gives lowest locant to the principle functional group followed by double and triple bonds.

e.g.
$$\begin{array}{c} & O \\ & 3 \\ CH_3 - CH - CH_2 - C - CH_2 - CH_3 \\ & CH_3 \\ & CH_3 \end{array}$$
(I) correct

(C = Ogroup gets number 4 which is not lowest)

2 Rules for chain terminating functional groups

(1) When a chain terminating functional group such as $-CHO, -COOH, -COOR, -CONH_2, -COCI, -C \equiv N$ etc. is present, it is always given number 1 (one.)

$$\overset{4}{C}H_{3} - \overset{3}{C}H_{2} - \overset{2}{C}H - CH_{3}$$

$$\overset{1}{1}\overset{1}{C}OOH$$

e.g.

2-Methylbutan-1-oic acid

$$CH_{3} - C_{4} \equiv C_{3} - CH_{2} - C_{1} - H_{2}$$
Pent-3-yn-1-al

(2) If a compound contains two or more like groups, the numerical prefixes di, tri, tetra etc. are used

e.g.
$$\begin{array}{c} CH_2 - CH - CH_2 \\ | & | & | \\ OH & OH & OH \\ Propane - 1,2,3 - triol \\ CH_3 - C - CH_2 - C - CH_3 \\ || & || \\ O & O \end{array}$$

(3) The name for benzene as substituent is phenyl. In case the phenyl ring is further substitued, the carbon atoms of the ring directly attached to the parent chain in such a ways that the substituent on the ring gets the least possible number. For example



1,1,1-Trichloro-2,2-diphenylethane



Ethyl- 2-methyl-2-(3-nitrophenyl) propanoate

(4) If the organic molecule contain more than one similar complexes substitutents, then the numerical prefixes such as di, tri, tetra etc. are replaced by bis, tris, tetrakis etc. respectively.

e.g.
$$HO - CH_2 - CH_2 - O$$
$$CH - COOH$$
$$HO - CH_2 - CH_2 - O$$

2, 2-Bis (2-hydroxyethoxy) ethanoic acid

Solved Examples

Ex.15 Write IUPAC Name

(a)

$$CH_{3}CH_{2} - CH - C - OCH_{3}$$

$$CH_{2} - CH_{2} - CH_{3}$$
(b) $(CH_{3})_{3}COH$
(c) $CH_{3} - CH - CH_{2} - COOH$

$$CH_{3} - CH - CH_{2} - COOH$$
(b) 2-Methylpropan-2-ol

(c) 3-Methylbutanoic acid

3 Rules for IUPAC nomenclature of polyfunctional compounds :

(1) When an organic compound contains two or more different functional groups than senior functional group is selected as the principal functional group while other groups are treated as substituents.

(2) Some functional group such as all halo groups (fluoro, bromo, chloro, iodo), nitroso (NO) nitro (– NO_2) and alkoxy (–OR) are always treated as substituent groups.

$$\mathbf{e.g.} \quad \begin{array}{c} \mathsf{NH}_2 \\ \mathbf{4} \\ \mathsf{CH}_3 \\ \mathsf{$$

4-Amino-3-chloropentan-2-ol $(-NH_2 \& -CI group treat as substituent)$

Numbering the principal chain order is

[Principal functional group > double bond > triple bond > substituents]

e.g.
$$CH_3 - C - CH_2 - COOH$$

 \parallel
O
3 Overhuten 1 eie asid

3-Oxobutan-1-oic acid

$$\begin{array}{c} O\\ 5\\ CH_3 - C - CH_2 - CH_2 - CH_2 - CHO\\ 4-Oxopentan-1-al \end{array}$$

$$[-COOH > -CO]$$

$$O = \stackrel{6}{C}H - \stackrel{5}{C}H_2 - \stackrel{4}{C}H_2 - \stackrel{3}{C} - \stackrel{2}{C}H_2 - \stackrel{1}{C}OOH$$

3, 6-Dioxohexanoic acid or 5-Formyl-3-oxopentanoic acid

(3) The longest possible chain of carbon atoms containing the functional group and the maximum number of multiple bonds is selected as parent chain.

e.g. (a)
$${}^{4}_{C}H_{3} - {}^{3}_{C}H_{2} - {}^{2}_{C}H - CH_{2} - CH_{3}$$

 $| \\ I_{1}H_{2}OH$

parent chain contains four rather than five carbon atoms.

(b)
$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{1}-O-C_{2}H_{5}$$
$$CH_{3}-CH_{2}-CH_$$

parent chain contains five rather than six carbon atoms

(c)
$$\begin{array}{c} CH_{3} - CH_{2} - C$$

Ethyl 3-methylpent-4-en-1-oate

$$(d) \begin{array}{c} & O \\ & CH_3 & 1 \\ & I \\ & I \\ & CH_3 - C \\ & CH_3 - C \\ & CH_3 - C \\ & CH_3 \\ & CH_3 \\ & CH_3 \\ & CH_3 \end{array} (CH_3 - CH_3 \\ CH_3 \\ & CH_3 \\ & CH_3 \end{array} (CH_3 - CH_3 \\ CH_3 \\ & CH$$

3,3 Dimethyl -2 - (1 - methylethyl) butanamide

(4) If more than one same chain terminating group are present then the principal chain is selected including the functional groups and numbring is done from that side which gives lowest locant to unsaturation substituent

e.g (a)
$$HOOC - CH_2 - CH_2 - COOH_1$$

Butane-1, 4-dioic acid

(b)
$$\begin{array}{c} 1 & 2 & 3 & 4 & 5 \\ NC - CH - CH - CH_2 - CH_2 - CN \\ | \\ CH_3 \\ 2 - Methylpentanedinitrile \end{array}$$

e.g. Write the IUPAC name of

$$CH_3 - CH_2 - C\ddot{H} - CH_2^4 - C\ddot{H} - CH_3$$

 $1 - 2 H_2 - CH_2 - CH_3 + 7 - 7 - CH_2 + 7 - CH_3 +$

- 1. The longest chain containing functional group is of 7 carbon atoms. Therefore, the word root is hept & the chain is numbered as shown.
- 2. There is no multiple bond in it. Hence, the primary suffix is **ane**.
- 3. The functional groups is CN. Hence, secondary suffix is **nitrile**
- 4. Moreover, there is a methyl group on carbon 5 and ethyl group on carbon 3.
- 5. The IUPAC name is, therefore,

3-Ethyl-5-methylheptanenitrile

e.g. Write the IUPAC name of

$${}^{7}_{C}H_{3} - C\overset{6}{H}_{2} - C\overset{5}{H}_{-}CH^{4}_{-}CH^{3}_{-}CH^{2}_{2} - CHO^{1}$$

- 1. The longest chain containing functional group is of **seven** carbon atoms. Therefore, word root is hept.
- 2. As C = C double bond is present in the molecule. Thus, the primary suffix is **ene**.
- 3. The secondary suffix is **al** because the presence of CHO group.
- 4. The chain is numbered as shown so that carbon atom of CHO groups gets number 1.

The methyl group is present on carbon 5 while position of double bond is 3. Thus, IUPAC name is

5-Methylhept-3-en-1-al.

e.g. Write the IUPAC name of

$$\begin{array}{c|ccccc} & \mathsf{NH}_2 & & & & & & 1\\ \mathsf{11} & & & \mathsf{9} & & & & 3 & & 2 & 1\\ \mathsf{CH}_3 - & \mathsf{CH} - & \mathsf{CH}_2 & \mathsf{CH}_3 & \mathsf{CH}_2 - & \mathsf{CH} - & \mathsf{CH}_3 \\ & & & & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & & & \\ \mathsf{10} & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & \\ \mathsf{10} & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10} & & & & & \\ \mathsf{10}$$

- Primary suffix is ene, due to presence of double bond between C₄ & C₅
- 2. Senior functional group is alcohol hence secondary suffix is **-ol**
- 3. Root word is undec
- 4. Chain is numbered as shown
- 5. 6-nitro-7-methyl-8-Bromo-10-amino are prefixes. Arrange them in alphabaetical order & give the name.

10 – Amino– 8 – bromo – 7 – methyl – 6 – nitroundec – 4 – en – 2 – ol

Ex.16 Write IUPAC Name

(a)
$$CH_3 - C - CH_2 - CH_2 - C - OH$$

(c)

$$CH_2 - CH = CH - CH_2 - CH_3$$
$$CH_3 - CH = CH - CH_2 - CH_2 - CH_2 - CH_2 - COOH$$

Ans. (a) 4-Oxopentanoic acid

- (b) Propane-1,2,3-tricarboxylic acid
- (c) 4-(But-2-enyl)non-6-enoic acid

Ex.17 Write IUPAC Name

$$\begin{array}{c} \mathsf{CH}_3 & \mathsf{O}\\ \mathsf{I}\\ \mathsf{H}\\ \mathsf{H}\\ \mathsf{H}\\ \mathsf{H}\\ \mathsf{H}\\ \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{CH}_2\mathsf{CH}_2\mathsf{CI} \end{array}$$

(b)
$$CH_3 - CH - CH_2 - CH_2 - OH$$

CI
(c) $CH_3 - OCH_2CH_2N < H$
CH₃

$$(\mathbf{d}) \operatorname{CH}_{3} - \operatorname{CH} - \operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{CH}_{3}$$
$$\overset{\mathsf{H}}{\underset{\mathsf{Br}}{\overset{\mathsf{H}}{\operatorname{H}}}} \operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{CH}_{3} - \operatorname{CH}_{3}$$

Ans. (a) 1-Chloro-5-methylhexan-2-one

- (b) 3-Chlorobutan-1-ol
- (c) N-methyl-2-Methoxyethan-1-amine
- (d) 3-Bromo-2-chloro-5-methyloctane

Nomenclature of Aromatic Compounds

The aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is the simplest hydrocarbon of aromatic series which has planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below.



(i) Nuclear Substituted –

The functional group is directly attached to the benzene ring in the IUPAC system, they are named as derivatives of benzene. The position of the substituents in disubstituted benzenes are indicated either by prefixes such as O–(ortho) for 1, 2, m–(meta) for 1, 3 and p (para) for 1, 4 position. However, many of their common names have also been adopted by the IUPAC system

(ii) Side - Chain Substituted -

The functional group is present in the side chain of the benzene ring in the IUPAC systems, these are usually named as phenyl derivatives of the corresponding aliphatic compounds.

The IUPAC and common names of a few important members of each family are given below.

(1) Aromatic hydrocarbons (arenes) hydrocarbons which contain both aliphatic and aromatic units are called arenes. These are of two types

(a) Hydrocarbon containing one ring only.

CH₃





1, 2 – Dimethyl benzene 1, 3 – Dimethyl benzene (o – Xylene) (m – Xylene)



(Styrene)







Phenylethyne

3-Phenylprop-1-yne (Propargyl benzene)

(b) Hydrocarbon containing condensed or fused ring



Naphthalene



Anthracene



(Phenanthrene)

2. Aryl Groups :



or p-Dichlorobenzene



1 - Bromo - 3 phenylpropane

1,4-Dichlorobenzene Phenyldicholoromethane (Benzyl chloride)



1 - chloro - 2 phenylethene

Organic Chemistry – Some Basic Principles and Techniques 4. Hydroxy derivaties

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

Phenols-monohydric (i)



Hydroxybenzene (phenol)

- 4-methyl phenol (p-cresol)
- Dihydric and polyhydric phenols (ii)





Benzene - 1, 2 - diol(Catechol)

Benzene - 1, 3 - diol (Resorcinol)



Benzene - 1, 4 - diol (Quinol)

(iii) Aromatic Alcohols



Phenyl methanol (Benzyl alcohol)



- Methoxy benzene (Anisol)
- Phenoxybenzene (Diphenyl ether)
- (v) Aldehydes



Benzenecarbaldehyde (Benzaldehyde)



2-Hydroxybenzenecarbaldehyde (Salicylaldehyde)



- 3-Phenylpropanal
- $(\beta phenylpropionaldehyde)$
- (vi) Ketones





Methyl phenyl ketone (Acetophenone) Diphenyl ketone (Benzophenone)

Nitrobenzene

1, 3 – Dinitrobenzene (m – Dinitrobenzene)





2, 4, 6 – Trinitrophenol

Benzene-1, 2-diamine

(T.N.P) (Picric acid)

2-Nitro toluene (O-Nitro toluene)

(viii) Amines

(a) Aryl amines





Benzenamine (Aniline)





- N, N–Dimethylbenzenamine N–Phenyl benzenamine (N, N–Dimethylaniline) (Diphenyl amine)
 - (b) Aryl alkyl amine



Phenylmethamine (Benzylamine)



2- Phenyl ethanamine $\beta-$ phenyl ethyl amine)

(ix) Arenediazonium Salts

Benzene diazonium chloride

Benzene diazonium hydrogen sulphate

(x) Cyanides and Isocyanides





Benzenecarbonitrile (Benzonitrile)

- Benzeneisonitrile (Phenyl isocyanide)
- (xi) Carboxylic Acids





Benzenecarboxylic acid

cid 2-Methylbenzene carboxylic acid (O-toluic acid)



Benzene – 1, 2 -dicarboxylic acid (Phthalic acid)

(xii) Anhydrides:



Benzenecarboxylic anhydride

(xiii) Esters :



4-Methylphenyl ethanoate

(xiv) Amides :



Benzenecarboxamide

Solved Examples

Ex.18 Write IUPAC name of following aromatic compounds



2-Methyl-3-phenylpropanal

CH₂OCH₃ **(b)**

Methoxyphenylmethane (Benzyl methyl ether)

Some Important 1993 Recommendations

of IUPAC Nomenclature of

Organic Compounds

1. Locants (numerals and / or letters) are placed immediately before the part of the name to which they relate. For example.

 $CH_3CH_2CH = CH_2$ should be named as but-1-ene CH_3CH_2OH should be named as ethan-1-ol similarly, a few more examples are given as following:



CH. _³CH = C _

2-Methylbut-2-en-1-ol

Cyclopent-2-en-1-ol

CH. 2,2-Dimethylpropan-1-ol

2. The locant 1 is often omitted when there is no ambiguity. For example.

	CH ₃ CH ₂ CHO			
Butanoic acid	Propanal			
CH ₃ CH ₂ CH ₂ CN				
Butanenitrile				

In all the above examples locant 1 for the functional group is omitted because the position of the functional group is unambiguous. However, in the following cases the position of the functional group must be mentioned.

CH₃CH₂CH₂OH CH₃CH₂CH₂NH₂ Propan-1-ol Propan-1-amine

Here, we cannot write simply propanol (or propanamine) because there are two propanols; propan-1-ol and propan-2-ol.

3. Arrangement of Prefixes

(i) Simple prefixes such as methyl, ethyl, chloro, nitro, hydroxy, etc. are arranged alphabetically.

The prefixes di, tri, etc. are however not considered for comparison.

 $\begin{array}{c}2 & 1\\CH_2CH_2\\ | & |\\CI & Br\end{array}$

1-Bromo-2-chloroethane

(ii) The name of a prefix for a substituted substituent is considered to begin with the first letter of its complete name.

e.g.

$$CI \\ I \\ CH - CH_2 - CH_3 \\ BCH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \\ I_4 \\ CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \\ I \\ CH_3 \\ 4-(1-Chloropropyl)-3-methyloctane$$

for the substituted 1-chloropropyl, 'C' is taken as the first letter.

(iii) When two or more prefixes consist of identical roman letters priority for citation is given to the group which contains the lowest locant at the first point of difference.

For example,

$$CI - CH - CH_3$$

 1
 1
 1
 2
 3
 $CH_2 - CH_2CI$

1-(1-Chloroethyl)-4-(2-chloroethyl)cyclohexane

Here, 1-chloroethyl gets priority over 2-chloroethyl.

ADDITIONAL ILLUSTRATIONS AND SOLVED EXAMPLES

Compound	Prefix	Wordroot	Pri. Suffix	Sec. Suffix	Name
$CH_3 - CH_2 - CH_2 - CH_3$	_	But	ane	_	Butane
$ \begin{array}{c} 1 & 2 & 3 & 4 \\ CH_{3} - CH - CH_{2} - CH_{3} \\ 1 \\ CH_{3} \end{array} $	2–Methyl	But	ane	_	2–Methylbutane
CH ₃ -CH=CH-CH ₂ -CH ₃	_	Pent	2-ene	_	Pent-2-ene
1 CH ₃ C=CHCH ₂ CH ₃ CH ₃	2–Methyl	Pent	2-ene	_	2-Methylpent-2-ene
$0CH \equiv C - CH_3$	_	Prop	yne	_	Propyne
$CH_3 - CH_2 - CH_2 - CH_2$ OH	_	But	ane	1–ol	Butan-1-ol
$\begin{array}{cccccc} 4 & 3 & 2 & 1 \\ CH_3 - CH - CH_2 - CH_2 \\ I & I \\ CH_3 & OH \end{array}$	3–Methyl	But	ane	1–ol	3–Methylbutan–1–ol
OH 5 4 3 2 1 CH ₃ -C=CH-CH ₂ -CH ₂ CH ₃	4 – Methyl	Pent	3–ene	1–ol	4-Methylpent-3-en-1-ol
$ \begin{array}{c} 3\\ CH \equiv C - CH_2\\ \\ OH \end{array} $	_	Prop	2-yne	1–ol	Prop–2–yn–1–ol
$CH \equiv C - C \equiv CH$	_	Buta	diyne	_	Butadiyne
CH_3 - CH = C = CH - CH_3	_	Penta	2, 3 diene	_	Penta-2, 3-diene
ОН	Cyclo	But	2-ene	1-ol	Cyclobut-2-en-1-ol
NO ₂	4-Nitro	Benz	_	oyl Bromide	4-Nitrobenzene carbonyl bromide

WOOD ROOTS

Number of Carbon Atoms	Word Root	Name
1	Meth	Methane
2	Eth	Ethane
3	Prop	Propane
4	But	Butane
5	Pent	Pentane
6	Hex	Hexane
7	Hept	Heptane
8	Oct	Octane
9	Non	Nonane
10	Dec	Decane
11	Undec	Undecane
12	Dodec	Dodecane
13	Tridec	Tridecane
14	Tetradec	Tetradecane
15	Pentadec	Pentadecane
16	Hexadeca	Hexadecane
17	Heptadec	Heptadecane
18	Octadec	Octadecane
19	Nonadec	Nonadecane
20	Icos	Icosane
21	Heneicos	Heneicosane
22	Docos	Docosane
23	Tricos	Tricosane
30	Triacont	Triacontane
31	Hentriacont	Hentriacontane
40	Tetracont	Tetracontane
50	Pentacont	Pentacontane
60	Hexacont	Hexacontane
70	Heptacont	Heptacontane
80	Octacont	Octacontane
90	Nonacont	Nonacontane
100	Cent & Hect	Centane or Hectane

FUNCTIONAL GROUPS IN DECREASING ORDER OF SENIORITY

	Class	Name	Suffix	Prefix
1	R – COOH	Alkanoic Acid	- oic Acid (carboxylic acid)	Carboxy
2	R – SO3H	Alkane sulphonic Acid	– sulphonic Acid	sulpho
3	$\frac{\mathbf{R} - \mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{R}}{\ \ }$	Alkanoic Anhydride	– anhydride	
	0 0			
4	R – COOR	Alkyl alkanoate	– alkanoate (carboxylate)	Alkoxy carbonyl
5	R - C - X	Alkanoyl halide	– oyl halide (carbonyl halide)	halo carbonyl
	0			
6	R - C - NH2	Alkanamide	– amide (carboxamide)	Carbamoyl
	0			
7	R – C ° N	Alkanenitrile	– nitrile (carbonitrile)	cyano
8	R - C - H	Alkanal	– al (carbaldehyde)	formyl / oxo
	0			
9	R - C - R	Alkanone	– one	Oxo / Keto
	0			
10	R – OH	Alkanol	– ol	hydroxy
11	R – SH	Alkanethiol	– thiol	mercapto
12	R – NH2	Alkanamine	- amine	amino

COMMON AND IUPAC NAMES OF SOME ORGANIC COMPOUNDS

S.No.	Compound	Common names	IUPAC name
1.	CH_4	Methane or Marsh gas or Fire damp or Carbane	Methane
2.	$H_3C - CH - CH_3$ CH ₃	Isobutane	2-Methylpropane
3.	$\begin{array}{c} H_3C-CH-CH_2-CH_3 \\ I \\ CH_3 \end{array}$	Isopentane	2-Methylbutane
4.	$CH_3 \\ \\ H_3C - C - CH_3 \\ \\ CH_3$	Neopentane	2, 2-Dimethylpropane
5.	CH ₃ CH ₃ – CHCH ₂ CH ₂ CH ₃	Isohexane	2-Methylpentane
6.	$CH_3 \\ \\ CH_3 - C - CH_2CH_3 \\ \\ CH_3 \\ CH_3$	Neohexane	2-2-Dimethylbutane
7.	$CH_2 = CH_2$	Ethylene	Ethene
8.	$CH_{3}CH = CH_{2}$	Propylene	Propene
9.	$CH_3CH_2 - CH = CH_2$	α-Butylene	But-1-ene
10.	$CH_{3}CH = CHCH_{3}$	β-Butylene	But-2-ene
11.	$CH_3(CH_2)_2CH = CHCH_3$	β-Hexylene	Hex-2-ene
12.	CH ₃ CH = CH ₂	Isobutylene	2-Methylpropene

		<u>Organic Chemistry – Some</u>	<u>Basic Principles and Techniques</u>
13.	$CH_2 = C = CH_2$	Allene	Propadiene
14.	HC = CH	Acetylene	Ethyne
15.	$H_3C - C \equiv CH$	Methyl acetylene	Propyne
16.	CH ₃ – Cl	Methyl chloride	Chloromethane
17.	CH ₃ – CH – CH ₃ I	Isopropyl iodide	2-Iodopropane
18.	CH ₃ CH ₂ – CH – CH ₃ CI	sec-Butyl chloride	2-Chlorobutane
19.	CH ₃ CH ₃ – CH – CH ₂ – CI	Isobutyl chloride	1-Chloro-2-methylpropane
20.	CH ₃ CH ₃ – C – CI CH ₃	tert-Butyl chloride	2-Chloro-2-methyl propane
21.	CH ₂ – Br CH ₂ – Br	Ethylene dibromide	1, 2-Dibromoethane
22.	CH ₃ – CH – Br Br	Ethylidene bromide	1, 1-Dibromoethane
23.	$CH_2 = CH - Cl$	Vinyl chloride	Chloroethene
24.	$CH_2 = CH - CH_2 - Br$	Allyl bromide	3-Bromo-1-propene
25.	$CH_3 - CH_2 - OH$	Ethyl alcohol or (Methylcarb inol)	Ethanol
26.	$CH_3CH_2CH_2 - OH$	n – Propyl alcohol or (Ethyl carbinol)	Propan-1-ol
27.	CH ₃ – CH – CH ₃ OH	Isopropyl alcohol	Propan-2-ol

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28.	$CH_2 = CH - CH_2 - OH$	Allylalcohol	Prop-2-en-1-ol
29.	$CH \equiv C - CH_2 - OH$	Propargyl alcohol	Prop-2-yn-1-ol
30.	СН ₃ – СН – СН ₂ ОН ОН	Propylene glycol	Propane-1, 2-diol
31.	$\mathrm{HO}-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{CH}_2-\mathrm{OH}$	Trimethylene glycol	Propane-1, 3-diol
32.	СН ₂ -СН-СН ₂ ОН ОН ОН	Glycerol or Glycerine	Propane-1, 2, 3-triol
33.	H – CHO	Formaldehyde	Methanal
34.	CH ₃ – CHO	Acetaldehyde	Ethanal
35.	$CH_3CH_2CH_2 - CHO$	n-Butyraldehyde	Butanal
36.	CH ₃ CH – CHO	Isobutyraldehyde	2-Methylpropanal
37.	$CH_2 = CH - CHO$	Acrolein	Propenal
38.	$CH_{3}CH = CH - CHO$	Crotonaldehyde	But-2-enal
39.	$CH_3 - CO - CH_3$	Dimethyl ketone or Acetone	Propanone
40.	$CH_3 - CO - CH_2CH_3$	Ethyl methyl ketone	Butanone
41.	$CH_3 - CO - CH_2CH_2CH_3$	Methyl n-propyl ketone	Pentan-2-one
42.	$CH_3CH_2 - CO - CH_2CH_3$	Diethyl ketone	Pentan-3-one
43.	$CH_{3}CO - CH = CH_{2}$	Methylvinyl ketone	But-3-en-2-one
44.	Н – СООН	Formic acid	Methanoic acid
45	СН – СООН	Acetic acid	Fthanoic acid
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-13.	$C_{11_3} = COOI1$		
46.	$CH_3CH_2CH_2 - COOH$	n-Butyric acid	Butanoic acid
47.	CH ₃ CH ₂ CH ₂ CH ₂ COOH	n-Valeric acid	Pentanoic acid
48.	CH ₃ CH – COOH	Iso-butyric acid	2-Methylpropanoic acid
49.	$CH_2 = CH - COOH$	Acrylic acid	Propenoic acid
50.	соон соон	Oxalic acid	Ethanedioic acid
51.	Н₂С СООН СООН	Malonic acid	Propanedioic acid
52.	H ₂ C – COOH H ₂ C – COOH	succinic acid	Butanedioic acid
53.	H_2C $CH_2 - COOH$ $CH_2 - COOH$	Glutaric acid	Pentanedioic acid
54.	Н Н ₃ С–С–СООН ОН	Lactic acid	2-Hydroxypropanoic acid
55.	О Н ₃ С – С – СООН	Pyruvic acid	2-Oxopropanoic acid
56.	носнсоон	Tartaric acid	2,3 – Dihydroxybutane dioicacid
57.	HOCHCOOH H₂C – СООН OH CCOOH CH₂ – СООН	Citric acid	2 – Hydroxypro pane – 1,2, 3 – tricarboxylic acid

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		Organic Chemistry – Some D	asic i i meipies and reeningues
58.	HO-CH-COOH	Malic acid	2 – Hydroxy – butan e dioic acid
	CH ₂ COOH		
59.	н соон	Maleic acid	cis-But-2-enedioic acid
	н_ссоон		
60.	н соон С	Fumaric acid	trans-But-2-enedioic acid
	HOOCH		
61.	$CH_2 = CH - COOH$	Acrylic acid	Propenoic acid
62.	$H_{3}C - CH = CH - COOH$	Crotonic acid	But-2-enoic acid
63.	H – COOCH ₃	Methyl formate	Methyl methanoate
64.	$H - COOC_2H_5$	Ethyl formate	Ethyl methanoate
65.	$CH_3 - COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
66.	H–COCl (unstable)	Formyl chloride	Methanoyl chloride
67.	CH ₃ – COCl	Acetyl chloride	Ethanoyl chloride
68.	(CH ₃ CO) ₂ O	Acetic anhydride	Ethanoic anhydride
69.	(CH ₃ CH ₂ CO) ₂ O	Propionic anhydride	Propanoic anhydride
70.	$H - CONH_2$	Formamide	Methanamide
71.	$CH_3 - CONH_2$	Acetamide	Ethanamide
72.	$CH_3 - CH_2 - CONH_2$	Propionamide	Propanamide
73.	$CH_3 - O - N = O$	Methylnitrite	Methylnitrite
74.	$CH_{3}CH_{2} - O - N = O$	Ethyl nitrite	Ethylnitrite

75.	$CH_3 - NH_2$	Methylamine	Methanamine
76.	(CH ₃ CH ₂) ₂ NH	Diethylamine	N-Ethylethanamine
77.	(CH ₃) ₃ N	Trimethylamine or N,N-Dimethylamino- methane	N,N-Dimethyl methan- amine
78.	$H_2N - SO_3H$	Sulphamic acid	Aminosulphonic acid
79.	$CH_3 - CN$	Methyl cyanide or Acetonitrile	Ethanenitrile
80.	$CH_3 - N^+ \equiv C^-$	Methyl isocyanide or Methyl carbylamine	Methane isocyanide
81.	$\mathrm{CH}_{3}\mathrm{CH}_{2}-\mathrm{N}^{+}\equiv\mathrm{C}^{-}$	Ethyl isocyanide or Ethyl carbylamine	Ethaneisocyanide
82.	$O \xrightarrow{H_2C - CH_2} O \xrightarrow{H_2C - H_2C} O$	Dioxane	1,4-Dioxacyclohexane
83.		Trioxane	1,3,5-Trioxacyclohexane
84.		Toluene	Methylbenzene or Toluene
85.		Xylene (o,m,p)	(o,m,p)Dimethylbenzene
86.	CH3 CH3 CH3	Mesitylene	1,3,5 – Trimethyl benzene
87.		Cumene	Isopropylbenzene

88.		Benzyl chloride	Chlorophenylmethane
89.		Benzal chloride	Dichlorophenylmethane
90.		Benzochloride	Trichlorophenylmethane
91.		Benzonitrile	Benzenecarbonitrile
92.		(Gammexane or Lindane or 666) BHC	Hexachlorocyclohexane
		[Benzene hexachloride]]	
93.	OH	Carbolic acid	Phenol
94.	ОНОН	Catechol	Benzene-1,2-diol
95.	ОН	Resorcinol	Benzene-1,3-diol





112.		Aniline	Aniline (Benzenamine)
113.		(o, m, p) Toluidine	Methylaniline
114.	OH CH ₃	(o, m, p) cresol	Methylphenol
115.	$\bigcirc \bigcirc$	Napthalene	Naphthalene
116.	OOO	Anthracene	Anthracene
117.		Phenanthrene	Phenanthrene
118.		Pyrene	Pyrene

INTRODUCTION

The name was given by Berzilius. Two or more than two organic compounds having the same molecular formula and molecular weight but different physical and chemical properties are called isomers and the phenomenon is called isomerism.



STRUCTRAL ISOMERISM

- 1. Chain Isomerism (CI) : The compounds which have same molecular formula, same functional group, same position of functional group or multiple bond or substituent but different arrangement of carbon chain (different parent name of compound) shows chain isomerism.
 - **Ex.** $CH_3 CH_2 CH_2 CH_3$ 1-Butane (4C)

2-Methyl propane (3C)

Ex. $CH_3 - CH_2 - CH = CH_2$ Butene (4C)

$$CH_2 = C - CH_3$$

 CH_3

2–Methyl-1-propene (3C)

Ex. $CH_3 - CH_2 - CH_2 - CH_2 - OH$ 1-Butanol (4C)

2-Methyl-1-propanol (3C)

2. Position Isomerism (PI): The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, shows position isomerism.

Ex.
$$CH_2 = CH - CH_2 - CH_3$$

But-1-ene
 $CH_3 - CH = CH - CH_3$

But-2-ene

Ex. $CH_3 - CH_2 - CH_2 - CH_2 - OH$ 1-Butanol $CH_3 - CH_2 - CH - CH_3$

2-Butanol

Ex.
$$CH_3 - CH_2 - CH_2 - CH_2 - CI_1$$

1-Chlorobutane

$$CH_3 - CH_2 - CH - CH_3$$

2-Chlorobutane

EXAMPLE OF CIAND PI

(i) C_4H_{10} have two isomers : Both butane and isobutane are chain isomers.

Ex.
$$CH_3 - CH_2 - CH_2 - CH_3$$

Butane
 $CH_3 - CH - CH_3$
 \downarrow
 CH_3
Isobutane

(ii) C_5H_{12} have three isomers : All of three structures are chain isomers because only carbon chain (parent) is different.

 $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

Pentane

$$CH_{3}-CH_{2}-CH-CH_{3}$$

$$CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}-CH_{3}-CH_{3}$$

2-Methyl butane

2,2–Dimethylpropane

(iii) C₆H₁₄ has 5 isomers

- (a) $CH_3CH_2CH_2CH_2CH_2CH_3$ Hexane
- (b) $CH_3 CH_2 CH_2 CH_3 CH_3$

2-Methyl pentane

(c)
$$CH_3 - CH_2 - CH - CH_2 - CH_3$$

 \downarrow
 CH_3

3-Methyl pentane

Organic Chemistry – Some Basic Principles and Techniques

$$\begin{array}{ccc} (d) & CH_3-CH-CH-CH_3\\ & & | & |\\ & CH_3 & CH_3 \end{array}$$

2,3–Dimethyl butane

(e)
$$H_3C - C - CH_2 - CH_3$$

 $H_3C - C - CH_2 - CH_3$
 CH_3

- $a-b, b-d, a-c, c-d \longrightarrow$ Chain Isomers 2,2–Dimethyl butane
- b-c, d-e \longrightarrow Position Isomers

(iv) C₇H₁₆ has 9 isomers

$$1. \rightarrow CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3} \qquad Heptane$$

$$2. \rightarrow CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{-}-CH_{3} \qquad 2-Methylhexane$$

$$3. \rightarrow CH_{3}-CH_{2}-CH_{2}-CH_{-}-CH_{3} \qquad 3-Methylhexane$$

$$4. \rightarrow CH_{3}-CH_{2}-CH_{2}-CH_{-}-CH_{3} \qquad 2,2-Dimethyl pentane$$

$$CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad 2,2-Dimethyl pentane$$

$$CH_{3} \qquad CH_{3} \qquad$$

(v) $C_{3}H_{6}Cl_{2}$ has 4 isomers : Position of chlorine atom is different in all the structure, so these are position Isomers.

1.
$$H_3C-CH_2-CH-Cl$$

1,1-Dichloropropane

Cl

$$I$$

2. H_2C — CH_2 — CH_2 — Cl
 $1,3$ –Dichloropropane

$$\begin{array}{c} CI \\ I \\ 3. \\ H_3C - C - CH_3 \\ I \\ CI \end{array}$$

2,2-Dichloropropane

4.
$$H_2^{Cl}$$
 - CH - CH₃
 H_2^{Cl} - CH - CH₃

1,2-Dichloropropane

(vi) $C_5H_{11}Cl$ has 8 isomers (vii) C_8H_{10} has 4 aromotic isomers





(viii) $C_6H_4X_2 \longrightarrow 3$ Aromatic isomers $C_6H_4XY \longrightarrow 3$ Aromatic isomers $C_6H_3X_3 \longrightarrow 3$ Aromatic isomers $C_6H_3XYZ \longrightarrow 10$ Aromatic isomers Solved Examples

- **Ex.19** Structures CH_3 — CH_2 — $CH=CH_2$ and CH_3 — $C=CH_2$ are :- CH_3
- Ans. Chain Isomers

Molecular formula	No. of Isomers
$C_{4}H_{10}$	2
C ₅ H ₁₂	3
$C_{6}H_{14}$	5
C_7H_{16}	9
$C_{8}H_{18}$	18
C ₉ H ₂₀	35
$C_{10}H_{22}$	75

3. Ring chain isomerism (RCI): Same molecular formula but different mode of linking (open chain or closed chain) of carbon atoms.

$$C_{3}H_{6}$$
 CH_{3} CH_{2} [open chain]
 $C_{3}H_{6}$ CH_{2} [closed chain or ring]

They have same molecular formula so they are Ring chain isomers.

Solved Examples

Ex.20 Relate a,b and c:-

$$\begin{array}{ccc}
\text{(a)} & H_3C-C \equiv CH \\
\text{(b)} & CH_2=C=CH_2 \\
\text{(c)} & CH_2-CH \\
\end{array}$$

Ans. $a-b \longrightarrow a-c, b-c \longrightarrow$

Functional Isomers Ring-chain Isomers, Functional Isomers

Special points :

• Alkenes with cycloalkane and alkynes (Alkadienes) with cycloalkenes show Ring-chain Isomerism.

 \rightarrow

• Ring-chain Isomers are also Functional Isomers but priority is given to Ring-chain Isomers.

(1) Ring-chain Isomers	(2) Chain Isomers
(3) Functional Isomers	(4) Position Isomers

Ans. (1)

OR

(1) Functional Isomers	(2) Position Isomers
(3) Chain Isomers	(4) Metamerism

Ans. (1)

OR

(1) Functional Isomers	(2) Position Isomers
(3) Ring-chain Isomers	(4) 1 and 3 Both

Ans. (4)

Ex.22 Relate structures a,b,c and d.

(a)
$$CH_3 - CH_2 - C \equiv CH$$

(b) $CH_2 = C = CH - CH_3$



a, b	\longrightarrow	Functional Isomers	

a, c. → Ring-chain Isomers and Functional Isomers

b, c
$$\longrightarrow$$
 Ring-chain Isomers and Functional Isomers

a, d.
$$\longrightarrow$$
 Ring-chain Isomers and Functional Isomers

c, d. \longrightarrow Chain Isomers

b, d.
$$\longrightarrow$$
 Ring-chain Isomers and Functional Isomers

Ex.23
$${}^{5}_{CH_{3}} - {}^{4}_{CH_{2}} - {}^{3}_{CH_{2}} - {}^{2}_{CH_{2}}$$
 and ${}^{1}_{1CN}$

Pentanenitrile

$${}^{4}_{\text{CH}_{3}}$$
 $-{}^{3}_{\text{CH}_{2}}$ $-{}^{2}_{\text{CH}_{-}}$ CH $_{3}$ are ?

2–Methyl butanenitrile

- **Ans.** Molecular formula same, Functional group same, position of Functional group same but different parent carbon atom chain so both are Chain isomers
- **Ex.24** How many minimum carbons required for Chain isomerism and Position isomerism in alkanes?

Ans. 4, 6

Ex.25 How many minimum carbons required for Chain isomerism and Position isomerism in alkenes?

Ans. 4, 4

Ex.26 How many minimum carbons required for Chain isomerism and Position isomerism in alkynes?

Ans. 5, 4

4. Functional Isomerism :- Same molecular formula but different functional groups.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

(i) Alcohol and ether
$$\longrightarrow$$

 $CH_3-CH_2-OH \text{ and } CH_3-O-CH_3$
(ii) Aldehydes and ketones \longrightarrow
 $CH_3-CH_2-C-H \text{ and } CH_3-C-CH_3$
 $\parallel O O$
(iii) Acids and ester \longrightarrow
 $CH_3-C-OH \text{ and } H-C-O-CH_3$
 $\parallel O$
(iv) Cyanide and isocyanide \longrightarrow
 $CH_3-CH_2-CH_2-CN \text{ and } CH_3-CH_2-CH_2-NC$

 $\begin{array}{c} & & \text{Organi} \\ \hline (v) \text{ Nitro and Nitrite} \longrightarrow \\ & & CH_3 - CH_2 - N \swarrow_O^O \quad \text{and} \\ & & CH_3 - CH_2 - O - N = O \\ \hline (vi) \text{ Keto and enol} \rightarrow \\ & & O \\ & CH_3 - C - CH_3 \quad \text{and} \quad \begin{array}{c} CH_2 = C - CH_3 \\ & OH \\ \hline (vii) \text{ Amide and Oxime} \rightarrow \\ & CH_3 - C - CH_3 \quad \text{and} \quad CH_3 - CH = NOH \\ & O \\ \hline (vii) \text{ Amide and Oxime} \rightarrow \\ & CH_3 - C - NH_2 \quad \text{and} \quad CH_3 - CH = NOH \\ & & O \\ \hline (viii) \quad 1^\circ, 2^\circ, 3^\circ \text{ amines} \\ & (i) CH_3 - CH_2 - CH_2 - NH_2 \\ & (ii) CH_3 - NH - CH_2 - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 - NH - CH_2 - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 - NH - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 - N - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 - N - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - CH_3 \\ - CH_3 \\ - CH_3 \\ - CH_3 \\ \hline (iii) \begin{array}{c} CH_3 \\ - C$

(ix) Alcoholic and phenolic compounds :

$$\bigcirc \ \ CH_2OH \\ \bigcirc \ \ CH_2OH \\ \bigcirc \ \ CH_3$$

(x) Alkyl halides do not show Functional isomerism.

5. Metamerism: Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group.

Polyvalent Functional group [More than one valency] are :

Ex.
$$CH_3 \longrightarrow O \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow CH_3;$$

 $CH_3 \longrightarrow O \longrightarrow CH \longrightarrow CH_3$
 \downarrow
 CH_3

Both are metamers.

1–Methoxypropane 2–Methoxypropane

- Both are metamers and Position isomer but priority is given to metamerism.
- Metamers may be Position isomer or Chain isomer but priority is given to metamerism.
- Ex. CH_3 — CH_2 —NH— CH_2 — CH_3 CH_3 —NH— CH_2 — CH_2 — CH_3 N—Ethyl ethanamine N—Methyl propanamine They are only metamers not CI

Ex.
$$CH_3$$
— NH — CH_2 — CH_2 — CH_2 — CH_3
 CH_3 — NH — CH_2 — CH — CH_3
 CH_3

Both are metamers and Chain isomer

Ex.
$$CH_3 - C - CH_2 - CH_2 - CH_2 - CH_3$$

2–Hexanone

$$CH_3 - CH_2 - C - CH_2 - CH_2 - CH_3$$

3-Hexanone

Both are metamers and Position isomer

Ex.
$$CH_3$$
-C- CH_2 - CH_2 - CH_2 - CH_3

2-Hexanone

$$\begin{array}{c} CH_3 {-\!\!\!\!-} CH_2 {-\!\!\!\!-} C {-\!\!\!\!-} CH {-\!\!\!\!-} CH_3\\ \parallel \quad \mid \\ O \quad CH_3 \end{array}$$

2-Methyl-3-pentanone

Both are Metamers, Chain and Position isomers

Ex.27 Structures
$$CH_3 - C - O - C_6H_5$$
 and

$$C_6H_5 - C - O - CH_3$$
 are

Ans. Both are metamers.

- 6. Tautomerism or Desmotropism : Tautomerism was introduced by "Laar". It's also called desmotropism.
 - Desmotroism means bond turning.

[Desmos = Bond; Tropos = Turn]

 Tautomers have same molecular formula but different structural formula due to wandering nature of active hydrogen between two atoms.

$$\begin{array}{c|c} CH_2 - C - H \\ \parallel \\ H & O \\ - Hydrogen \text{ or active } H \end{array} - H of carbonyl compound is active H$$

Ex.



Ex.

$$\begin{array}{cccc} CH_{3}-C-CH_{2} & \rightleftharpoons & CH_{3}-C=CH_{2} \\ & & & & & \\ O & H & & & O-H \\ & & & & & O-H \end{array}$$
keto
$$ene+ol=enol$$

Note :

(1) Tautomers are also F. I. and exist in dynamic equilibrium [1 is used to show tautomerism]

(2) By shifting of H-atom π bond also change its position.

(a)For carbonyl compounds :- Carbonyl compounds having atleast one α -H show tautomerism

(i)
$$CH_3 - C - H$$

(i) $CH_3 - C - CH_3$
(ii) $CH_3 - C - CH_3$
(iii) $CH_3 - C - CH_3$
(iii) $CH_3 - CH - C - H$
(iv) $CH_3 - CH - C - H$

(iv)
$$H - C - H$$
 No α H, No tautometrism

(v)
$$\bigcirc^{C-H}$$
 No α H, No Tautomerism

(vi)
$$\overset{O}{\underset{C-CH_{3}}{\parallel}}$$
 3 α H,

shows tautomerism (Aceto phenone)

(vii)
$$Ph-C-Ph$$
 No α H,
 \parallel
O
No tautomerism (Benzophenone)

shows tautomerism

(ix) $H \to H H H$ 4 α H, shows tautomerism

(x)
$$H \xrightarrow{O}_{H} H$$
 α -H, attached sp² carbon

does not take part in tautomerism

Solved Examples

Ex.28 Which of the following show keto enol tautomerism.



(1), (2) and (4)Ans.

> (b) For nitro compounds : Nitro compounds having at least one α – H show tautomerism

$$CH_2 = N_0$$
 $CH_2 = N_1$

Nitro form

Aci nitro form (acidic form so soluble in base)

Note : Nitro compounds with at least one α -H are soluble in NaOH.

Solved Examples

Ex. 29 Which of the following show tautomerism.

(1) CH₃CH₂—NO₂ (2) (CH₃)₂CH—NO₂ $(3) (CH_3)_3 C - NO_2$ (4) Ph—CH₂—NO₂

Ans. 1, 2 and 4

Ex.30 Which of the following do not soluble in NaOH.

(1) CH_3CH_2 —NO ₂	$(2) (CH_3)_2 CH - NO_2$
(3) $(CH_3)_3C-NO_2$	(4) Ph— CH_2 — NO_2
s Only 3	

Ans. Only 3

(c) H—C \equiv N and H—N \equiv C are tautomers [also Functional isomers] while $R - C \equiv N$ and $R - N \equiv C$ are only Functional isomers.

$$H - C \equiv N \implies C \equiv N - H$$
Active H
$$(d) H - N \bigcirc O \quad and$$

$$H - O - N = O \text{ are tautomers.}$$

$$ENOL CONTENT$$

$$1. \quad CH_2 - C - H \qquad \longrightarrow \qquad CH_2 = C - H$$

$$H \quad O \quad OH$$

$$"keto" (\approx 99\%) \qquad "enol" (\approx 1\%)$$

$$2. \quad CH_3 - C - CH_2 \qquad \longrightarrow \qquad CH_3 - C = CH_3$$

Less stable or unstable

 $\approx 1\%$

$$\geq$$
 OH

"keto" ($\approx 1\%$)

 $\approx 99\%$

1.

2.

4.

,0 `OH

> "enol" (stable by resonance and aromatic nature) ($\approx 99\%$)

Aceto acetic ester (AAE)

$$\begin{array}{c} CH_3 - C = CH - C - OC_2H_5 \\ \downarrow & \parallel \\ OH & O \end{array}$$

AAE
$$aqueous solution$$
 keto : enol = 93 : 7
liquid state keto : enol = 25 : 75

$$\begin{array}{c} CH_3 - C - CH_2 - C - O - C_2H_5 \\ \parallel & \parallel \\ O & O \\ \vdots & \vdots \\ H - O - H & H - O - H \end{array}$$

– In liquid state

• Keto from is stablised by intermolecular H-Bonding.

<u>Organic Chemistry – Some Basic Principles and Techniques</u> Other Examples

$$\begin{array}{c} CH_3 {-\!\!\!\!-} C = CH {-\!\!\!\!-} C {-\!\!\!\!-} OC_2H_5 \\ \downarrow \\ O {-\!\!\!\!-} H {\cdot} \cdots O \end{array}$$

• Enol form is stabilised by intramolecular H–Bonding.

KEY POINT

- (1) Enol content \propto number of >C=O group.
- (2) If number of >C=O groups are equal then proportional to number of α -H.
- (3) Group —OH attached to sp² carbon or double bond is less stable or unstable.
- (4) More active H, more take part in tautomerism.
- (5) Stability of enol form depnds on (i) Resonance and (ii) H – Bond.

Solved Examples

Ex. 31 Arrange the following in correct order of enol content.



Ex.32 Which have maximum stable enol form



(1) $C_4H_{10}O$ Isomers r7[4 alcohol and 3 ethers] total 7 isomers are possible.

Alcohol:
$$CH_3$$
— CH_2 — CH_2 — CH_2 — OH_2 — OH_3
 CH_3 — CH_2 — CH — CH_3
 OH
 CH_3 — CH — CH_2 — OH
 CH_3
and CH_3 — CH_3
 $CH_$

Ethers:
$$CH_{3}$$
—O— CH_{2} — CH_{2} — CH_{3} .
 $C_{2}H_{5}$ —O— $C_{2}H_{5}$, CH_{3} —O— CH — CH_{3}
 I
 CH_{3}

(2) $C_{5}H_{12}O$ Isomers r [8 alcohols and 6 ethers] total 14 isomers are possible. (i) CH_{3} —O— CH_{2} — CH_{2} — CH_{2} — CH_{3} (ii) CH_{3} —O—CH— CH_{2} — CH_{3} (iii) CH_{3} —O— CH_{2} — $CH_{-}CH_{3}$ (iv) $C_{2}H_{5}$ —O— $C_{3}H_{7}$ (v) CH_{3} —O— $C_{-}CH_{3}$ (v) CH_{3} —O— $C_{-}CH_{3}$ (vi) CH_{3} — CH_{2} —O— $CH_{-}CH_{3}$ (vi) CH_{3} — CH_{2} —O—CH— CH_{3} (vi) CH_{3} — CH_{2} —OCH— CH_{3} (vi) CH_{3} — CH_{2} —O—CH— CH_{3} (vi) CH_{3} — CH_{2} —O—CH— CH_{3} (vi) CH_{3} — CH_{2} —O—CH— CH_{3} (vi) CH_{3} — CH_{3}

(i)
$$CH_3 - CH_2 - CH_2 - CH_2 - H$$

(ii)
$$CH_3 - CH - C - H$$

 $CH_3 - CH_3$
(iii) $CH_3 - C - CH_2 - CH_3$

(4) C₄H₈O₂ (2 acids and 4 esters) total 6 isomers are possible. *Corganic Chemistry – Some Basic Principles and Techniques Solved Examples*

(i)
$$CH_{3}-CH_{2}-CH_{2}-C-OH$$

(ii) $CH_{3}-CH_{2}-OC_{2}H_{5}$
(iii) $CH_{3}-CH-C-OH_{2}-OH_{3}$
(iv) $C_{2}H_{5}-C-OCH_{3}$
(v) $H-C-OC_{3}H_{7}$

(vi)
$$H - C - O - CH - CH_3$$

 CH_3

(5) Aromatic isomers of $C_7 H_8 O$.



Note : Alcoholic and phenolic groups are Functional isomers.

Ex.33
$$CH_3 - CH_2 - CH_2 - C - OH$$
 and

$$CH_3-CH_2-CH-CH-H$$
 are
OH

(a) Position isomers	(b) Functional isomers
(c) Geometrical isomers	(d) Chain isomers

Ans. (b) Functional group different so Functional isomers.

Note : If Functional group is changed then they will be never Chain, Position isomer and metamers.

Ex.34
$$CH_3$$
—S— CH_2 — CH_3 and CH_3 — CH_2 —S— CH_3 are –

Ans. Identical

Ex.35
$$\begin{array}{c} 0 & 0 \\ \parallel & \parallel \\ CH_3 - C - 0 - C - C_6H_5 \end{array}$$
 and $\begin{array}{c} 0 & 0 \\ \parallel & \parallel \\ CH_2 - C - 0 - C - CH_6 \end{array}$ are -

Ans. Identical

STEREO ISOMERISM

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

(A) CONFIGURATIONAL ISOMERISM :

Stereo isomers which have following characteristics.

- 1. Stereo isomer which cannot interconvert in each other at room temperature due to restricted rotation known as Geometrical isomerism.
- 2. Stereo isomer which cannot super impose on each other due to chirality know as optical isomerism.

GEOMETRICAL ISOMERISM (G. I)

Alkenes (>C=C<), oximes (>C=N—) and azo compounds [-N=N-], show G. I. due to restricted rotation about double bond while cycloalkanes show G. I. due to restricted rotation about single bond.

G. I. IN ALKENES

Reason :- Restricted rotation about double bond : It is due to overlapping of p-orbital.

Restricted Rotation

Free Rotation







Ex.



cis-2-butene

C = C

trans-2-butene

Note : cis 1 trans is possible only when π bond break.

Condition for Geometrical isomerism

Only those alkenes show G. I. in which "Each sp² 1. carbon have different atoms or groups"

$$\begin{pmatrix} a & a \\ b & b \end{pmatrix} C = C \begin{pmatrix} x \\ y \end{pmatrix}$$

$$b > C = C < y$$



Not Geometrical isomers Not Geometrical isomers

Solved Examples

- EX.36 Which of the following show Geometrical isomerism-
 - (1) 1,1-diphenyl-1-butene
 - (2) 1,1-diphenyl-2-butene
 - (3) 2,3-dimethyl-2-butene
 - (4) 3-phenyl-1-butene

Ans.(2)

NOMENCLATURE SYSTEMS **OF GEOMETRICAL ISOMERS**



(a) Cis-Trans System : If same groups at same side then cis and if same groups at different side then trans.

$$a > C = C < a > b > C = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b > c = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C < b = C <$$

[Same groups, same side] [Same groups different side]





trans



cis







trans-2-pentene

It does not show Geometrical isomers So no cis-trans

<u>Organic Chemistry – Some Basic Principles and Techniques</u> Priority Rules :

Pro	perties of Cis-1r	ans isoi	mers:
(i)	Stability	_	cis < trans
	[less repulsio	n betwee	en similar groups in trans]
(ii)	Dipole moment	—	cis>trans
(iii)	Polarity		cis>trans
			[more μ , more polarity)
(iv)	Solubility		cis>trans
			[because $\mu_{cis} > \mu_{trans}$]
(v)	Boiling point		cis>trans
			[ionic character]
(vi)	Melting point	_	cis < trans
		[more p	packing capacity of trans.]

Dipole moment [µ] :



Solved Examples

Ex.37 If dipole moment of chlorobenzene is μ , then dipole

moment of Cl is –

trans $\mu \neq 0$

Ans. Zero

(b) E - Z System:

E (Entgegen) : When high priority groups are opposite side.

Z(**Zussaman**): When high priority groups are same side.



HP-High priority and LP-Low priority

Rule I : Priority is proportional to atomic number of atom which is directly attached to sp² carbon.



Rule II : If rule-I is failed then consider next atom



'Z' dec

decreasing order of atomic number

Rule III :- If multiple bond is present then consider them as :-



Prioity order for some groups is : $Br > Cl > OH > NH_2 > COOH > CHO >$ $CH_2OH > CN > C_6H_5 > C$ $\equiv CH > C(CH_3)_3 > CH \equiv CH_2 > CH(CH_3)_2$ Rule IV : If isotopes are present then consider atomic weight.



GEOMETRICAL ISOMERS IN OXIMES [>C = N]

'E'

• Oximes show G. I. due to restricted rotation about double bond.

[I, H, H]

 Only those oximes show Geometrical isomerism in which sp² carbon have two different groups.

$$[CH_{3} - CH = O + H_{2}N - OH] \longrightarrow CH_{2} - CH = N - OH \text{ (oxime)}$$

Ex. Acetaldoximes has two Geometrical isomers -

$$\begin{array}{ccc} CH_3-C-H & CH_3-C-H \\ \parallel & \parallel \\ N-OH & HO-N \\ syn & anti \end{array}$$

When H and OH are on the same side When H and OH are on the opposite side

Ex. Ph—CH=N—OH -∥ N—OH [syn.] Benzaldoxime [Anti] HO

Solved Examples

Ex.38 Which of the following show Geometrical isomerism-

(1)CH₃—CH₂—CH=N—OH
(2)H₂C=N—OH
(3) CH₃—C—CH₃
$$\parallel$$

N—OH
(4) CH₃—C—CH₂CH₃
 \parallel
N—OH

(1), (4)Ans.



GEOMETRICAL ISOMERS IN CYCLOALKANES

Cycloalkanes show Geometrical isomers due to restricted rotation about single bond. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.



Solved Examples

Ex.39 Which of the following show Geometrical isomerism-



Ans. (1), (2) and (4)

NUMBER OF GEOMETRICAL ISOMERS IN POLYENES

 R_1 —CH=CH—CH=CH CH=CH— R_2

- (a) If $R_1 \neq R_2$ then number of Geometrical isomers = 2^n [n = number of double bonds.]
- Ex. CH_3 —CH=CH—CH=CH—CH=CH— CH_2CH_3
 - As n = 3 r number of Geometrical isomers = $2^3 = 8$
- (b) If $R_1 = R_2$ then number of Geometrical isomers = $2^{n-1} + 2^{p-1}$

where
$$p = \frac{n}{2}$$
 (when n is even)
and $p = \frac{n+1}{2}$ (n is odd)

Ex.
$$CH_3$$
— CH = CH — CH = CH — CH = CH — CH_3
[n=3]

Number of Geometrical isomers

$$= 2^{2} + 2^{1} r 2^{n-1} + 2^{p-1} [p = \frac{3+1}{2}]$$
$$= 4 + 2 = 6$$

Special Point :

 $CH_2 = CH - CH = CH_2$ [1,3-butadiene] show Geometrical isomerism due to resonance.



Introduction and Definitions

(I) Optical activity & plane-polarised light : Ordinary light is an electromagnetic wave, which has oscillation in all the directions perpendicular to the path of propagation. When ordinary light is passed through Nicol prism it has all its oscillations in the same plane and is called plane-polarised light.

Certain compounds rotate the plane of polarised light in a characteristic way when it is passed through their solutions. These compounds are referred to as optically active compounds. The angle of rotation can be measured by an instrument called polarimeter.

(II) dextrorotatory compounds : If the substance rotates plane-polarised light to the right i.e. in clockwise direction it is called dextrorotatory & indicated by 'd' or (+).

(III) laevorotatory compounds: If light is rotated towards left i.e. in anticlockwise direction the substance is said to be laevorotatory and indicated by '1' or (-)



(IV) Specific rotation [α]. Specific rotation is the number of degrees of rotation observed if a 1-dm (10-cm) tube is used and the compound has concentration 1 gm/mL. Thus specific rotation [α] is

$$\left[\alpha\right]_{t}^{\lambda} = \frac{\theta}{\ell \times C}$$

 $[\alpha] =$ Specific rotation

 θ = observed angle of rotation (degree)

$$\ell = \text{Pathlength}(\text{dm})$$

c = concentration (gm/ml)

$$\lambda =$$
 wavelength (nm)

 $t = temperature (25^{\circ}C)$

CAUSE OF OPTICAL ACTIVITY

The foundation of modern theory of stereochemistry was laid by Louis Pasteur when he observed two different kind of crystals, which were mirror images of each other. In aqueous solutions of both types of crystals showed optical rotation that was equal in magnitude but opposite in direction. Pasteur believed that this difference in optical activity was associated with the three dimensional arrangement of atoms in the two types of crystals.

Later van't Hoff and LeBel proposed that all the four valencies of carbon are directed towards the four corners of regular tetrahedron, and if all the four substituent attached to such a carbon are different the resulting molecule lack symmetry and such a molecule is referred to as asymmetric molecule and asymmetry of the molecule is responsible for optical activity in such organic compounds.

ELEMENT OF SYMMETRY AND CONCEPT OF MOLECULAR DISSYMMETRY/ ASYMMETRY AND CHIRALITY.

(I) Plane of symmetry :

It is an imaginary plane which bisects the molecule in two equal halves in such a way that each half of the molecule is the mirror image of the other half.



Plane of symmetry

(II) Centre of symmetry :

The centre of symmetry is defined as the point in a molecule through which if a straight line is drawn from any part of the molecule this line encounters identical groups at equal distances in opposite direction.



(III) Asymmetric and dissymmetric compounds :

A molecule which does not possess any element of symmetry (there are all 23 elements of symmetry) is called asymmetric. A molecule which does not possess plane of symmetry and centre of symmetry is called dissymmetric.

(IV) Condition for optical activity :

The minimum condition for a compound to show optical activity is molecular dissymmetry i.e. absence of plane of symmetry and centre of symmetry.

(V) Chirality :

A compound which is non-superimposable to its mirror image is called chiral while a compound which is superimposable to its mirror image is called achiral. All dissymmetric (or asymmetric) compounds are chiral & vice-versa.

(VI) Chiral centre :

A compound in which a carbon is atttached with four different groups lacks symmetry and is called chiral carbon or asymmetric carbon. It is represented by C^* . e.g.

(a)
$$CH_3 - CH - CH_3$$
 (2-chloropropane):
 $|$
Cl





I has no chiral centre since two groups (a & b) are identical. Its is superimposable on its mirror image II (\equiv III).

(b)
$$CH_3 - CH - C_2H_5$$
 (2-chlorobutane):





I has one chiral centre it is asymmetric & it is not superimposable to its mirror image II (\equiv III).

The necessary condition for chirality is not just the presence of asymmetric carbon atoms but the asymmetry of the molecule as a whole.

Solved Examples

Ex.40 Which of the following compounds has chiral carbon?

$$(A) CH_3 - CH = CH - CH_3$$

$$(B) CH_3 - CHOH - CH_2 - CH_2$$

$$(C) \xrightarrow{CH_3} C = N - OH$$

(D) All of these

Sol. The starred carbon is chiral carbon because all the four substituents are different

$$CH_3 - CH_2 - CH_3$$

Ex.41 Mark the asymmetric carbon atoms in the following compounds

(A) $CH_3 - (CHOH)_2 - COOH$ (B) $HOCH_2 - (CHOH)_4 - CHO$

H H
| |
Ans.
$$(A) CH_3 - C^* - C^* - COOH$$

| |
OH OH

PROJECTION FORMULA IN OPTICAL ISOMERISM

(I) Wedge-dash projection formula :

It is a convenient way of depicting three dimensional structure in two dimension. In this projection four bonds of a tetrahedral molecule is shown by two lines (in the plane) one wedge (up the plane) one dash (down the plane)



(II) Fischer projection formula :

It is also a convenient way of depicting three dimensional structure in two dimension.

Rules for writing Fischer projection formula :

(i) The molecule is drawn in the form of cross (+) with the chiral carbon at the intersection of horizontal & vertical lines.

(ii) On vertical line, main chain is taken with first carbon at the top.

(iii) The horizontal lines represent the bonds directed towards the viewer and vertical lines away from the viewer e.g.

(a)
$$\begin{array}{c} * \\ CH_2 - CH - CHO \\ | & | \\ OH & OH \end{array}$$
 (glyceraldehyde)

can be represented in two different Fischer projection as



(b)
$$CH_3 - CH - COOH (Alanine)$$

|
NH₂

can be represented in two different Fisher projections as



Solved Examples

Ex.42 Draw the wedge-dash projection formula of



CONFIGURATIONAL NOMENCLATURE

IN OPTICAL ISOMERS

Relative configuration : the experimentally determined relationship between the configurations of two molecules, even though we may not know the absolute configuration of either. Relative configuration is expressed by D-L system.

Absolute configuration : The detailed stereochemical picture of a molecule, including how the atoms are arranged in space. Alternatively the (R) or (S) configuration at each chirality centre.

(I) D - L System (Relative configuration) :

This method is used to relate the configuration of sugars and amino acids by the help of enantiomers of glyceraldehyde. The configuration of (+)-glyceraldenyde has been assigned as D and the compounds with the same relative configuration are also assigned as D, & those with (-) glyceraldehyde are assigned as L.



Examples :





Sugars have several asymmetric carbons. A sugar whose highest numbered chiral centre (the penultimase carbon) has the same configuration as D - (+) - glyceraldehyde (– OH group on right side) is designated as a D-sugar, one whose highest numbered chiral centre has the same configuration as L-glyceraldehyde is designated as an L-sugar.



(II) R and S configurations in Fischer projection : (absolute configuration)

D-Fructose

D-Mannose

Rule I: The priorities of groups which are attached with the asymmetric C-atom are assigned by sequence rule.

Rule II : The lowest priority group is brought to the bottom of Fischer projection by two or even simultaneous exchanges.

Rule III : Then an arrow is drawn from first priority group to second priority group to third priority group. If the arrow is clockwise the configuration assigned to the projection is \mathbf{R} & If it is anticlockwise the configuration assigned is \mathbf{S} .

Solved Examples

Ex.43 (i)
$$\overset{(3)}{\underset{(1)}{\text{Br}}} \overset{(3)}{\underset{(1)}{\overset{(3)}{\underset{(1)}{\text{H}_2}}}} \overset{(3)}{\underset{(1)}{\overset{(3)}{\underset{(1)}{\overset{(3)}{\underset{(1)}{\text{H}_2}}}}} \overset{(3)}{\underset{(1)}{\underset{(1)}{\underset{(1)}{\overset{(3)}{\underset{(1)}{\underset{($$







Ex.44 Assign Ror S configuration to each of the following compounds



Organic Chemistry – Some Basic Principles and Techniques Solved Examples

CONVERTINGA WEDGE-DASH FORMULA INTO FISCHER PROJECTION FORMULA

Step 1 : Decide the priority of groups by sequence rule.

Step 2 : Bring the lowest prior group to dash by even simultaneous exchanges.

Step 3 : Draw an arrow from first prior group to second prior group till third prior group.

Step 4 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

Step 5 : Draw the Fischer projection formula having equivalent configuration to the wedge-dash formula.

Examples :



Here the lowest prior group is already on dash, there is no need for exchanges.





ENANTIOMERS

Stereoisomers which are non-superimposable mirror images of each other are called enantiomers.

e.g. in all the following molecules there is no centre of symmetry or plane of symmetry. Therefore their two mirror image isomers are non-superimposable and hence enantiomers. **Ex.45** 2-Chlorobutane:



















PROPERTIES OF ENANTIOMERS

	Properties	Remarks
(1)	Molecular formula	Same
(2)	Structural formula	Same
(3)	Stereochemical formula (str. formula with orientation)	Different
(4)	Dipole moment	Same
(5)	Physical properties (m.p., b.p., density, solubility, refractive index etc.)	Same
	Chemical properties	
(6)	(a) with optically inactive compound	Same
	(b) with optically active compound	Different

RACEMIC MIXTURE

A mixture of equal amounts of enantiomers is called a racemic mixture or racemic modification. A racemic modification is always optically inactive when enantiomers are mixed together, the rotation caused by a molecule of one enantiomer is exactly cancelled by an equal and opposite rotation caused by a molecule of its enantiomer.

The prefix (\pm) is used to specify the racemic nature of the particular sample. e.g. (\pm) Lactic acid, (\pm) Alanine.

OPTICAL PURITY

Sometimes we deal with mixtures that are neither optically pure nor racemic mixture. In these cases we specify the optical purity of the mixture. It is defined as the ratio of its rotation to the rotation of pure enantiomer.

 \Rightarrow Optical purity

 $= \frac{\text{observed optical rotation}}{\text{optical rotation of pure enantiomer}} \times 100$

e.g. If we have some 2-butanol with observed rotation of +9.72, we compare this rotation with +13.5 rotation of the pure (+) enantiomer.

optical purity = $\frac{9.72}{13.5} \times 100 = 72\%$.

That means 72% is pure (+) 2-Butanol and 28% is (\pm mixture)

Total(+) isomer = 72 + 14 = 86%, (-) isomer = 14%

ENANTIOMERIC EXCESS

To compute the enantiomeric excess of a mixture we calculate the excess of predominant enantiomer as a percentage of the entire mixture. The calculation of enantiomeric excess gives the same result as the calculation of optical purity.

 \therefore optical purity = enantiomeric excess

$$= \frac{|\mathsf{d}-\ell|}{\mathsf{d}+\ell} \times 100$$

 $= \frac{\text{excess of one enantiomer over other}}{\text{entire mixture}} \times 100$

Thus for above example

optical purity = enantiomeric excess = $d - \ell = 72\%$ & $d + \ell = 100\%$ so $2d = 172 \Rightarrow d = 86\%$ & $\ell = 14\%$ (composition of mixture)

OPTICAL DIASTEREOMERS

The optical isomers which are neither mirror image nor superimposable to each other are called diastereomers. Diastereomers have different physical and chemical properties and they can be easily separated by physical methods.

e.g Let us consider the stereoisomers of 3-chlorobutan-2-ol



There are 4 stereoisomers of 3-chlorobutan-2-ol. In which (I & II) & (III & IV) are enantiomeric pairs. (I & III) or (I & IV) or (II & III) or (II & IV) all the isomers in each pair are neither mirror image nor superimposable to each other. Therefore these pairs are optical diastereomers.

MESO COMPOUND

A meso compound is one whose molecules are superimposable on their mirror images even though they contain chiral centres. A meso compound is optically inactive since it has a plane of symmetry. A meso compound is nonresolvable.

e.g. Let us consider the stereoisomers of 2, 3-Butanediol



In all the possible isomers I & II are enantiomers. But III & IV are not enantiomers since they have plane of symmetry they are superimposable to each other (all symmetrical compounds are superimposable to their mirror images).

Thus III & IV are identical & meso compounds.

Thus total stereoisomers of 2, 3-butanediol is 3. Two enantiomers and one meso isomer.

NUMBER OF OPTICAL ISOMERS

(STEREOISOMERS)

Nature of compound	No. of optical isomers (n = no. of chiral centres)
I : Compounds having dissimilar ends	2 ⁿ
II : Compounds having similar ends with even chiral centres	$2^{n-1} + 2^{\frac{n}{2}-1}$ (enantiomers = 2^{n-1} meso compounds = $2^{\frac{n}{2}-1}$)
III : Compounds having similar ends with odd chiral centres	2^{n-1} (meso isomers = $2^{\frac{n-1}{2}}$ enantiomers = $2^{n-1} - \frac{n-1}{2}$)

e.g. Let us draw the total isomers of

n = 3 (odd chiral centres with similar ends.)

Total isomers $= 2^{3-1} = 2^2 = 4$





REACTION OF CHIRAL MOLECULES WITH OPTICALLY ACTIVE REAGENT (OPTICAL RESOLUTION)

Resolution refers to the method of separating a racemic mixture into its enantiomeric constituents. A racemic mixture is allowed to react with another optically pure compound. This changes a racemic mixture into a mixture of diastereomers which have different melting and boiling point and solubilities. These can be separated from one another by conventional method of separation of compounds. The separated diastereomers is then broken down to give pure enantiomers. Suppose a racemic mixture (\pm) A is to be separated. It is reacted with an optically pure compound (+) B. Thus the schematic diagram for resolution will be.



Example:





(I) Case of allene :

(a) Allenes with even π bonds :

e.g.
$$a = C = C = c = b$$

the orbital diagram of this structure will be



Since the groups at the end of allene are in perpendicular plane, it will not show geometrical isomerism. The molecule lacks centre of symmetry as well as plane of symmetry. Overall the structure has molecular dissymmetry which is the sufficient condition for optical activity. The molecule will exist in two enantiomeric forms.



(b) Allenes with odd π bonds :

Organic Chemistry – Some Basic Principles and Techniques (IV) Case of ortho-ortho-tetrasubstituted biphenyls :



the orbital diagram of this structure will be



The groups at the end of allene structure lie in same plane (ZX plane). Therefore it will have a plane of symmetry (ZX plane). The molecules lacks molecular dissymmetry & it will not show optical activity hence optical isomerism. But the compound will exist in two geometrical diastereomeric forms.



(II) Case of spiranes : A similar case like allenes is observed in spiranes. The spiranes with even rings and different groups at terminal carbons show optical activity & optical isomerism, while the spiranes with odd rings shows geometrical isomerism.

(a) spiranes with even rings :



shows optical isomerism.

(b) spiranes with odd rings :



shows geometrical isomerism.

(III) Case of cycloalkylidene :





becomes non-planar at room temperature in order to have minimum electronic repulsion among the substituent. In this orientation (phenyl planes perpendicular to each other) the free rotation of C - C single bond is restricted and molecule shows optical activity due to molecular disymmetry. e.g.



COMPOUNDS HAVING CHIRAL CENTRES OTHER THAN CARBON

The tetrahedral atom with four different groups attached to it is a stereocentre (chiral centres). Thus when atom like nitrogen, phosphorous, sulphur, silicon, germanium has four different groups attached with them they are chiral and show optical activity & hence optical isomerism. e.g.



ASYMMETRIC NITROGEN AMINE INVERSION

Amines with all different groups attached to N-atom have chiral centres $(R_1R_2R_3\dot{N})$ as nitrogen atom. Since the geometry of the molecule is tetrahedral it has molecular dissymmetry. It will exist as two enantiomers but the two enantiomers of amines

Organic Chemistry – Some Basic Principles and Techniques rapidly **Newman projection :**

cannot be separated because they rapidly interconvert to each other. Therefore they always exist as racemic mixture.

e.g. Ethylmethyl amines CH₃NHC₂H₅.



Mirror plane

Interconvertible ethylmethylamine enantiomers (non resolvable)

CONFORMATIONAL ISOMERISM

Free rotation :

For defining free rotation let us consider the bonding in ethane.



We find that the σ -bond joining the carbon atoms is cylinderically symmetrical about the line joining the two carbon nuclei; if the energy does not differ much in different arrangements the molecule can rotate about this carbon-carbon σ bond, we describe this freedom to change by saying that there is free rotation about the carbon-carbon single bond.

Conformations:

Different arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations.

Conformational isomers :

There are infinite arrangement (conformations) which arise due free rotation around carbon-carbon σ bond, different conformations corresponding to energy minima are called conformational isomers. The conformational isomerism arises due to free rotation along a bond.

For conformational analysis, a special type of structural formula is convenient to use which is called newman projection formula and another type is a sawhorse formula.



To write newman projection formula we imagine ourselves taking a view from one carbon atom directly along the selected bond axis to the next atom. The front carbon and its other bonds are represented



Dihedral angle :

The angle between C - X and C - Y in X - C - C - Y when it is visualised along C - C bond.



Staggered, eclipsed and skew conformations :

(I) The staggered conformation of a molecule is that conformation where the dihedral angle between the bonds at each atom of carbon-carbon bond is 180°.

(II) In then eclipsed conformation the atoms bonded to carbons at each end of carbon-carbon bond are directly opposite to one another. The dihedral angle between them is 0°.



(III) Skew conformation : All conformations other than staggered or eclipsed are skew conformations.

Factors affecting stability of conformations :

(I) Angle strain : Any atom tends to have bond angles that match those of its bonding orbitals. For example 109°.28′ for sp³-hybridized carbon. Any deviation from "normal" bond angles are accompanied by angle strain.

(II) Torsional strain : Any pair of tetrahedral carbons attached to each other tend to have their bonds staggered for minimum repulsion between their bonds. Any deviation from the staggered conformation are accompanied by torsional strain.

(III) van der Waals strain : Non bonded atoms or groups that just touch each other i.e. they are about as far apart as the sum of their van der Waals raddii, attract each other. If brought any closer together they repel each other. Such crowding together is accompanied by van der Waals strain.

Conformational analysis of ethane :

Ethane molecule contains a carbon-carbon σ bond and each carbon is further attached to 3 H-atoms. It exists in two extreme conformations i.e.

- (i) eclipsed conformation
- (ii) staggered conformation



The potential energy barrier between the two conformations of ethane is about 12.5 kJ/mol.

The potential energy of ethane molecule is at a minimum for the staggered conformation, increase with rotation and reaches a maximum at the eclipsed conformation most ethane molecules, naturally exist in the most stable. staggered conformation. There are only three energy minima, that is ethane has only three conformers. Since they are indistinguishable they are degenerate.

Energy profile of Eclipsed and Staggered forms of ethane



Conformational analysis of butane :

If we consider rotation about the C2 - C3 bond of butane, we find that there are six important conformations shown as I - VI below :



Energy profile of conforminations of butane :



Strains and stability in n-butane				
Conformation of n-butane	dihedral angle (φ)	Torsional strain	vander Waal strain	Stability
I : Anti	180°	Absent	Absent	Maximum
II : Partially eclipsed	120°	Maximum	Present (between – CH₃ & – H grps)	Intermediate - 1
III : Gauche	60°	Absent	Present (between two – CH ₃ grps)	Intermediate - 2 (> Intermediate1)
IV : Fully eclipsed	0°	Maximum	Maximum (between two – CH ₃ grps)	Minimum

The stability order will be :

Anti > Gauche > Partially eclipsed > Fully eclipsed. n-Butane exists as **three conformational** isomers one anti (I) and two gauche (III & V). The gauche conformers III and V are mirror images of each other and hence are (conformation) enantiomers. Gauche conformations (III & V) and anti conformation (I) are not mirror images of each other and hence are conformational diastereomer n-butane spends the greater part of its time as the anti conformer, and divides the smaller part equally between the two gauche conformers. As a result of the rapid inter conversion these isomers can't be separated.

Case of intramolecular hydrogen bonding :

In case of $G - CH_2 - CH_2 - OH$, where G = -OH, - NH_2 , - F, - NR_2 , - NO_2 , - COOH, - CHO the Gauche form is more stable than the anti form due to intramolecular hydrogen bonding i.e.



stability : Gauche form > anti form.

REACTION MECHANISM

ORGANIC CHEMISTRY

The study of hydrocarbons and the compounds which would be thought of as their derivative.

NATURE OF COVALENT BOND

A **covalent bond** is formed by the progressive overlapping of two bonding orbitals. For the stable bond formation, the condition is that the electrons should have opposite spins.

SIGMA BOND (σ)

The molecular orbital formed by the overlapping of two s-atomic orbitals or one s-and one p-orbital is called a **sigma bond**. Overlapping of hybridised orbitals also leads to the formation of sigma bond. σ -bonds are stronger as they result from the effective axial overlapping.

Order of strength of σ -bond :-

(i) $sp^3-sp^3 > sp^3-sp^2 > sp^2-sp^2 > sp^2-sp > sp-sp$ (ii) $sp^3-s > sp^2-s > sp-s$
(iii) sp ³ -p>sp ² -p>sp-p
(iv) p-p>s-p>s-s

The relative energies of different orbitals :-

More is the s-character associated with the orbital less will be its energy $p > sp^3 > sp^2 > sp > s$

PI-BOND

The molecular orbital formed by the sideways overlapping of two p-atomic orbitals is called **Pi bond**.

Relative to σ -bond, π -bond is weaker as there is only partial overlapping in the later case.

 π -electrons are mobile. Hence π -bond is more reactive as compared to sigma bond. π -bond is always accompanied by the formation of a σ -bond.

HYBRIDISATION

In hybridisation phenomenon, the orbitals of different shapes, but almost of equal energies blend up to give the same number of new orbitals of another shape and of identical energies (give stronger, more directional and stable bonds) e.g. sp³, sp², sp

Example :-

1 2 3 4 5 1 2 3 4 (a) CH=C-CH=CH-CH₃ and (b) CH₂=C=CH-CH₃ (hybridisation state of carbon, number of σ and π -bonds)

(a)	C ₁ ,	C ₂ ,	C ₃ ,	C_4	C_5
	sp,	sp,	sp²,	sp^2	sp ³
σ	2,	2,	3,	3,	4
π	2,	2,	1,	1,	0
(b)	C ₁ ,	C_2	C ₃ ,	C_4	
	sp²,	sp,	sp²,	sp ³	
σ	3,	2,	3,	4	
π	1,	2,	1,	0	

GEOMETRY OF CARBON

Four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron with carbon atom situated at the centre (Le Bel and vant Hoff, angle 109°28').

The square pyramidal and square planar structures of carbon have not been accepted

BOND LENGTH

The distance between the nuclei of the two bonded atoms is termed as **bond length** e.g. C–C bond length

(i) $C_2H_6(1.54\text{\AA})$ (ii) $C_2H_4(1.34\text{\AA})$ (iii) $C_2H_2(1.20\text{\AA})$ (iv) $C_6H_6(1.39\text{\AA})$

Order of bond length

(i)
$$C-C > C-N > C - O$$

(ii) $C=C > C=N > C=O$
(iii) $C=C > C = N$
(iv) $-\frac{1}{c} - \frac{1}{c} - - -C = C - -C = C - C$
(v) $=C=C=>-C = C - C = C - C$
(vi) $\Rightarrow C-C=>C = C = C - C =$



(xiv) All the C–C bond distance in benzene are equal [1.39 Å] (resonance). In acetate ion both the C–O bonds are of equal length [1.26 Å] (resonance) Determination of bond length :

X-ray analysis, spectroscopy

Organic Chemistry – Some Basic Principles and Techniques BOND DISSOCIATION ENERGY

Bond energy may be defined as the energy released when two atoms get bonded or the energy needed to break the bond to form neutral atoms.

Example:

(i) C-C (80 k.cal-mole⁻¹) (ii) C=C (142 k.cal - mole⁻¹) (iii) C=C (190 k.cal-mole⁻¹) Order of bond energy :-(i) C=C > C=C>C-C (ii) H-H > O -H > C-H (iii) C=N > C=N > C-N (iv) C-Cl > C -Br > C-I (v) C-O (ketone) > C=O [CH₃CHO] > C=O [HCHO] | (vi) =C-H > = C-H > -C-H | (vii) C=O (CO₂) > C=S (CS₂) (viii) O=O > N = N (xi) O-H > N -H > C-O > C-N [110.6] [93.0] [85.5] [73.0] (k.cal-mole⁻¹]

Values of bond dissociation energy

(k.cal mole⁻¹)

С–Н [99.0]	N=N [100.3]
О–Н[110.6]	C=O (CO ₂) [192]
N–H [93.6]	C=O (ketone) [179]
С–О [85.5]	C=O[HCHO][166]
CCl [81.1]	C=N [147.2]
C–Br [68.0]	N=O [145.1]
C–I [51.1]	$C=S(CS_2)[128]$
O–F [45.2]	C≡C [200]
OCl[52.1]	C≡N [212.4]
O–Br [48.2]	C=C [142]
C–C [80]	О–О [119]

BOND ANGLE

The angle between two adjacent bonds, in a molecule is known as bond angle, e.g.

	Compound	Angle	Number
(i)	acetylene	H–C–C (180°)	two
(ii)	ethylene	H–C–C (120°)	six
(iii)	ethane	Н–С–С (109° 28')	twelve
(iv)	benzene	H C C C C C C C C C C C C C C C C C C C	eighteen
(v)	alcohol	R–O–H (105.5°)	one
(vi)	ether	R–O–R (110°)	one

COVALENT BOND BREAKING

- (1) Heterolysis, heterolytic fission or heterolytic cleavage
- (2) Homolysis, homolytic fission or homolytic cleavage

1. Heterolytic Fission

When the covalent bond breaks in such a way that the both the electrons of the bond pair remain with only one of the two atoms, the process is called **heterolysis** or **heterolytic fission** or **ionic fission** or **unsymmetrical fission** or **polar cleavage**.

Heterolysis of a sigma bond forms a cation and an anion as ionic intermediate species.

$$A : B \longrightarrow A + : B$$

or
$$A : B \longrightarrow A : + B$$

It is clear that heterolysis of a pi bond should form a bipolar species, as follows.

$$A = B \longrightarrow A - B$$
:

2. Homolytic Fission

When the covalent bond breaks in such a way that the electrons of the bond pair are distributed between the two atoms i.e. each atom gets a share of one electron, the process is called **homolysis** or **homolytic fission** or **nonionic fission** or **symmetrical fission** or **free radical cleavage**. Homolysis of a sigma bond forms free radical intermediate species

$$A:B \longrightarrow A\bullet + \bullet B$$

Homolysis of a pi bond forms a biradial intermediate species

$$A = B \longrightarrow \dot{A} - \dot{B}$$

CARBOCATIONS

When a carbon atom in an organic compound is covalently bonded to a more electronegative atom. Z, the bonding electrons are more shifted towards Z than carbon atom. Therefore, this covalent bond has greater tendency to undergo heterolysis in such a way that the electron pair goes to Z which develops negative charge while carbon atom develops positive charge as shown below

$$\xrightarrow{\delta \oplus}_{C} \xrightarrow{\delta \Theta}_{Z} \xrightarrow{Heterolysis} \xrightarrow{O}_{C} + :Z$$

The species formed by heterolysis of a covalent bond in an organic compound and having positively charged carbon atom is known as a **carbocation**

The positively charged carbon atom in an alkyl carbocation has six electrons in its outermost energy level and this carbon atom is in a state of sp^2 hybridisation. Due to sp^2 hybridisation, the geometry around the positive carbon atom is trigonal and the value of bond angles is 120° as shown below.



1. Type or carbocations

Carbocations are classified into three categories.

(i) Primary or 1° carbocations

- (ii) Secondary or 2° carbocations
- (iii) Tertiary or 3° carbocations

(i) Primary or 1° carbocations have positive charge on primary carbon atom. For example

[⊕]CH₃

Methyl carbocation

 $\mathrm{CH}_3-\overset{\scriptscriptstyle\oplus}{\mathsf{C}}\mathsf{H}_{_2}$

Ethyl carbocation

 $CH_3 - CH_2 - \overset{\oplus}{\mathsf{C}}\mathsf{H}_2$

n-Propyl carbocation

$$CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2$$

n-Butyl carbocation

CH₃

 $CH_3 - CH - \overset{\oplus}{C}H_2$

Isobutyl carbocation

(ii) Secondary or 2° carbocations have positive charge on secondary carbon atom. For example

CH₃-[⊕]_{CH}-CH₃

Isopropyl carbocation

 $\mathrm{CH}_{3} – \mathrm{CH}_{2} - \overset{\scriptscriptstyle\oplus}{\mathsf{C}}\mathsf{H} – \mathrm{CH}_{3}$

sec-Butyl carbocation

(iii) Tertiary or 3° carbocations have positive charge on tertiary carbon atom. For example

$$CH_3 - \overset{\bigoplus}{C} - CH_3$$
 (tert. Butyl carbocation)
I
CH_3

2. Stability of Carbocations

Carbocations are reactive due to positive charge on the carbon atom. Increase in positive charge increases their reactivity and decreases their stability. The order of stability of alkyl carbocations is as follows

Tertiary > Secondary > Primary

This order of stability is explainable on the basis of increase in the electron-donor (or + I effect due to hyperconjugation) with increase in the number of alkyl groups on the cationic carbon atom. as shown below





Isopropyl carbocation (Secondary)

Η		Ð
H		С
F	/	

Methyl
carbocation
(Primary)

(ii) Stability of Aryl Carbocations

The increase in the number of phenyl groups on the cationic carbon atom results in tremendous increase in the stability of the aryl carbocations. This is because of resonance due to which the positive charge of carbon atom gets delocalized to o-, p- and o –positions of the benzene rings.

$$(C_{6}H_{5})_{3}\overset{\oplus}{C} > (C_{6}H_{5})_{2}\overset{\oplus}{C}H > C_{6}H_{5}\overset{\oplus}{C}H_{2} > CH_{2}$$
$$= CH - \overset{\oplus}{C}H_{2} > 3^{\circ} > 2^{\circ} > 1^{\circ} > \overset{\oplus}{C}H_{3} (1^{\circ})$$

[Stability ∞ No. of resonating structures]

Examples: $\overset{\cdot}{\mathsf{C}}\mathsf{H}_3$, $\mathsf{CH}_3\overset{\cdot}{\mathsf{C}}\mathsf{H}_2$, $(\mathsf{CH}_3)_2\overset{\cdot}{\mathsf{C}}\mathsf{H}$, $(\mathsf{CH}_3)_3\overset{\cdot}{\mathsf{C}}$
3. Formation of carbonium ion

(i)
$$(CH_3)_3C$$
-Cl \rightarrow $(CH_3)_3C$ +Cl⁻

[Heterolytic fission]

(ii) CH₃OH
$$\xrightarrow{H^+}$$
 CH₃ $\overset{+}{O}$ H₂ $\xrightarrow{-H_2O}$ $\overset{+}{C}$ H₃
[Protonation]

(iii) $CH_3 - CH = CH_2 \xrightarrow{H^+} CH_3 - \overset{+}{C}H - CH_3$

[Protonation]

(iv) Abstraction of halide ion by lewis acid

$$CH_3 \longrightarrow Br + FeBr_3 \longrightarrow CH_3 + FeBr_4$$

Lewis acid

$$C_2H_5$$
 $(-CI) + AICI_3 - CH_3CH_2 + AICI_4$



(v) Removal of N₂ from diazonium cation

$$CH_3 \longrightarrow CH_3 + N_2$$

Reactions :

- (i) Nucleophilic substitution of 3° alkyl halide
- (ii) Markownikoff reaction
- (iii) Dehydration of alcohols
- (iv) Hydrolysis of acetyl chloride

Examples :-

Ethyl alcohol $\xrightarrow{\text{conc. } H_2SO_4}$ ethene

Mechanism

$$CH_{3}-CH_{2}OH \xrightarrow{H^{\oplus}} CH_{3}-$$

$$CH_{2}\overset{\oplus}{O}H_{2} \xrightarrow{-H_{2}O} CH_{3}- \overset{\oplus}{C}H_{2} \xrightarrow{-H^{\oplus}} CH_{2} = CH_{2}$$

Resonance in allyl carbocation :

$$CH_2 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow CH_2 CH_2 CH_2$$

| I wo su uctures |

Organic Chemistry – Some Basic Principles and Techniques Resonance in benzyl carbocation :



[Four structures]

Obviously benzyl carbocation is more stable as compared to allyl carbocation.

(ii) Stability ∞ Reduction of positive charge on the carbon



CARBANIONS

When a carbon atom is bonded to a more electron donor atom or group Z. in an organic molecule. The shared pair of electrons is more shifted towards the carbon atom. This bond during chemical reaction can undergo heterolysis in such a way that the electron pair remains with carbon atom and Z does not receive the share of the electron pair. Thus carbon atom acquires a positive charge and Z acquires a negative charge as shown below

$$C \mid -z \stackrel{\Theta}{\longleftrightarrow} C: + \overset{\Theta}{Z}$$

The organic species obtained as above, having negative charge on carbon atom is known as carbanion. The negatively charged carbon atom of a carbanion has eight electrons in its outermost energy level. The carbanion carbon atom of an alkyl carbanion is in a state of sp³ hybridisation. The geometry of the methyl carbanion is trigonal pyramidal similar to that of ammonia molecule.



1. Types of carbanions

(i) Primary Carbanions

⊝ CH₃	$\operatorname{CH}_{3}-\operatorname{\ddot{C}H}_{2}$	$CH_3 - CH_2 - \ddot{C}H_2$
Methyl	Ethyl	n-propyl
carbanion	carbanion	carbanion

(ii) Secondary Carbanions

⊖	©
CH ₃ −ĊH−CH ₃	CH ₃ −CH ₂ −CH ₂ −CH ₃
Isopropyl carbanion	sec-Butyl carbanion

(iii) Tertiary Carbanions

$$CH_3 - \ddot{C} - CH_3$$

|
 CH_3
tert-Butyl carbanion

2. Stability of Carbanions

Carbanions are reactive due to negative charge on the carbon atom. Increase in negative charge increases their reactivity and decreases their stability. Similarly decrease in negative charge decrease the reactivity of the carbanions and increases their stability. If the hydrogen atom present on the negatively charged carbon atom of a carbanion is substituted by an electron-donor group. There is an increase in the electron density on the carbanion carbon and thus decrease in the stability.

 $\stackrel{\Theta}{:CH_{3}}$ > 1° > 2° > 3°

Examples : CH_3 , $(CH_3)_2 CH, CH_3 CH_2$, CH_2CHO

(i)
$$\overset{\Theta}{\mathsf{C}}\mathsf{H}_3 > \mathsf{C}\mathsf{H}_3 \overset{\Theta}{\mathsf{C}}\mathsf{H}_2 > (\mathsf{C}\mathsf{H}_3)_2 \overset{\Theta}{\mathsf{C}}\mathsf{H} > (\mathsf{C}\mathsf{H}_3)_3 \overset{\Theta}{\mathsf{C}}$$

Explanation :- Stability of alkyl carbanions can be explained by inductive effect. Greater the number of alkyl group [+ I effect] attached to the carbon atom bearing negative charge, lesser is the stability.

 $3^{\circ} < 2^{\circ} < 1^{\circ} < \overset{\scriptscriptstyle \Theta}{\mathsf{CH}}_{2}$

(ii)
$$\overset{\Theta}{\mathsf{C}}\mathsf{H}_2 - \mathsf{NO}_2 > \overset{\Theta}{\mathsf{C}}\mathsf{H}_2 - \mathsf{CHO}$$

(iii)
$$+ - - \overset{\Theta}{\mathsf{C}}\mathsf{H}_2 < - + - \overset{\Theta}{\mathsf{C}}\mathsf{H}_2$$

(iv)
$$\overset{\Theta}{\mathsf{CH}}_2 - \mathsf{CHO} > \overset{\Theta}{\mathsf{CH}}_3$$

(v)
$$\overset{\Theta}{C}H_2 - CH_2 - NO_2 > CH_3 - \overset{\Theta}{C}H - NO_2 > (CH_3)_2 \overset{\Theta}{C}H$$

$$(vi) F - \overset{\Theta}{C}H_2 > CI - \overset{\Theta}{C}H_2$$

(vii) Resonance exists in ${}^{\circ}_{C}H_2$ -C=N, hence it is stable carbanion

$$\begin{array}{c} & & \\ & &$$

(viii) Carbanion in which negative charge and double bond are in conjugation

Note : Carbanions are nucleophile

3. Formation of Carbanion

(i)
$$\overset{\circ}{O}H + H \longrightarrow \overset{\circ}{C}H_2 \longrightarrow CHO$$

(ii)
$$C_2H_5$$
 $H \longrightarrow CH_2COOC_2H_5 + C_2H_5OH$

Reactions :

- (i) Aldol condensation
- (ii) Claisen condensation
- (iii) Decarboxylation

Example:

$$RCOOH \xrightarrow{\text{soda-lime}} RH$$

ORGANIC FREE RADICALS

When a carbon atom in an organic compound is covalently bonded to an atom or a group. Z which is electroneutral or very weakly electron-donor or very weakly electron-acceptor. The electron pair of the covalent bond is almost equally shared by C and Z. Such a covalent bond has a tendency to undergo homolysis during chemical reaction to form electroneutral species. Each having one unpaired electron and are known as **free radicals**. The reactive intermediate organic species having an odd or unpaired free electron on a carbon atom is called an **organic free radical**.

Example

$$H \xrightarrow{H} C - Z \iff H \xrightarrow{H} C \cdot + Z \cdot$$

Example

 $-C \cdot, CH_{3} \cdot, (C_{6}H_{5})_{3} C \cdot, CH_{2} = CH-CH_{2} \cdot, (CH_{3})_{2} CH \cdot, CH_{3}CH_{2} \cdot$

1. Formation of free radicals

(i)
$$Cl_2 \xrightarrow{hv} Cl \cdot + Cl \cdot [Homolytic fission]$$

(ii) $CH_3COCH_3 \xrightarrow{hv} CH_3 \cdot + CH_3CO \longrightarrow CO + \cdot CH_3$
(iii) $(C_2H_5)_4 Pb \xrightarrow{140^{\circ}C} Pb + 4C_2H_5 \cdot$
(iv) $CH_3 - N = N - CH_3 \rightarrow N_2 + 2CH_3 \cdot$
(v) $C_6H_5 - \overset{O}{C} - O - O - \overset{O}{C} - C_6H_5$
 $\xrightarrow{\Delta} 2C_6H_5COO \cdot \rightarrow 2C_6H_5 \cdot + 2CO_2$
(vi) $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH + HO \cdot$
[Fenton's reagent]
(vii) $RCOO^- \xrightarrow{anode} RCOO \cdot + e \longrightarrow R \cdot + CO_2$

Salient features

(i) Free radical reactions are catalyzed by light, heat etc.

(ii) Free radical reactions proceed in vapour phase or in nonpolar solvents.

(iii) Free radical reactions are frequently autocatalytic

- (i) Chlorination of alkanes
- (ii) Pyrolysis of alkanes
- (iii) Wurtz reaction
- (iv)Anti-Markownikoff rule
- (v) Kolbe electrolytic synthesis
- (vi) Polymerisation initiated by free radical

Example

 $CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$ Step - I [initiation]

$$Cl_2 \longrightarrow Cl_{\bullet} + Cl_{\bullet}$$

Step - 2 [propagation]

 $CH_4+Cl \bullet \longrightarrow CH_3 \bullet + HCl and CH_3 \bullet +$

$$Cl_2 \longrightarrow CH_3Cl + Cl$$

Step-3 [termination] $Cl \cdot + Cl \cdot \rightarrow Cl_2$ or $CH_3 \cdot + CH_3 \cdot \rightarrow CH_3 - CH_3$

or $CH_3 \cdot + Cl \cdot \rightarrow CH_3 - Cl$

2. Order of stability of free radicals

$$\begin{aligned} (C_6H_5)_3 C \bullet > (C_6H_5)_2 CH \bullet > C_6H_5 CH_2 \bullet > CH_2 \\ = CH - CH_2 \bullet > 3^\circ > 2^\circ > 1^\circ > CH_3 \bullet \end{aligned}$$

Explanation – Lesser is the bond dissociation energy, greater is the ease with which the free radical is formed (greater its stability)

 $\begin{array}{l} \mathrm{CH}_{3}-\mathrm{H} \rightarrow \mathrm{CH}_{3} \bullet + \mathrm{H} \bullet \ ,\\ \Delta\mathrm{H}=435 \mathrm{kJ} \\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{H} \rightarrow \mathrm{CH}_{3}-\mathrm{CH}_{2} \bullet + \mathrm{H} \bullet \ ,\\ \Delta\mathrm{H}=411 \mathrm{kJ} \\ (\mathrm{CH}_{3})_{2} \mathrm{CH}-\mathrm{H} \rightarrow (\mathrm{CH}_{3})_{2} \mathrm{CH} \bullet + \mathrm{H} \bullet \ ,\\ \Delta\mathrm{H}=395 \mathrm{kJ} \\ (\mathrm{CH}_{3})_{3} \mathrm{C}-\mathrm{H} \rightarrow (\mathrm{CH}_{3})_{3} \mathrm{C} \bullet + \mathrm{H} \bullet \ ,\\ \Delta\mathrm{H}=381 \mathrm{kJ} \end{array}$

It is apparent that 3° free radical is formed easily.

Order of the potential energy of the free radicals

t-butyl < isopropyl < ethyl < methyl

Stability on the basis of resonance

Stability ∞ Number of resonating structures

Triphenyl methyl free radical has the maximum number of resonating structures. Hence it is the most stable free radical

Resonance in allyl free radical

$$CH_2 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow CH_2 CH \longrightarrow CH_2$$

Resonance in benzyl free radical :



Geometry 3.

(i) Trigonal planar



- $(CH_3)_3$ \dot{C} or $(C_6H_5)_3$ \dot{C} $[sp^2]$
- (ii) Planar : $CH_2 = \dot{C} CH_2 [sp^2]$

(iii) Free radicals are electrophiles

INTERMEDIATE CARBENE SPECIES

The central carbon atom of a carbene species is neutral or uncharged. This carbon atom has two sigma bonds and two nonbonding electrons. i.e. there are six electrons or an incomplete octet in its outermost energy level.



Example-1: Photolysis of diazomethane forms a carbene species, called methylene intermediate.

$$\mathsf{CH}_2\mathsf{N}_2 \xrightarrow{ \ \mathsf{hv} } :\!\! \mathrm{CH}_2 \!+\! \mathsf{N}_2$$

Example-2: Reaction of metallic zinc on methylene dibromide or diiodide also forms methylene intermediate

$$CH_2Br_2 \xrightarrow{hv} : CH_2 + ZnBr_2$$

The carbon atom of the methylene intermediate referred to in the above two examples has two bond pairs and two nonbonding electrons. The two odd electrons occupy two separate orbitals and have parallel spins. Therefore such a methylene species may be regarded as a **biradical** that can act as a normal free radical in two steps as follows

- + •Z \longrightarrow •CH₂ –Z (i) $\bullet CH_2 \bullet$ Intermediate
- biradical radical free radical (ii) $\bullet C \dashv - 7 +$ •7

Free

$$(II) \bullet CH_2 = Z \quad f \quad \bullet Z \longrightarrow Z = CH_2 = Z$$

Product

 $CH_2 = C = O \xrightarrow{\Lambda} : CH_2 + CO$ Example-3 ketene

Methylene

Example-4
$$CCI_3 + 4$$

 $OH \rightarrow H_2O + :CCl_2$;

Two forms of carbenes

 $: \overline{C}Cl_3 \rightarrow : \overline{C}l + : CCl_2$



Reactions

(i) Hofmann carbylamine reaction

(ii) Riemer Tiemann reaction

(iii) Formation of cyclopropane from ethene and diazomethane

Example

$$\begin{array}{rcl} \mathrm{CH}_{2}\mathrm{N}_{2} \rightarrow & : \mathrm{CH}_{2} + \mathrm{N}_{2} \\ \mathrm{CH}_{2} = & \mathrm{CH}_{2} + : \mathrm{CH}_{2} \rightarrow & \overset{\mathsf{CH}_{2}}{\swarrow} & \overset{\mathsf{CH}_{2}}{\swarrow} & \overset{\mathsf{CH}_{2}}{\swarrow} \end{array}$$

INTERMEDIATE NITRENE SPECIES

In a nitrene species the central nitrogen atom is neutral i.e. it bears no charge. This neutral nitrogen atom has one sigma bond and two lone pairs, i.e. a total of six electrons in three pairs in its outermost energy level. In order to complete its octet the nitrogen atom of a nitrene species tries to acquire two electrons from somewhere and form a covalent bond thereby behaves as an electrophile.

— N: Partial structure Formula of Nitrenes

Example -

Reaction : Hofmann bromide reaction.

Formation - Amide + bromine + caustic potash

$$CH_{3} \xrightarrow{C} NH_{2} + Br_{2} + 2\bar{O}H \xrightarrow{O}$$

$$H_{3} \xrightarrow{O} N : + 2H_{2}O + 2\bar{B}r^{\Theta}$$

$$H_{3} \xrightarrow{O} N : + 2H_{2}O + 2\bar{B}r^{\Theta}$$

(Acylnitrene)

Rearrangement



ELECTROPHILICAND NUCLEOPHILIC REAGENTS





Nucleophile

Electrophile

Electrophile 1.

 $A - B + \overset{\scriptscriptstyle\oplus}{X} \to A - X + \overset{\scriptscriptstyle\oplus}{\mathsf{B}}$

$\mathbf{\tilde{x}}$ - Electrophile

These are positively charged ions or neutral molecules containing electron deficient atom. They are Lewis acids.

Examples : Positively charged species

$$\overset{+}{H}$$
, $\overset{+}{C}H_3$, H_3O^+ , $\overset{+}{N}O_2$, $\overset{+}{N}O$, $\overset{+}{B}r$, $C_6H_5\overset{+}{N}_2$,
 $CH_3\overset{+}{C}O$, $CH_3\overset{+}{N}_2$

Neutral Species :

Starred atom :

Note : In *I-Cl, chlorine is more electronegative than iodine [EN(Cl) > EN(I)] as such an electron deficient centre is created on iodine indicated by star.

For SO₂, electrophilic nature can be understood by its structure.



Clearly a positive centre is developed at the site of the sulphur atom.

2. Nucleophile

$$\mathbf{A} - \mathbf{B} + \stackrel{\Theta}{\mathbf{Y}} \longrightarrow \mathbf{A} - \mathbf{Y} + \stackrel{\Theta}{\mathbf{B}}$$

Y-Nucleophile

These are negatively charged ions or neutral molecule with unshared pair of electrons. They are electron rich or Lewis bases.

Examples - Negatively charged ions

 $\mathring{C}I$, $\mathring{B}r$, \mathring{I} , $\mathring{O}H$, $\mathring{C}N$, $\mathring{O}R$, $R\mathring{S}$, $\mathring{C} \equiv CH$, $N\mathring{O}_2$, $HS\mathring{O}_4$ Neutral Species - NH_3 , $R - NH_2$, R_2NH , R_3N . H_2O , ROH R_2O , R_2S Starred atom: $C_{2}H_{5}Li$, $C_{2}H_{5} - MgBr$,

3. Reaction

In fact the reaction is the mutual attack of an electrophile on nucleophile or vice-versa.

electrophile + nucleophile \rightarrow product

$$(CH_3)_3 \overset{\oplus}{\mathsf{C}} + \overset{\Theta}{\mathsf{O}}_{\mathsf{H}} \rightarrow (CH_3)_3 - OH$$

t-butyl alcohol

 $C_{H_3}^{\oplus} + {}_{CN}^{\Theta} \rightarrow CH_3CN$

methyl cyanide

$$\mathrm{CH}_{3} - \overset{\oplus}{\mathrm{CH}}_{2} + :\mathrm{NH}_{3} \to \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{NH}_{2} + \overset{\oplus}{\mathrm{H}}$$

ethylamine

4. The strength of electrophile follows the order

(i)
$$\overset{+}{C}H_{3} > CH_{3}\overset{+}{C}H_{2} > (CH_{3})_{2}\overset{+}{C}H > (CH_{3})_{3}\overset{+}{C}$$

(ii) $\overset{+}{N}O_{2} > \overset{+}{N}O$ (iii) $\overset{+}{C}I > \overset{+}{B}r > \overset{+}{I}$

5. The strength of nucleophile follows the order

(i) $\bar{O}C_2H_5 > \bar{O}H > CH_3CO\bar{O}$

(ii)
$$I^- < Br^- < Cl^-$$

(iii) $CH_{3}^{-} > NH_{2}^{-} > OH^{-} > F^{-}$

6 Electrophile and nucleophile at a glance

S.No.	Electrophile	Nucleophile
1.	Accepts the	Supplies the
	electron pair	electrons pair
2.	Electron deficient	Electron rich
3.	Attacks the points	Attacks the
	of high electron	point of low
	density	electron density
4.	Lewis acid	Lewis base
5.	Possesses an	Possesses an
	empty orbital to	electron pair
	receive the	which is loosely
	electron pair	held and can be
		supplied easily
6.	Usually positively	Usually
	charged	negatively
	species	charged
	-	species
7.	Forms an extra	Increases its
	bond with the	covalency by
	nucleophile	oneunit

Electron displacement along a carbon chain due to the presence of an attached substituent is known as inductive effect. It is a permanent effect and decrease rapidly with the length of carbon chain.

C-C-C-C-Z 4 3 2 1

1. Inductive effect is of following types -

(i) Negative Inductive Effector - I Effect

Some atoms or groups have a greater tendency to attract the shared electron of the covalent bond. Such atoms or groups acquire partial negative charge by receiving electron density from the covalent bonds of the chain. Therefore, these are classified as the groups exerting **negative inductive (–I) effect**. For example

$\stackrel{\oplus}{NH}_3$, $\stackrel{\oplus}{NR}_3$, $-NO_2$, $-C=N$, $-COCI$, $-COOH$
–CHO , –COOR, –F, –Cl, –Br, –I, –C≡CH
-CH=CH ₂ , -CO-R, -OH, -SH, -NH ₂ , -NHR,
$-NR_2$, $-NH-CO-R$, $-CF_3$, $-CCl_3$, etc.

The decreasing order of negative inductive effect of some important atoms and groups is given below

Order of - I effect

 $\begin{array}{l} \stackrel{\oplus}{-\mathsf{NH}_3} > \stackrel{\oplus}{\mathsf{N}}(\mathsf{CH}_3)_3 > -\operatorname{NO}_2 > -\operatorname{C} \equiv \!\! \mathrm{N} > -\!\! \mathrm{F} > -\!\! \mathrm{Cl} \\ > -\!\! \mathrm{Br} > -\!\! \mathrm{I} > -\!\! \mathrm{CF}_3 > -\!\! \mathrm{CCl}_3 > -\!\! \mathrm{OH} > -\!\! \mathrm{OCH}_3 > - \\ \operatorname{C}_6 \!\! \mathrm{H}_5 > -\!\! \mathrm{H} \end{array}$

(ii) Positive Inductive Effect or +I Effect

Some groups are electron donor and therefore acquire partial positive charge by increasing electron density in the covalent bonds of a chain. Such groups exert **positive inductive (+I) effect**. Alkyl radicals are the best examples of this type of groups.

The decreasing order of positive inductive effect of some alkyl groups with respect to hydrogen is given below.

Order of +I Effect

 $(CH_3)_3C \rightarrow (CH_3)_2CH \rightarrow CH_3CH_2 \rightarrow CH_3 \rightarrow H 3^{\circ}$ 2° 1° 1°

- 2. **Examples** [applications] :-(i) $HCOOH > CH_{,}COOH$ (ii) $CCl_2COOH > CHCl_2COOH >$ $CH_2CICOOH > CH_2COOH$ (iii) $CH_3CH_2CHCOOH > CH_2CH_2COOH$ (iv) $CH_2CH_2OH > CH_2CH_2OH$ CI (v) p-Nitrophenol > Phenol $(vi) CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$ (vii) $CH_2CH_2OH > CH_2CH_2OH > CH_2CH_2OH$ F CI Br (viii) HCOOH > CH, COOH > $C_{2}H_{5}COOH > n-C_{3}H_{7}COOH$
- 3. Order of basic character :-

(i) $NH_3 > CINH_2$ (ii) $(CH_3)_2NH > CH_3NH_2$ (iii) $C_2H_5NH_2 > C_6H_5NH_2$

4. Other examples :-

(i) Order of acid strength : CH₄ < CH₃I < CH₃Br < CH₂CH < CH₃F

 (ii) Order of acid strength of β-halo acids
 β-fluoroethyl alcohol > β-chloroethyl alcohol >
 β-bromoethyl alcohol
 (iii) Order of acid strength of aromatic alcohols
 : p-nitrobenzyl alcohol > benzyl alcohol

(iv) Order of acid strength in water

- (a) $\text{HCCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CH}_3\text{Cl} > \text{CH}_4$
- (b) $HCOOH > CH_3OH > CH_4$

Solved Examples

Ex.50 Why is formic acid stronger than acetic acid?

Sol. In formic acid, COOH group is bonded to the hydrogen atom, which does not exert any inductive effect. In acetic acid, COOH group is bonded to a methyl group, which exerts +I effect. The acetate ion formed due to ionisation of acetic acid is more reactive due to increase in the electron density on oxygen atom. This makes acetate ions react faster with hydrogen ions shifting the equilibrium in backward direction. Thereby decreasing the concentration of hydrogen ions. Therefore acetic acid is weaker than formic acid.

- **Ex.51** Discuss the decreasing order of acid strength of trihalogenated derivatives of acetic acid.
- **Sol.** The acid strength of the trihalogenated acetic acids increases with increase in the –I effect of the halogen substituents. Three fluorine atoms have greater –I effect than the other three halogens. Therefore trifluoroacetic acid ionises more than the other analogues. Thus, the decreasing order of acid strength is as follows

$$\label{eq:CF3} \begin{split} CF_3 & -COOH > CCl_3 - COOH > CBr_3 - COOH > \\ & CI_3 - COOH \end{split}$$

- **Ex.52** Discuss the relative order of acid strength of acetic acid and benzoic acid.
- Sol. Benzoic acid is a stronger acid than acetic acid. This is because methyl group present in acetic acid has a weak donor (+I) effect and phenyl group present in benzoic acid has a weak acceptor (–I) effect

 $C_6H_5 \rightarrow COOH > CH_3 \rightarrow -COOH$

5. Comparison of Base strength

Aliphatic amines are stronger bases than aromatic amines. The basic behaviour of amines is due to availability of lone pair of electrons present on the nitrogen atom. The positive inductive effect of methyl group increases electron density on nitrogen atom, due to which electron pair on nitrogen atoms is more readily available to the attacking acid. Therefore, alkylamines are more basic than ammonia. In aromatic amines, the NH₂ group is bonded to the aromatic ring, which exerts a weak –I effect. That is why, aniline is a weaker base than ammonia.

$$\begin{split} R & \longrightarrow - NH_2 & > H - NH_2 \\ & > C_6H_5 - \leftarrow NH_2 \\ (+I \, effect \, of \, R) & (No \, effect \, of \, H) \\ & (-I \, effect \, of \, C_6H_5) \end{split}$$

However, the major cause of much lower base strength of aniline than ammonia is resonance. A partial positive charge develops on the nitrogen atom of aniline due resonance, thereby the availability of electron density on nitrogen atom in aniline decreases.

Organic Chemistry – Some Basic Principles and Techniques Solved Examples

ELECTROMERIC EFFECT

Transfer of an electron pair from one location to the other in the structural formula of an organic compound under the influence of a reagent, is known as **electromeric effect**. Electromeric effect is a temporary effect that does not take place of its own, but occurs on the demand of the attacking reagent. This effect vanishes on the completion of the reaction. The electromeric effect is symbolized by a curved

arrow (\bigcap). Electromeric effect can normally take place in the following three ways

(a) Transfer of pi electron pair to the adjacent atom in the form of nonbonded electron pair

In the above representation, the two electrons of the pi bond situated between atoms A and B get transferred to atom B as lone pair.

(b) Transferred of nonbonded electron pair to the same atom in the form of pi electron pair

(c) Transfer of pi electron pair to the adjacent atom in the form of pi electron pair

RESONANCE

Many polyatomic molecules and ions having pi bonds can be represented by more than one structural formula. But none of these structural formulae truly stands for that molecule or ion. because none of them can explain its properties. These hypothetical or nonexistent structural formulae are known as resonating structures or contributing structures or **canonical structures**. The actual or existent structure is the hybrid of all the canonical structures and is called resonance hybrid structure. This property is known as resonance, In resonance, the positions of the nuclei of the atoms do not change, but the pi electrons are continuously moving or delocalized. Thus, the delocalization of pi electrons is the cause of resonance. Since the pi electrons constantly move, it becomes more difficult for the reagent to attack then and therefore the molecule or ion undergoing resonance acquires greater stability. This is called **resonance stabilization**.

Ex.53 Indicate resonating structural formulae of carbon dioxide

1. Resonance Energy

Due to resonance, the per mole energy of the resonance hybrid of a molecule or ion is less than the per mole energy calculated for the most stable of the canonical structures. This energy difference is known as **resonance energy**. Higher the value of resonance energy, greater is the resonance stabilization.

Solved Examples

- **Ex.54** What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene
- **Sol.** The values of resonance energy for benzene, naphthalene and anthracene are 36, 76 and 85 Kcal per mole respectively. It is clear from these values that the resonance stabilisation of naphthalene is more than that of benzene and less than that of anthracene. Thus, the increasing order of resonance stabilisation is as follows.



2. Resonance Effect or Mesomeric Effect (R or M Effect)

When an atom or a group of atoms or a substituent present in a molecule exerts electromeric displacement of a $\dot{p}i$ electron pair or a lone pair and thus initiates resonance in the rest of the molecule. The phenomenon is known as **Mesomeric effect or resonance effect**. The electron pair donor substituent is said to exert positive resonance (+R) effect or positive mesomeric (+M) effect. The electron pair acceptor substituents are said to exert negative resonance (-R) or negative mesomeric (-M) effect.

(i) Groups Exerting +R or +M Effect

Following are a few examples of the groups exerting positive mesomeric effect.

-OH, -NH₂, -OR, -NHR, -NR₂, -O, -CH₂, -Cl If a +M group is present on benzene ring, it increases electron density on o-and p-location, due to which the attacking electrophile largely forms a mixture of o- and p- electrophilic substitution products. Therefore in aromatic electrophilic substitution reactions, the groups exerting +M effect are mainly o- and p- directing, as illustrated below by taking the example of phenol.



A mixture of $o_{-} + p_{-} S_{E}$ products

(ii) Groups Exerting –R or –M effect

Following are a few examples of groups exerting negative mesomeric effect.

When a substituent exerting -M effect is bonded to the benzene nucleus, it reduces electron density at the ortho and para locations. Therefore, the electrophile cannot attack the positively charged ortho and para positions, but can collide with the electroneutral meta position slowly. Hence, in aromatic electrophilic substitution reactions the groups exerting -M effect exhibit meta-directing influence. This is illustrated below by taking the example of nitrobenzene.







Resonance hybrid structure m-SE product

Few points [M and R effect]

This effect operates in unsaturated molecules in which ► - There is a conjugated system of double bond.

- Negative charge is in conjugation with double (or multiple) bond.

- Lone pair of electron in conjugation with double (or multiple) bond.

- There is complete transfer of electron pair during the operation
- The reactivity of compounds is affected by the presence of

 $-NO_2$, $-C \equiv N$, > C = O, -CI, NH_2 etc. groups.

There is relay of π -electron from one end to the ► other end through a conjugated system of double bond.

Other Illustrations :

Π

 \therefore III < II < I

Order of stability of canonical forms :

(a) Vinyl chloride :

$$H_{2}C=CH - \ddot{C}I: \longleftrightarrow$$

$$I$$

$$H_{2}\overset{\Theta}{C} - CH = \overset{\oplus}{C}I: \longleftrightarrow H_{2}\overset{+}{C} - CH = \ddot{C}I:$$

$$II$$

$$III - least stable \quad [carbon is electron deficient]$$

$$II - less stable \quad [charge separation]$$

$$I - stable \quad [no charge separation]$$

HYPERCONJUGATION OR BAKER-NATHAN EFFECT

In an organic molecule, the transfer of a sigma electron pair (heterolysis) or a single electron from a sigma bond (homolysis) may also be responsible for initiation of resonance in the rest of the molecule. This is referred to as **hyperconjugation** or **Baker-Nathan effect**. It was also called **no-bond resonance** because in the canonical structure of the molecule, no bond is shown between the two atoms from where the sigma electrons/s has/ have been transferred. It can also be called σ , π -**conjugation** because a sigma electron/s is/are transformed into a pi pair in this type of resonance. However, for the first time, **Mulliken** in 1941 gave the name hyperconjugation to this phenomenon.

Solved Examples

In the above structural part (I), the sigma electron pair present between H and C–1 atoms shifts between C–1 and C–2 atoms as pi electron pair. Simultaneously, the pi electron pair present between C-2 and C-3 shifts to C-3 as a lone pair. As a result of these electron pair transfers. positive charge develops on hydrogen atom and negative charge develops on C-3 atom. Note that no bond is shown between H and C–1 atom in the canonical structural formula (II)

1. Applications of Hyperconjugation

(a) Explanation of Electron Donor Property of Alkyl Radicals

The cause of electron donor effect or +I effect of alkyl radicals is actually hyperconjugation.



<u>Organic Chemistry – Some Basic Principles and Techniques</u> (b) Explanation of Order of Stability of Alkyl Carbocations

The stability of alkyl carbocations decreases in the order $3^\circ > 2^\circ > 1^\circ$. For example

$$(CH_3)_3 \overset{\oplus}{\mathsf{C}} > (CH_3)_2 \overset{\oplus}{\mathsf{CH}} > CH_3 - \overset{\oplus}{\mathsf{CH}}_2 > \overset{\oplus}{\mathsf{CH}}_3$$

Larger the number of locations for delocalisation of the positive charge in the structural formula of the carbocation, lower is the reactivity or higher is the stability of that carbocation.

Methyl carbocation is least stable amongst alkyl carbocations, because of only one possible location for positive charge. Thus, methyl carbocation has only one structural formula

Ethyl carbocation is more stable than methyl carbocation, because of four possible locations for its positive charge i.e., one carbon atom and three α -hydrogen atoms. Thus, ethyl carbocation can be represented by the following four structural formulae.



(c) Explanation of Stability of Alkyl Free Radicals

The stability of alkyl free radicals is also similar to that of alkyl carbocations. i.e. $3^\circ > 2^\circ > 1^\circ$, because here also methyl, ethyl, isopropyl and tert-butyl free radicals can also be represented by one, four, seven and ten structural formulae. respectively.

$$(CH_3)_3 \overset{\bullet}{C} > (CH_3)_2 \overset{\bullet}{C} H > CH_3 - \overset{\bullet}{C} H_2 > \overset{\bullet}{C} H_3$$

STERIC HINDRANCE

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result that the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called steric hinderance.

Example :-

1. $(C_2H_5)_3 N \supseteq$ is less basic than $(CH_3)_3 N \supseteq$ Protonation easier : (Smaller size of CH₂ group)

$$\begin{array}{c} \mathsf{CH}_{3} \\ | \\ \mathsf{CH}_{3} - \overset{\mathsf{N}}{\underset{\mathsf{N}_{3}}{\mathsf{N}}} \xrightarrow{\mathsf{+H}^{+}} \\ | \\ \mathsf{CH}_{3} \end{array} \xrightarrow{\mathsf{CH}_{3}} [(\mathsf{CH}_{3})_{3}] \operatorname{N-H}]^{+}$$

Protonation difficult : [Bigger size of CH₃CH₂ group]⁺

$$CH_{3}CH_{2} \xrightarrow{\mathsf{CH}_{2}CH_{3}} \overset{\mathsf{H}^{*}}{\underset{\mathsf{CH}_{2}CH_{3}}{\overset{\mathsf{H}^{*}}{\overset{\mathsf{H}^{*}}{\longrightarrow}}} [(CH_{3}CH_{2})_{2}N - H]^{*}$$

ORGANIC REACTIONS AND MECHANISM

Types of reaction :-

- Organic substrate + Reagent \rightarrow Product Mainly four types of reactions are
- (a) Substitution
- (b)Addition
- (c) Elimination
- (d) Rearrangement or isomerisation

1. Substitution Reaction

It involves replacement of one substituent by another

$$A - B + x - y \rightarrow A - x + B - y$$



Organic Chemistry – Some Basic Principles and Techniques Example :

$$S_N$$
, $CH_3Br + CN^- \rightarrow CH_3CN + Br$
 S_E , $C_6H_6 + Br^+ \rightarrow C_6H_5Br + H^+$
 S_E , $CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$

(i) S_N reaction or nucleophilic substitution reaction

$$\stackrel{\scriptscriptstyle \delta^+}{\mathsf{R}} \xrightarrow{\to} - \stackrel{\scriptscriptstyle \delta^-}{\mathsf{X}} + \stackrel{\scriptscriptstyle \Theta}{\mathsf{N}} u \ \xrightarrow{\to} \ \mathsf{R} - \mathsf{N} u + \stackrel{\scriptscriptstyle \oplus}{\mathsf{X}}$$

alkyl halide nucleophile

Here : R-alkyl group X⁻ - leaving group

(halide ion)

Nu : attacking species [It is a weaker nucleophile, being conjugate base of hydrohalic acid]

Example:



(a) $[S_N 1]$ or unimolecular nucleophilic Substitution Reaction

[substrate–3° or tertiary halide]

Alkaline hydrolysis of tertiary butyl chloride

 $(CH_3)_3 C - Cl + OH^- \rightarrow (CH_3)_3 C - OH + \overline{C}I$

Mechanism

Step - 1 (Slow)

$$(CH_3)_3 C - Cl \rightarrow (CH_3)_3 \overset{\oplus}{C} + \overset{\Theta}{Cl}$$

Step - 2 (fast)

$$(CH_3)_3 \stackrel{\oplus}{\mathsf{C}} + OH^- \rightarrow (CH_3)_3 C - OH$$

t-butyl alcohol

Rate equation :-

V = k [t - butyl halide] Molecularity - 1,

Note :- Here the carbonium ion is planar [sp² hybridised] The nucleophile can attack the planar carbonium on either side to give t-butyl alcohol.



If the three groups attached to positively charged carbon are different than the product will be racemic.

(b) $[S_N 2]$ or Bimolecular Nucleophilic Substitution Reaction

[substrate-methyl or 1° halide]

Alkaline hydrolysis of methyl chloride : $CH_3Cl + OH^ \rightarrow CH_3OH + Cl^-$

Mechanism : (Concerted one step process)



Rate equation : $V = k [CH_3Cl] [OH^-]$

Molecularity - 2

Note : In the slow or rate determining step two species are taking part. Hence it is a bimolecular reaction. Further OH⁻ attacks from the rear (back) side and as such **inversion takes place.**

Supposing in place of methyl chloride there is optically active primary halide then the product obtained will be reverse of the original substrate as inversion takes place.

Orbital picture of transition state :



at the point of at the point of bond making bond breaking

(c) $S_N 1$ or $S_N 2$ reaction

[Substrate-2° halide]

Non polar medium $S_N 2$ reaction

Polar medium S_N1 reaction

Transition state and Intermediate

Transition state : A transition state refers to an imaginary state and cannot be isolated $(S_N 2)$

Intermediate : Intermediate is a stable real species and can be isolated under specific condition $[S_N 1 \text{ (carbocation)}]$

(ii) S_E reaction or electrophilic substitution reaction Benzene usually show electrophilic substitution reaction







Here the starred carbon (in benzene) C^* is in sp^2 hybridisation state. Electrophile attacks and arenium ion is formed as an intermediate.



Since in the rate determining step two species electrophile and benzene participates so it is a **bimolecular reaction.**

Rate = k [benzene]. [electrophile]

Example 1. Methylation of benzene

$$C_6H_6 \xrightarrow{CH_3CI/AICI_3} C_6H_5CH_3$$

Mechanism

Step-1 :
$$CH_3$$
- Cl + $AlCl_3 \rightarrow \overset{\oplus}{C}H_3 + \bar{A}lCl_4$

Step-2 (Slow)

$$\mathsf{CH}_{3}^{\oplus} + \mathsf{C}_{6}\mathsf{H}_{5} - \mathsf{H} \rightarrow \left[\underbrace{\overset{H}{\overbrace{\bigcirc} \oplus }}_{\overset{\bullet}{\overbrace{\bigcirc} \to }} \right] \xrightarrow{\mathsf{C}_{6}\mathsf{H}_{5}\mathsf{CH}_{3} + \overset{H}{\mathsf{H}}}_{toluene}$$

carbocation (σ -complex intermediate)

Step-3 :
$$\overset{\oplus}{H} + AlCl_4 \rightarrow AlCl_3 + HCl$$

Example 2. Nitration of benzene :

$$C_6H_6 \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} C_6H_5\text{NO}_2 + H_2O$$

Mechanism :

Step-1 :

$$2H_2SO_4 + HO - NO_2 \rightarrow NO_2 + 2HSO_4^- + H_3O_2^{\oplus}$$

Step-2 :
$$\overset{\oplus}{NO_2} + C_6H_5 - H \longrightarrow$$

$$\longrightarrow C_6H_5NO_2 + H$$

 $(\sigma$ -complex)

Step-3 :
$$\stackrel{\oplus}{H}$$
 + $HSO_4 \longrightarrow H_2SO_4$

Example 3: Sulphonation of benzene :

$$C_6H_6 \xrightarrow{\text{conc.H}_2SO_4} C_6H_5 - SO_3H + H_2O$$

Mechanism :

Step-1 :
$$H_2SO_4 \implies H_2O + SO_3$$

Step-2:
$$SO_3 + C_6H_5 - H \longrightarrow$$

$$\rightarrow C_6H_5 - S\bar{O}_3 + \overset{\oplus}{H} \Longrightarrow C_6H_5SO_3H$$

(\sigma-complex)

(iii) Free radical substitution S_F – Chlorination of methane is the example of free radical substitution

Reaction :-

$$CH_4 + Cl_2 \rightarrow CH_3 - Cl + HCl$$

Mechanism :-

(1) Step-1 (Chain initiation step)

 $Cl-\!\!\!-\!\!Cl \longrightarrow Cl \, {\boldsymbol{\cdot}} + Cl \, {\boldsymbol{\cdot}}$

(2) Step-2 (Chain propagation step)

$$Cl \cdot + CH_4 \rightarrow CH_3 \cdot + HCl$$

 $CH_3 \cdot + Cl_2 \rightarrow CH_3Cl + Cl \cdot$
(2) Step 2 (Classical states)

(3) Step-3 (Chain termination step) $CH_3 \cdot + CH_3 \cdot \rightarrow CH_3 - CH_3$ $CH_3 \cdot + Cl \cdot \rightarrow CH_3 - Cl$ $Cl \cdot + Cl \cdot \rightarrow Cl_3$

2. Addition reaction : Usually unsaturated molecule undergoes addition reaction. In this type of reaction one π -bond is broken and two σ -bonds are formed

$$[1\sigma, 1\pi]$$
 $[3\sigma]$

(i) Electrophilic addition reaction Substrate - Alkene, Alkyne

$$>C=C < + E \longrightarrow Nu \longrightarrow > C \longrightarrow C <$$

Mechanism :

trans-addition

It should be noted that :

- When polar molecular attacks the double bond of alkene, then π -electrons of the double bond shift to one of the carbon atom due to electromeric effect

 $>C \stackrel{\frown}{=} \stackrel{\frown}{C} <$, the electrophile attaches to that carbon atom and carbocation is formed

Organic Chemistry – Some Basic Principles and Techniques aches to **Example :- Addition of HCN at acetone :**

 The nucleophilic part of the reagent attaches to positively charged carbon and forms the end product. This is of course a trans-addition.

- Since the initial attack is of a electrophile this is referred as **electrophilic additio**

Other example :-

$$CH_2 = CH_2 + H - OH \xrightarrow{H^+} CH_3 - CH_2OH$$



1- methyl cyclohexene trans-2-methyl cyclohexanol

(ii) Nucleophilic addition reaction

[Substrate - Aldehyde, Ketone]

General Mechanism

$$>C = O + E - Nu \rightarrow >C -OE$$

Nu

$$>\overset{\delta t}{C} = \overset{\bullet}{O} \xrightarrow{\text{Electromeric}} \overset{\oplus}{effect} \xrightarrow{\oplus} \overset{\Theta}{O}$$

EN(O)> EN(C)
$$\downarrow \overset{\oplus}{E}\overset{\Theta}{N}_{u}$$

$$\downarrow \overset{\Theta}{E}\overset{\Theta}{N}_{u}$$

$$>C - \overset{\Theta}{O} + E^{\oplus}$$

$$\stackrel{\Theta}{N}_{u}$$

$$\Rightarrow \overset{\oplus}{C} - O + \overset{\Theta}{N}_{u}$$

attack

less stable

(does not form)

Oxygen bearing negative charge more stable (forms)

$$\downarrow \\ > C - OE \\ | \\ Nu$$

Mechanism :

HCN
$$\xrightarrow{\text{Base in}}_{\text{small quantity}} H^{\oplus} + CN^{\oplus}$$



(iii) Free radical addition : Anti-Markownikoff's reaction-peroxide effect

Addition of HBr to propene in presence of peroxide

$$CH_3 - CH = CH_2 + HBr$$
 _____eroxide

Mechanism :-

$$R \xrightarrow{O-O} R \xrightarrow{Homolysis} 2RO$$

(i) Chain initiation :-

 $RO + HBr \rightarrow ROH + Br$

(ii) Chain propagation : (two steps)

$$CH_3$$
- $CH=CH_2+Br \rightarrow CH_3-CH-CH_2Br$
2° free radical

$$CH_3 - \dot{C}H - CH_2Br + HBr \rightarrow CH_3 - CH_2 - CH_2Br + Br$$

(iii) Chain termination :

$$Br + Br \text{ or } 2CH_3 - \dot{C}H - CH_2Br$$
 or

$$CH_3 - \dot{C}H - CH_2Br + Br$$

Addition of Br₂ to Ethene ;

$$\begin{array}{c} H_2C = CH_2 + Br_2 \xrightarrow{hv} CH_2 - CH_2 \\ \downarrow \\ Br & Br \end{array}$$

Mechanism :

$$\begin{array}{cccc} Br_{2} & \xrightarrow{hv} & 2Br \\ CH_{2} = CH_{2} + & Br \bullet & \rightarrow & \bullet CH_{2} - CH_{2} - Br & \xrightarrow{+Br \bullet} \\ & & Br - CH_{2} - CH_{2} - Br \end{array}$$

3. Elimination reaction : Elimination is reverse of addition. In this type of reaction two σ -bonds are broken and 1 π bond is formed.

$$\begin{array}{c} \mathbf{A} \longrightarrow \mathbf{B} \longrightarrow \mathbf{A} = \mathbf{B} + \mathbf{x} - \mathbf{y} \\ | & | \\ \mathbf{x} & \mathbf{y} \end{array}$$

(three σ) (one- σ and one- π) (one- σ)

(i) Dehydration :

$$CH_{3}CH_{2}OH \xrightarrow{Conc. H_{2}SO_{4}} CH_{2}=CH_{2}+H_{2}O$$

(ii) Dehydrobromination :

$$CH_3$$
- $CH_2Br \xrightarrow{alc. KOH} CH_2 = CH_2 + HBt$

(iii) Debromination :

$$CH_{2}Br \xrightarrow{Zn} CH_{2} = CH_{2} + ZnBr_{2}$$
$$CH_{3}CHBr_{2} + 2Zn + Br_{2}CHCH_{3} \rightarrow CH_{3} - CH$$
$$= CH - CH_{3} + 2ZnBr_{2}$$

(iv) Dehydrogenation :

$$CH_3 - CH_2OH \xrightarrow{Cu} CH_3 - CHO + H_2$$

Examples of Cycloalkenes :

(v) Dehydration of Cyclohexanol :



(vi) Dehydrocholorination of clohexylchloride



(v) Debromination of 1,2-dibromocyclohexane



These reactions have been divided into two classes

- (1) E2 reaction
- (2) E1 reaction

- E2 reaction : Elimination bimolecular
- Reaction involves one step only
- Base pulls out a proton from the β -carbon atom,

- Simultaneously, a halide ion leaves and the double bond is formed



Rate equation :

(i)

v=k[halide][:B]

Molecularity - 2

(ii) E1 reaction :- Elimination unimolecular

Step-1 Heterolysis of substrate gives carbocation and halide ion (slow)

Step-2 Carbocation gives up proton to a base immediately and alkene is formed



Rate equation :

$$v = k [RX]$$

Molecularity - 1

4. Rearrangement reaction : Substituents change their positions



Examples :



Phenylhydroxylamine

p-Amino phenol

(ii)
$$CH_3 - C - \ddot{N} \longrightarrow O = C = N - CH_3$$

Acetyl nitrene Methyl isocyanate



Sodium phenyl carbonate Sodium Salicylate





Sulphanilic acid

(v)
$$H-N = C = O \rightarrow N \equiv C - O - H$$

Isocyanic acid Cyanic acid

(vi)
$$CH_3 - CH_2 - \overset{\oplus}{C} H_2 \rightarrow CH_3 - \overset{\oplus}{C} H - CH_3$$

1° Carbonium

2° Carbonium



p-Hydroxy acetophenone

(viii) $\begin{array}{ccc} N-OH & O\\ \parallel & 0\\ CH_3-C-CH_2CH_3 \rightarrow CH_3-NH-C-CH_2-CH_3 \end{array}$

Methyl ethyl ketoxime

N-Methyl propionamide

Organic Chemistry – Some Basic Principles and Techniques REACTIONATA GLANCE

Class of compounds

(i) Alkene, alkyne
(ii) Aldehyde, ketone
(iii) Aldehyde
(iv) Aromatic compounds
(v) Alkane
Electrophilic addition
Nucleophilic substitution
Electrophilic substitution
Free radical substitution

Type

MARKOWNIKOFF'S RULE AND PEROXIDE EFFECT

Markownikoff's Rule : When an unsymmetrical reagent adds to an unsymmetrical unsaturated hydrocarbon, the negative part of the addendum adds on to the carbon containing less number of hydrogen atom.

$$(CH_3)_2C=CH_2 + HCl \rightarrow (CH_3)_2C-CH_3$$

|
Cl

Mechanism •



[3° carbonium ion]

$$(CH_3)_2 \stackrel{\oplus}{\overset{C}{\mathsf{C}}} - CH_3 + \stackrel{\Theta}{\overset{C}{\mathsf{C}}} \xrightarrow{\text{fast}} (CH_3)_3 C - Cl$$

Second rule :

In the addition of HCl to vinyl chloride the chlorine, attaches itself to the carbon on which the chlorine atom is already present. $CH_2=CHCl + HCl \rightarrow CH_3CHCl_2$

Mechanism :

$$CH_{2} = CH - CI - CH_{2} - CH = CI$$

$$\bigoplus_{\substack{CI + CH_{3} - CH - CI}} CH_{2} - CH = CI$$

$$\bigoplus_{\substack{H - CI}} CH_{2} - CH - CI$$

$$\bigoplus_{\substack{H - CI}} CH_{2} - CH - CI$$

Peroxide effect :

In the presence of air or peroxides addition of hydrogen bromide to unsymmetrical unsaturated hydrocarbon takes place reverse to that of Markownikoff's rule [Kharash effect]

 $(CH_3)_2C = CH + HBr \xrightarrow{\text{peroxide}} (CH_3)_2 CH - CH_2Br$ It should be noted that HCl and HI do not show peroxide effect.

Organic Chemistry – Some Basic Principles and Techniques ELECTRONIC EFFECTS, ACID-BASE STRENGTH

AND REACTION INTERMEDIATES

ELECTRONIC EFFECTS

The effect which appears due to electronic distribution is called electronic effect.

Classification :



1. The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-chloro butane, Here due to more EN of Cl atom C – Cl bond pair is slightly displaced towards Cl atom hence creating partial negative $(\delta -)$ charge over Cl atom and partial positive $(\delta+)$ charge over C₁ atom.

Now since C_1 is slightly positive, it will also cause shifting of $C_1 - C_2$ bond pair electrons towards itself causing C_2 to acquire small positive charge. Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

Diagram showing I effect

$$C_{4} \xrightarrow{\delta\delta\delta^{+}}_{3} \xrightarrow{\delta\delta^{+}}_{2} \xrightarrow{\delta\delta^{+}}_{1} \xrightarrow{\delta^{+}}_{1} \xrightarrow{\delta^{-}}_{1} CI$$

The arrow shows electron withdrawing nature of – Cl group.

Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

- (a) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.
- (b) It is also called transmission effect.
- (c) It causes permanent polarisation in molecule, hence it is a permanent effect
- (d) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
- (e) The electrons never leave their original atomic orbital.
- (f) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.
- (g) The inductive effect is always operative through σ bond, does not involve π bond electron.

2. Types of inductive effect :

(a) - I Effect : The group which withdraws electron cloud is known as - I group and its effect is called - I effect. Various groups are listed in their decreasing - I strength as follows.

$$\begin{array}{l} \overset{\textcircled{\mbox{\boldmath Θ}}}{-\operatorname{\mathsf{NR}}}_3 > - \overset{\textcircled{\mbox{\boldmath Θ}}}{-\operatorname{\mathsf{SR}}}_2 > & - \overset{\textcircled{\mbox{\boldmath Θ}}}{-\operatorname{\mathsf{NH}}}_3 > - & \operatorname{NO}_2 > \\ -\operatorname{SO}_2 R > & - \operatorname{CN} > - & \operatorname{CHO} > - & \operatorname{COOH} > \\ & - & F > - & \operatorname{Cl} > \\ - & \operatorname{Br} > - & I > - & \operatorname{OR} > - & \operatorname{OH} > & - & \operatorname{C} \equiv & \operatorname{CH} > \\ - & \operatorname{NH}_2 > - & \operatorname{C}_6 \operatorname{H}_5 > & - & \operatorname{CH} = & \operatorname{CH}_2 > - & \operatorname{H}. \end{array}$$

(b) + I effect : The group which release electron cloud is known as + I group and effect + I effect.

$$-O^{\Theta} > -COO^{\Theta} > -C(CH_3)_3 > -CH(CH_3)_2$$
$$> -CH_2 - CH_3 > -CH_3 > -D > -H$$

The hydrogen atom is reference for + I and - I series. The inductive effect of hydrogen is assumed to be zero.

Solved Examples

Ex.56 Since $-NO_2$ is -I group it pulls or withdraws electron from cyclohexane ring making it electron deficient



Let us consider effect of COOH & – COO[–] in carbon chain

Ex.57
$${}^{\Theta}$$
OOC $\rightarrow {}^{\delta-}$ H₂ $\rightarrow {}^{\delta\delta-}$ CH₂ $\rightarrow CH_3$

Ex.58 HOOC $\leftarrow \overset{\delta^+}{CH}_2 \leftarrow \overset{\delta\delta_+}{CH}_3$

Due to e⁻ donating nature of $-COO^{\Theta}$ carbon chain has become partially negative but -COOH is -Igroup therefore carbon chain has become partially positive.

Ex.59 (a)
$$CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow \overset{\oplus}{\underset{c}{\overset{\bullet}{\mathsf{S}}}_{\mathsf{CH}_3} \leftarrow CH_3$$





$$(e) CH_2 \Longrightarrow C \Longrightarrow O$$

(I)
$$CH_3 \rightarrow CH_2 \rightarrow Br$$

(g) $CH_3 \rightarrow CH \leftarrow CH_2 \leftarrow CH_3$
 $\downarrow F$
 $CH_3 \rightarrow C \leftarrow CH_2 \leftarrow CH_3$
(h) $\downarrow O$
(i) $CH_3 \rightarrow C \leftarrow CH_2 \leftarrow CH_3$
 $\downarrow O$
(i) $CH_3 \rightarrow C \leftarrow CH_2 \rightarrow C \leftarrow CH_3$

3. Applications of Inductive effect :

(a) In deciding acidic strength of aliphatic carboxylic acids.

-I effect \propto Acidic strength (presence of -I groups increases acidic character)

+ I effect ∞ Basic strength (presence of + I groups increases basic character)

The Bronsted - Lowry Definition of Acids and Bases

According to the Bronsted - Lowry theory : An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Acidic strength is directly related to stability of conjugate base –I stabilises conjugate base amd +I destabilises conjugate base.

Solved Examples

Ex.60 (I)
$$\begin{array}{c} H_{3}C-H_{2}C-H_{2}C-CH-COOH \\ \downarrow \\ CI \end{array}$$
(II)
$$\begin{array}{c} CH_{3}-CH_{2}-CH-CH_{2}-COOH \\ \downarrow \\ CI \end{array}$$
(III)
$$\begin{array}{c} CH_{3}-CH-CH_{2}-CH_{2}-COOH \\ \downarrow \\ CI \end{array}$$
(IV)
$$\begin{array}{c} CH_{3}-CH_{2}-CH_{2}-CH_{2}-COOH \\ \downarrow \\ CI \end{array}$$
(IV)
$$\begin{array}{c} CH_{3}-CH_{2}-CH_{2}-CH_{2}-COOH \\ \downarrow \\ CI \end{array}$$
Acid strength order
$$I > II > III > IV$$

Explanation :

We know that -I effect increases acidic strength. But it is distance dependent effect so where the -I group is nearest to -COOH, It exert strong effect and makes acid stronger.

```
Ex.61 (I)O_2N - CH_2 - COOH
(II) F - CH<sub>2</sub> - COOH
(III) H<sub>3</sub>CO - CH<sub>2</sub> - COOH
(IV) CH<sub>3</sub> - CH<sub>2</sub> - COOH
Acid strength order
I > II > IV
```

Explanation :

Since NO₂ has strong – I effect its influence will make corresponding acid strongest (– I effect ∞ acid character).

(b) Acidic Character of Alcohol : Greater - I effect results in greater acidic character. Similarly greater + I effect lowers acidic character.

Solved Examples

Ex.62 (a) Acidity:
$$CH_3 - CH_2 - OH < CH_2 - CH_2 - CH_2 - OH < CH_2 - CH_2 - CH_2 - OH < CH_2 - CH_2 - OH$$

 $OH < CH_2 - CH_2 - OH < CH_2 - CH_2 - OH$
(b) Acidity: $CH_3 - OH > CH_3 + CH_2 - OH$

(c) **Dipole moment :** Greater I effect results in greater dipole moment.

$\text{Ex.63}\ \mu$: CH_3NO_2 > CH_3COOH > CH_3F > CH_3OH

(d) Stability of carbocation : Carbocations are electron deficient species and they are stabilised by + I effect and destablised by – I effect. Because + I effect tends to decrease the positive charge and – I effect tends to increases the positive charge on $\rightarrow C^+$ (carbocation)

Ex.64 Stability :
$$CH_3^{\oplus} < CH_3^{\oplus} CH_2^{\oplus} < (CH_3)_2 \overset{\oplus}{C}H$$

< $(CH_3)_3 C^{\oplus}$

(e) Stability of carbon free radical : Carbon free radical are stabilised by + I effect.

Ex.65 Stability : $CH_3^{\bullet} < CH_3 \rightarrow CH_2^{\bullet} < CH_3$

$$\rightarrow \begin{array}{c} \dot{\mathbf{C}} \mathsf{H} \ < \ \mathrm{CH}_{3} \ \rightarrow \ \begin{array}{c} \dot{\mathbf{C}} \\ \uparrow \\ \mathsf{CH}_{3} \end{array} \begin{array}{c} \leftarrow \ \mathrm{CH}_{3} \end{array} \begin{array}{c} \mathrm{CH}_{3} \end{array}$$

(f) Stability of carbanion stabilised by -I effect and destabilised by +I effect.

Resonance & Mesomeric effect

1. **Definition :** Resonance is the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structure.

Resonating structure are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybrid is more stable than any resonating structure. The P.E. difference between the most stable resonating structure and resonance hybride is called resonace energy. The stability of molecule is directly proportional to resonance energy.

$$CH_{2} = CH - CH = CH_{2} \leftrightarrow CH_{2} - CH = CH - CH_{2}$$

$$CH_{2} - CH - CH - CH_{2} \leftrightarrow CH_{2} - CH - CH - CH_{2}$$

$$CH_{2} - CH - CH - CH_{2}$$

$$CH_{2} - CH - CH - CH_{2}$$

$$Resonance hybrid$$
Fig.1

The most stable resonating structure contribute maximum to the resonance hybrid and less stable resonating structure contribute minimum to resonance hybrid.

Solved Examples



2. **Resonance Hybrid :-** It is the actual structure of the species without violating the rules of covalence maxima for the atoms.



3. **Resonance Energy:-** The difference in energy between the hybrid and the most stable canonical structure is referred as the resonance energy. (as shown in Fig.2)

(Most stable resonating structure) Energy R.E = 36 Kcal Resonance hybrid **Resonance Energy of Benzene**

Fig.2

The resonance energy of a resonance hybrid is the difference between the theoritical and experimental value of heat of hydrogenation of the compound.



Cvclohexene

```
(-28.6 Kcal/mol)
```

Accordingly,

$$+ 3H_2 \xrightarrow{\text{Catalyst}} + 3 \times 28.6 =$$

(-85.8 Kcal/mole)

Therefore, benzene has [-85.8-(-49.8)] Kcal/mol less energy than expected for a typical compound with three double bonds. Hence resonance energy of benzene molecule is -85.8 + 49.8 = -36.0 Kcal/ mole.

let us see resonating structures of given molecules

Solved Examples

Write resonating structure for each of the following molecules : **Ex.67**

(a)
$$CH_3 - CH = CH - C = CH_3$$

(b) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$
(c) $H_2 \overset{\cdots}{N} - CH = CH - C = N$

Organic Chemistry – Some Basic Principles and Techniques



3 The Rules of Resonance

(a) All the canonical forms (resonating structure) must have proper lewis structure. For instance none of them may have a carbon atom with five bonds.



(b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structures 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atoms and this is not permitted :



(c) All atoms taking part in the delocalisation must lie in a plane so that orbitals overlaping become parallel to each other.



(d) All canonical forms must have the same number of unpaired electron.

(e) The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.

(f) All canonical forms do not contribute equally to the true molecule. The more stable structure is the greater contribution to its resonance hybrid. (a) **Nonpolar (uncharged) structure are most stable.** Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.

$$\overrightarrow{CH_2} = CH - \overrightarrow{CH} : \overrightarrow{CH_2} - CH = \overrightarrow{CH}^{\oplus}$$
(I)
(II)

(b) Structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are especially stable and make large contributions to the hybrid.

Solved Examples



(c) Structures with more covalent bonds are more stable than other structures

$$\begin{array}{c} CH_2 = CH - CH = CH_2 & \longleftrightarrow & CH_2 - CH = CH - \overline{C}H_2 \\ (I) & (II) \\ \hline This structure is the most stable because it contains more covalent bonds. \\ \hline & \overleftarrow{C}H_2 - CH = CH - \overrightarrow{C}H_2 \\ (III) \end{array}$$

(d) Structure that carry negative charge on a more electronegative atom and positive charge on less electronegative atom are comparatively more stable.

Ex.70
$$\begin{array}{c} \overbrace{CH_2}^{\ominus} - C - H & \longleftrightarrow \\ CH_2 = C - H \\ \overbrace{O}^{||} & O^{-} \\ I \\ (II \text{ is more stable than I}) \end{array}$$

Ex.71
$$: \stackrel{\checkmark}{\text{Br}} \stackrel{\checkmark}{=} CH \stackrel{\checkmark}{=} \stackrel{\checkmark}{CH}_2 \longleftrightarrow \stackrel{\oplus}{\text{Br}} = CH - \stackrel{\oplus}{CH}_2$$

I II
(I is more stable than II)

5. Mesomeric effect : Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond.

Solved Examples

Ex.72
$$: \overbrace{I}^{\bigcirc} CH = CH_2 \longleftrightarrow : \overbrace{II}^{\bigoplus} = CH - \widecheck{C}H_2$$

I and II are resonating structures of $Cl - CH = CH_2$. This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

Ex.73
$$\bigvee_{O}^{H} H = CH_2 \leftrightarrow \bigcup_{O}^{O} N = CH - \overset{\oplus}{C}H_2$$

6 Conjugation: - A given atom or group is said to be in conjugation with an unsaturated system if:-

(i) It is directly linked to one of the atoms of the multiple bond through a single bond.

(ii) It has π bond, positive charge, negative charge, odd electron or lone pair electron.

- (a) $CH_2 = CH CH = CH_2$ (Conjugation between C = C and C = C)
- **(b)** $CH_2 = CH CH_2$

(Conjugation between +ve charge and C = C)

- (c) $CH_2 = CH \dot{N}H_2$ (Conjugation between lone pair and C = C)
- (d) $CH_2 = CH \dot{C}H_2$

(Conjugation between odd electron and C = C)

(e)
$$CH_2 = CH - CH = CH - \overrightarrow{CH}_2$$

(Conjugation between negative charge and C = C)

7. Types of Mesomeric Effect : This is of two types

(a) + m effect (b) – m effect

(a) Positive Mesomeric effect (+ m effect) : When the group donates electron to the conjugated system it shows + m effect.

Solved Examples

Ex.74 (I)
$$X \stackrel{\frown}{I} CH \stackrel{\frown}{=} CH_2 \longleftrightarrow X = CH \stackrel{\odot}{-} CH_2$$

(II)
$$H_2 \stackrel{\bullet}{C} = CH \stackrel{\bullet}{=} CH \stackrel{\bullet}{=} CH \stackrel{\bullet}{=} CH \stackrel{\bullet}{=} OH_2 \stackrel{\bullet}{\longleftrightarrow} H_2 \stackrel{\bullet}{\longleftrightarrow} H_2 \stackrel{\bullet}{\longleftrightarrow} H_2 \stackrel{\bullet}{\longleftrightarrow} H_2 \stackrel{\bullet}{\boxtimes} H_2 \stackrel{\bullet}{\longrightarrow} H_2 \stackrel{\bullet}{\longrightarrow}$$















 $\overset{\bigoplus}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}{\overset{\mathsf{NH}_2}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}{\overset{\mathsf{NH}_2}}}}}}$

Groups which shows '+ m' effect are :

 $\begin{array}{c} - O^{\odot} > - NH_{2} > - NHR > - NR_{2} > - OH > - OR \\ > - NH - C - R > - O - C - R > - Ph, - CH = CH_{2} \\ \parallel & \parallel \\ O & O \end{array}$ $\begin{array}{c} > - F > \\ - Cl > - Br > - I, - N = O. \end{array}$

(b) Negative Mesomeric Effect (- m effect) : When the group withdraws electron from the conjugated system, it shows - m effect

Groups which can show - m effect are

$$-NO_2 > -C \equiv N > -SO_3H > -CHO > -C-R$$

 $\parallel O$
 $> -C-OH$
 $\parallel O$

Solved Examples

Ex.75
$$\overrightarrow{O} = \overrightarrow{C} \underbrace{\checkmark}_{CH} = \overrightarrow{CH_2} \underbrace{\leftrightarrow}_{O} - \overrightarrow{CH} = \overrightarrow{CH}_2$$

Ex.76 $\begin{array}{c} \textcircled{\bigcirc} - \widecheck{N} = \widecheck{\bigcirc} : \\ \hline{\bigcirc} - \widecheck{N} = \overbrace{\bigcirc} : \\ \hline{\bigcirc} - \widecheck{N} = \overbrace{\bigcirc} : \\ \hline{\bigcirc} - \widecheck{N} - \overbrace{\bigcirc} \\ \hline{\bigcirc} - \widecheck{N} - \overbrace{\bigcirc} \\ \hline{\bigcirc} \\ \hline{\bigcirc} \\ \hline \end{array}$



Ex.77
$$H_2C \stackrel{\frown}{=} CH \stackrel{\frown}{=} C \stackrel{\frown}{=} N: \longleftrightarrow H_2C \stackrel{\oplus}{=} CH = C \stackrel{\oplus}{=} \stackrel{\frown}{N}:$$

Ex.78 By drawing resonating structures of following molecules, Judge whether the group attached to ring exerts +m or -m effect.



Sol. (a)
$$_{-NH-C-CH_3}^{O}$$
 (+m group)





(b)
$$-C-CH_3$$
 (-m effect group)



Note:

1. When a +m group and -m group are at metapositions with respect to each other then they are not in conjugation with each other, but conjugation with benzene ring exists.



 +m group increases electron density in benzene ring while -m group decreases electron density in the benzene ring.

Solved Examples

Ex.79 Write electron density order in the following compound.







Ans. IV > I > III > II

8. Difference between Inductive and Mesomeric effects:-

Inductive effect	Mesomeric effect
(1) It is found in	(1) It is found in
saturated and	unsaturated compounds
unsaturated	especially having
compounds.	conjugated system.
(2) It involves partial	(2) It involves complete
shifting of sigma	shifting of pi-electrons
electrons.	of pi-bonds or lone pair
	of electrons.
(3) The electron pair	(3) The electron pair is
is slightly displaced	completely transferred
from its position and	and thus full positive
thus partial charges	and negative charges are
are developed.	developed.
(4) It is transmitted	(4) It is transmitted from
over a quite short	one end to other end of
distance. The effect	the chain provided
becomes negligible	conjugation is present. It
after third atom in the	is distance independent.
chain (distance	
dependent).	

9. Important points :

(a) If any π -bond has more than one π bond in conjugation, then only one π bond will take part in delocalisation.

$$\mathsf{CH}_2 = \mathsf{CH} - \mathsf{C} \equiv \mathsf{CH} \\ \downarrow$$

Out of two π bonds only one π bond will take part in delocalisation.

(b) If any conjugate position has more than one lone pair then only one lone pair will take part in the delocalisation.

$$\mathsf{CH}_{2} = \mathsf{CH} - \overset{{}_{\scriptstyle \leftarrow}}{\overset{\scriptstyle \leftarrow}{O}} - \mathsf{CH}_{3}$$

Out of the two lone pair 's only one will take part in delocalisation.

(c) If any conjugate position has π bond and any of the positive charge, negative charge, odd electron, lone pair electrons then only π bond will take part in delocalisation.



Nitrogen has π bond as well as lone pair, but only π bond of nitrogen will take part in delocalisation.

(d) Electrons of negative charge or lone pair behave as 2π electrons if it is in conjugation to π bond.



Hyperconjugation

1. Hyper conjugation : It is delocalisation of sigma electron with p-orbital. Also known as $\sigma \pi$ -conjugation or no bond resonance. It may takes place in alkene, alkynes, carbocation, free radical, benzene nucleus.

Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

2. Hyperconjugation in alkene



3. Hyperconjugation in carbocation



4. Hyperconjugation in radical





(a) The effect of electron displacement due to this type of resonance is called hyperconjugative effect.

(b) Since canonical forms of this resonance may not contain any bond between H and C so hyperconjugation is also known as no bond resonance.

(c) These resonating structures only suggest that
 * There is some ionic character between C-H bond.

* Carbon - carbon double bond acquires some single bond character.

(d) Number of no bond resonating structures due to hyperconjugation = Number of α -hydrogens (In aliphatic systems)

Solved Examples

Ex.80

Structure	Number of - hydrogens	Number of resonating structures
$CH_3 - CH = CH_2$	3	4
$CH_3 - CH_2 - CH = CH_2$	2	3
$CH_3 - CH = CH - CH_3$	6	7
$CH_3 - CH_2$	3	4
$H_3C - C - CH_3$ CH_3	9	10

6. Applications of hyperconjugation

(a) Stability of Alkenes :- More is the number of hyperconjugative structures more stable is the alkene.

"More alkylated alkenes are more stable".

Stability of alkenes ∞ no. of hyperconjugative structures.

Example



Stability	in	decreasing	order
- construction of the second sec		4001040119	0.00.

(b) Heat of hydrogenation : Greater the number of α hydrogen results greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation

Stability of alkenes ∞ no. of hyperconjugative

structures
$$\propto \frac{1}{\Delta H_{Hydrogenation}}$$

Solved Examples

 $\mathbf{Ex.81} \text{ CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 (\Delta \text{H}_{\text{Hydrogenation}})$

(c) Bond Length : Bond length is also affected by hyperconjugation

Solved Examples

Ex.82
$$H_{2C} \xrightarrow{H} HC \xrightarrow{C} HC \xrightarrow{H}_{2} \xrightarrow{H} HC \xrightarrow{H}_{2$$

(i) Bond length of C(II) - C(III) bond is less than normal C–C bond.

(ii) Bond length of C(II) - C(I) bond is more than normal C=C bond.

(iii) C–H bond is longer than normal C–H bond.

(d) **Dipole moment :** Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule.

Solved Examples

Ex.83 (I)
$$CH_2 = CH_2 < CH_3 - CH = CH_2$$

(Dipole moment)

(II)
$$H - CH = O < CH_3 - CH < CH_3 - CH =$$

 $CH - CH - CH$ (Dipole moment)

(e) Stability of carbocation :

More hyperconjugation more is the stability.

Solved Examples

Ex.84 (a)
$$\stackrel{\oplus}{C}$$
H₃ < CH₃ $\stackrel{\oplus}{C}$ H₂ < CH₃ $\stackrel{\oplus}{C}$ HCH₃ < (CH₃)₃ $\stackrel{\oplus}{C}$
(b) CH₃ - $\stackrel{\oplus}{C}$ H₂ > CH₃ - CH₂ - CH₂ - $\stackrel{\oplus}{C}$ H₂ > $\stackrel{CH_3}{\underset{CH_3}{\longrightarrow}}$ CH - $\stackrel{\oplus}{C}$ H₃ > $\stackrel{CH_3}{\underset{CH_3}{\longrightarrow}}$ CH - $\stackrel{CH_3}{\underset{CH_3}{\longrightarrow}$ CH - $\stackrel{CH_3}{\underset{CH_3}{\longrightarrow}$ CH - $\stackrel{$

(due to resultant of inductive effect and hyperconjugation)

(f) Stability of free radical : Greater the number of α -hydrogen results greater stability of carbon free radical

Solved Examples

Ex.85 (a)
$$\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H - CH_3 < CH_3$$

$$(b) CH_{3} - \dot{C}H_{2} > CH_{3} - CH_{2} - \dot{C}H_{2} > CH_{3} - CH_{2} - \dot{C}H_{3} > CH_{3} - \dot{C}H_{3} - \dot{C}H_$$

(due to resultant of inductive effect and hyperconjugation, both operates in same direction)

ACIDS AND BASES

Organic Chemistry – Some Basic Principles and Techniques Relative acidity of hydrocarbons

(a) The Bronsted - Lowry Definition of Acids and Bases

According to the Bronsted - Lowry theory, an acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :

H – Ö:	+ H – <u>Ċ</u> l: -	→ H Ö ⁺ H +	- :ċi:-
H	۸ aid	H H	Conjugato
Base	Acia	Conjugate	Conjugate
(proton	(proton	acid	base of
acceptor)) donor)	of H ₂ O	HCI

Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion (H_3O^+) and a chloride ion (Cl⁻). The molecule or ion that forms when an acid loses its proton is called the **conjugate base** of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the **conjugate acid** of that base.

(b) The Lewis Definition of Acids and Bases

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors. For example aluminiumchloride, reacts with ammonia in the same way that a proton donor does. Using curved arrows to show the donation of the electron pair of ammonia (the Lewis base), we have the following examples:



Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C - H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hence

$$HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$$

Acidity of Phenols

When phenol ionises the phenoxide ion is more stabilised by resonance than the unionised phenol. In phenol unlike charges are spread and so it is less stable.



Groups which are -I, -m increases acidic character of phenol of effectively dispersing negative charge of phenoxide ion.

Alternatively + I and + m groups decreases acid strength.

Solved Examples



step 1, III will be least acidic as it has no dispersion

of negative charge (No mesomerism).

step 2 since -I, -m group will increase acid strength, Nitrophenol will be most acidic followed by phenol,

step 3 Amongest cresol and methoxyphenol, methoxyphenol has +m effect of $-OCH_2$, which increases e⁻density hence decrease acidic strength



acid strengh order : I > III > II > IV

Step 1 : Notice that CH₃ have + I effect so all methylphenols (cresols) are less acidic than phenol **(I)**.

Step 2: Now amongest cresols p- and o- CH₃ are increasing the e⁻ density due to their hyper conjugation but ortho isomer has viable + I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only + I works it as least e density amongst the cresol





П

acid strength order : II > IV > III > I

Step 1 In nitrophenols – I effect of NO₂ will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols

Step 2 Only – I effect is applicable in meta nitrophenol it will be number three. Now -o, -phave both - I and - m effect of NO, group over OH and in this particular case para isomer is more acidic



(i) $R - C - O^{\odot}$ (I) exists as two equivalent cannonical

structures I(A) and I(B). This ion is resonance stablised and resonance hybrid structure is I(C).



(ii) $R - C = O^{\Theta}$ ion is more stable due to resonance,

hence carboxylic acids are acidic in nature.

(iii) Electron withdrawing group (-I effect) stablises the anion and hence, increases acidic nature.



Solved Examples

Ex.89
$$F - CH_2 - COOH > Cl - CH_2COOH >$$

Br - CH,COOH > I - CH,COOH

Increasing acid strength

$$Cl - CH_2COOH > CH_3COOH$$

- Increasing acid strength
- (iv) Electron releasing group (+ I effect) destablises the anion and hence decreases acidic nature.



H is trapped by NO, group.

than ortho since

Now

Solved Examples

Ex.91
$$HCOOH > CH_3COOH > CH_3 - CH_2 - COOH$$

Ex.92
$$\begin{array}{c} \text{COOH} \\ \text{COOH} \\ \text{COOH} \end{array} > \begin{array}{c} \text{COOH} \\ \text{COOH} \\ \text{COOH} \end{array} > \begin{array}{c} \text{CH}_2 \\ \text{COOH} \\ \text{CH}_2 \\ \text{COOH} \end{array} > \begin{array}{c} \text{CH}_2 \\ \text{COOH} \\ \text{CH}_2 \\ \text{COOH} \end{array}$$

Ortho effect

It is common observation that generally ortho substituted benzoic acids are highly acidic as compared to their isomers and benzoic acids itself. This is called ortho effect in benzoic acid. However exceptions are seen.



acid strength order : II > IV > III > I

Explanation the ortho isomer will be most acidic due to ortho effect.

Ex.93 (1) (G = -m, -I)





K_a order = ortho > para > meta > benzoic acid

(2) G = (-I > +m) - CI, Br, F, I



K_a order = ortho > meta > para > benzoic acid

(3)
$$G = (+m > -\mathbf{I}) \dots OCH_{3}$$



 K_{a} order = meta \approx ortho > benzoic acid > para

(4) G = (+I, H.C.) R (Alkyl group)



K_a order = ortho > benzoic acid > meta > para Comparison between two geometrical isomers



K₁^f

 K_2^{f}



Now $\mathbf{K}_{1}^{m} > \mathbf{K}_{1}^{f}$ Since the conjugate base is stabilised by

intramolecular H bonding. But $\mathbf{K}_{2}^{f} > \mathbf{K}_{2}^{m}$ Since in maleate ion, after donation of H^{\oplus} two – COO^{\odot} groups faces each other and makes system unstable. In fumarate ion this repulsion is minimised.

Organic Chemistry – Some Basic Principles and Techniques BASES

Aliphatic Bases

Ease of protonation is the basic nature

Increasing strength of nitrogenous bases is related to readiness with which they are prepared to take up protons.

Consider the following molecules

$$\ddot{N}H_3$$
, Me $\rightarrow NH_2$, Me $\rightarrow NH$, Me $\rightarrow N \leftarrow Me$
 $\downarrow \qquad \qquad \uparrow$
Me Me

By visiting + I effect of methyl in above example we may expect basic nature as

$$\label{eq:Mentry} \begin{split} \mathrm{NH}_3 &< \mathrm{MeNH}_2 < \mathrm{Me}_2\mathrm{NH} < \mathrm{Me}_3\mathrm{N} \\ & \textbf{(Which is not true always)} \end{split}$$

This is due the fact that basic strength of an amine in water is determined not only by ease of electron donation (protonation) of N atom but also by the extent to which cation so formed can undergo **SOLVATION** and become stabilised by H atom attached to N atom greater is possibility of solvation via H bonding by water. Alkyl groups are hydrophobic and inhibits H bonding hence solvation.



Thus, due to two opposite effect viz. solvation of cation and + I effect. The jumbled order comes to be

 $Me_2NH > Me - NH_2 > Me_3N > NH_3$

It is also interesting to note that in gas phase basicity order of amines follows the usual order of

 $Me_3N > Me_2NH > MeNH_2 > NH_3$

Since only + I effect works and no solvation effect persists.

Similarly : On the same reasons ethyl amines and other amine follows the following order for basic strength:

$$Et_3N > Et_2NH > EtNH_2 > NH_3$$

(gas phase)
 $Et_2NH > Et_3N > EtNH_2 > NH_3$
(water as solv

(water as solvent)

Aromatic amines (Ph – $\ddot{N}H_2$) or Anilines



When the lone pair lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that system can get resonance stabilisation. Aniline is a weaker base than NH_3 because it has delocalised lone pair.

Solved Examples

Ex.95 Which of them is strong base



In pyrole lone pairs are involved in resonacne therefore it is less basic. But in pyridine lone pairs are in perpendicular plane of π orbitals therefore no tinvolved in resonance



Ex.96 Which of them is stronger base

$$CH_3 - NH_2$$
 \bigcirc NH_2

Since ease of donation of lone pair of N is basicity, $CH_3 - NH_2$ is more basic due to + I effect of $- CH_3$ group. Aryl amine aniline is very less basic since lone pair of N is involved in resonance.



(a) Ortho-substituted anilines are mostly weaker bases than aniline itself.

(ortho effect):

(b) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
(c) The small groups like -NH₂ or -OH do not experience (SIR) due to small size.

Solved Examples

Ex.97 (1) $G = (-M, -I); NO_2$



(Aniline > p > m > o) Only (–I) decides the order.

(4) G = (+I, HC); If $R = -CH_3$ (Toluidines)



$$K_{b}$$
 order : p > Aniline > o > m

REACTION INTERMEDIATE

Dissociation of a Covalent Bond

Homolysis and Heterolysis fission of Covalent Bonds

Reactions of organic compounds always involve the making and breaking of covalent bonds. A covalent bond may break in two fundamentally different ways. The bond may break so that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital. This kind of cleavage, called heterolysis (Gr: hetero-different + lysis-loosening or cleavage), produces charged fragments or ions. The bond is said to have broken heterolytically:

$$A : \stackrel{(}{:} \stackrel{\bullet}{B} \rightarrow \underbrace{A^{+} + : B^{-}}_{\text{lons}} \text{ Heterolytic bond cleavage}$$

The other possibility is that the bond breaks so that each fragments takes away one of the electrons of the bond. This process, called homolysis (Gr. homothe same + lysis), produces fragments with unpaired electrons called radicals.

$$A \stackrel{\frown}{\underset{\text{Radicals}}{\overset{\bullet}{\overset{\bullet}}}} \stackrel{\bullet}{\xrightarrow{}} A \stackrel{\bullet}{\underset{\text{Radicals}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}}} Homolytic bond cleavage$$

Heterolysis of a bond normally requires that the bond be polarised.

$${}^{\delta +}\!A \stackrel{\frown}{:} B^{\delta -} \to A^+ + : B^-$$

Polarisation of a bond usually result from different electronegatives of the atoms joined by the bond. The greater the difference in electronegativity, the greater the polarisation. In the given instance, atom B is more electronegative than A.

Even with a highly polarised bond, heterolysis rarely occurs without assistance, because heterolysis requires separation of oppositively charged ions but oppositively charged ions attract each other, their separation requires considerable energy. Often, heterolysis is assisted by a molecule with an unshared pair that can form a bond to one of the atoms :

$$Y: + \stackrel{\delta^+}{\to} \stackrel{f}{\to} \stackrel{b^{\delta^-}}{\to} \stackrel{f}{\to} \stackrel{f}{\to} - A + : B^-$$

Formation of the new bond furnishes some of the energy required for the heterolysis.

Carbanion

Definition : A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

Solved Examples

Ex.98	Θ CH₃,	Methyl carbanion
Ex.99	$CH_3 - \overset{}{C}H_{_2}$	Ethyl carbanion
Ex.100	(CH ₃) ₂ ён	Isopropyl carbanion

Organic Chemistry – Some Basic Principles and Techniquesn may beKeto and Enol Tautomers

Hybridisation : Hybridisation of carbanion may be sp³, sp² & sp.

Hybridisation Example sp^{3} $\stackrel{\circ}{C}H_{3}, CH_{3} - \stackrel{\circ}{C}H_{2}$ sp^{2} $H_{2}C = \stackrel{\circ}{C}H, CH_{2} = CH - \stackrel{\circ}{C}H_{2}$ sp $HC = \stackrel{\circ}{C}$

Stability of carbanion :

Carbanions are stabilised by electron withdrawing effect as

- (i) -I effect (ii) -m effect
- (iii) Delocalisation of charge

Carbanions are Lewis bases. In their reactions they seek a proton or some other positive centre to which they can donate their electron pair and thereby neutralize their negative charge.

$$\begin{array}{ccc} -\overset{I}{\underset{l}{\overset{\leftarrow}{\overset{}}}} & + & -\overset{I}{\underset{l}{\overset{\diamond}{\overset{}}}} & \overset{\bullet}{\underset{l}{\overset{\leftarrow}{\overset{}}}} & \longrightarrow & -\overset{I}{\underset{l}{\overset{}{\overset{}}} -\overset{I}{\underset{l}{\overset{}{\overset{}}} - & + & :L^{-} \\ \text{Carbanion} & Lewis acid \end{array}$$

Solved Examples

Ex.101 $\overset{\Theta}{C}_{H_3} > CH_3 \xrightarrow{\Theta}_{CH_2} > CH_3 \xrightarrow{\Theta}_{CH_2} \xrightarrow{\Theta}_{CH_2} \xrightarrow{\Theta}_{CH_3} > CH_3 \xrightarrow{\Theta}_{CH_3} \xrightarrow{\Theta}_{CH_3} (Stability order)$

Ex.102
$$CH_2 = CH - \overset{\Theta}{C}H_2 < C_6H_5 - \overset{\Theta}{C}H_2 < (C_6H_5)_3 \overset{\Theta}{C}$$
 (Stability increasing order.)

TAUTOMERISM

Definition : Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen. The keto and enol forms of carbonyl compounds are constitutional isomers, but of a special type, because they are easily interconverted in the presence of traces of acids and bases, chemists use a special term to describe this type of constitutional isomerism. Interconvertible keto and enol forms are said to be tautomers, and their interconversion is called **tautomerization**.

Under most circumstances, we encounter keto - enol tautomers in a state of equilibrium. (The surfaces of ordinary laboratory glassware are able to catalyze the interconversion and establish the equilibrium). For simple monocarbonyl compounds such as acetone and acetaldehyde, the amount of the enol form present at equilibrium is very small. The greater stability of the following keto forms of monocarbonyl compounds can be related to the greater strength of the carbon-oxygen π bond compared to the carbon - carbon π bond (~ 364 versus ~ 250 kJ mol⁻¹):

Keto Form

Enol Form

Acetaldehyde







Acetone





Cyclohexanone



Organic Chemistry – Some Basic Principles and TechniquescarbonylNitro-Acinitro system :

In compounds whose molecules have two carbonyl groups separated by one $- CH_2 - group$ (called β -dicarbonyl compounds), the amount of enol present at equilibrium is far higher. For example, pentane-2, 4 -dione exists in the enol form to an extent of 76% in the liquid.



The greater stability of the enol form of β -dicarbonyl compounds can be attributed to stability gained through resonance stabilization of the conjugated double bonds and (in a cyclic form) through hydrogen bonding:



Resonance stabilisation of the enol form

The conversion of a carbonyl compound into its enol is called enolization.

Lactum-Lactim system :



The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



The stability of the nitro form as compound to the acinitro form due to stabilised by resonance.



Nitroso-Isonitroso system :

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.

Ex.104 $CH_3 - CH_2 - CH_2 - NO \implies$ Nitrosopropane

$$CH_{3} - CH_{2} - CH = NOH, \qquad CH_{3} - CH - CH_{3} \iff$$
oxime 2-Nitrosopropane

 $CH_3 - C - CH_3$ NOH Acetoneoxime

Imine - Enamine system :

 $\begin{array}{cc} R_2 CH - CR = NR & \longleftrightarrow & R_2 C = CR - NH - R \\ \\ Imine & \\ \end{array}$

Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

Process of interconversion :

(a) Base-catalyzed enolization involves the intermediate of an enolate ion, and is thus a consequence of the acidity of the α -hydrogen.





Carbanion enolate ion (conjugate base of both carbonyl compound and enol)



Protonation of the enolate anion by water on the α carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

(b) Acid-catalyzed enolization

Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the α -carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.





(c) Exchange of α -hydrogens from deuterium as well as racemization at the α -carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.



Carbocation

Definition : A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.

Solved Examples

Ex.105 $\stackrel{\oplus}{C}H_3$, Methyl carbocation CH₃ - $\stackrel{\oplus}{C}H_2$ Ethyl carbocation
Hybridisation : Carbocation may be $sp^2 \& sp$ hybridised

Hybridisation Example sp^2 $\overset{\oplus}{C}H_3$ sp $H_2C = \overset{\oplus}{C}H$, $HC = \overset{\oplus}{C}$

Stability : Carbocation are stabilised by

(i) + I effect	(ii)+m effect
(iii) Hyperconjugation	

Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations are Lewis acids. In this way they are like BF_3 and $AlCl_3$. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair, that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):



Because carbocations are electron seeking reagents, chemists call them electrophiles. Electrophiles are reagents which in their reactions seek the extra electrons that will give them a stable valence shell of electrons. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of neon.

Ex.106
$$CH_{3} \rightarrow CH_{3} \rightarrow CH_{3}$$

 $CH_{3} \rightarrow CH_{2} > CH_{3}$

t-Butyl carbocation has +I effect of three Me – groups and also Hyperconjugation effect which makes it most stable.



In Benzyl cation, Extensive Resonance is seen which stabilises C^{\oplus} .

In Ethyl carbocation + I and Hyperconjugation of Me – group stabilizes carbocation, in vinyl carbocation stability decreases rapidly since carbon of $'CH_2'$ is sp² hybridized which is slightly more electronegative hence acts as – I atom which increases (+) charge.

Rearrangement : Whenever an Intermediate carbocation is formed in reaction it rearranges to a more stable one.

Not all carbocations rearrange but only those which can produce more stable species can only rearrange. Consider the following reactions.

(a)

$$CH_{3} - CH \stackrel{f}{=} \stackrel{e}{C}H_{2} + H_{-}Br \longrightarrow CH_{3} - CH_{3$$

This reaction involves formation of carbocation but no rearrangement.

(b)
$$CH_3 - CH - CH \stackrel{\frown}{=} CH_2 + H - Br \longrightarrow$$

 $CH_3 - CH_3 - CH_2 - CH_3 \stackrel{H^- shift}{\longrightarrow} CH_3 - CH_2 - CH_3$

(c)
$$CH_3 - CH_3 - CH = CH_2 + H-CI \rightarrow CH_3$$

$$\begin{array}{c} \mathsf{CH}_{3} \bigoplus \limits_{\mathsf{C}} \mathsf{CH}_{-} \mathsf{CH}_{-$$

Carbocation rearrangement can also occur by ring expansion.







One very stable carbocation reported is cyclopropylmethyl carbocation. This unique stabilisation is seen in this case of three member ring only.

$$\sim \overset{\oplus}{\mathsf{C}}\mathsf{H}_2$$
 (more stable than Benzyl)

cyclopropyl methyl carbocation

Ionic reactions are those in which covalent bonds break heterolytically and in which ions are involved as reactants, intermediates, or products.

Another broad category of reaction mechanisms that involve homolysis of covalent bonds with the production of intermediates possessing unpaired electrons called radicals (or free radicals):

$$A : B \xrightarrow{\land} B \xrightarrow{homolysis} A \cdot + \cdot B$$

Radicals



	Carbon free radical	Carbocation	Carbanion
	Cuill	Cuint	
Shape	trigonal planar	trigonal planar	Pyramidal
Hybridisation	sp ²	sp²	sp³
No. of electronsin outermost shell	7	6	8

Solved Examples

Ex.108
$$H_{3}C-C^{+}_{CH_{3}} > CH_{3}$$

$$H_3C - CH - CH_3 > H_3C - CH_2 > CH_3$$

(Stability order)

$$Ex.109 \quad (C_{6}H_{5})_{3}C^{\bullet} > (C_{6}H_{5})_{2}C^{\bullet} > C_{6}H_{5} - CH_{2}$$

>
$$CH_2 = CH - \dot{C} - CH_3$$
 (Stability order)
|
 CH_3

Organic Chemistry – Some Basic Principles and Techniques

Divalent Carbon intermediates : Carbenes

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon compounds are called carbenes. Most carbenes are highly unstable compounds that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules. The reactions of carbenes are especially interesting because, in many instances, the reactions show a remarkable degree of stereospecificity.

Methods of preparation of carbene :

$$CHCl_{3} + HO^{\odot} \xrightarrow{-HCl} : CCl_{2}$$

$$CH_{2}I_{2} + Zn \xrightarrow{-ZnI_{2}} : CH_{2}$$

$$CH_{2}N_{2} \xrightarrow{h \cup \text{ or } \Delta} N_{2} \uparrow + : CH_{2}$$

$$CH_{2} = C = O \xrightarrow{\Delta} : CH_{2} + CO \uparrow$$

Types of carbene

Singlet

– Ç –

Table : 2

Shape	Bent	Linear
Hybridisation	sp ²	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Diamagnetic	Diradical

The nitrogen analog of carbenes are nitrenes. They are very reactive since in them octet of N is incomplete.

In nitrenes only one valencies of N are satisfied.

Benzyne

F

Nitrenes

The benzene ring has one extra C – C π bond in benzyne



Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp² since the overlap between these orbitals is not so much effective.