GENERAL ORGANIC CHEMISTRY

1. GENERAL ORGANIC CHEMISTRY

1.1 Introduction

In 1807, Berzelius proposed the term 'Organic Chemistry' for the study of compounds derived from natural sources. This was based on the theory of **vitalism** which said that all living systems possessed a 'vital force' which was absent in non-living systems. Compounds derived from living natural sources (organic) were thought to be fundamentally different from inorganic compounds.



No Vita Force

Living Systems

Non-living Systems

The vital force could be philosophically thought as the mysterious force God instilled in the living systems.

In 1823, Friedrich Wohler joined Berzelius as his student. In 1828, Wohler made a discovery which changed the definition of organic chemistry. Wohler conducted the following experiment.

$$\begin{array}{c} \stackrel{\leftrightarrow}{\text{Display}}_{\text{Ammonium Cyanate}} (\text{Inorganic}) \xrightarrow{\text{evaporation}} O = C(\text{NH}_2)_2(s) \\ \stackrel{\text{Urea Crystals}}{\text{Urea Crystals}} (\text{Organic}) \end{array}$$

Wohler successfully synthesized an organic compound starting from an inorganic compound. Following this, many others synthesized organic compounds starting from inorganic compounds. Thus, the theory of vitalism and the definition of organic chemistry lost its meaning.

But what was common in all the above compounds synthesized was the presence of carbon. Carbon shows a special property **catenation**. Carbon can connect with other carbon atoms to form long chains and rings (selfcatenation) and can connect with atoms of many other elements in the periodic table (cross-catenation). Because of this reason, carbon can form a wide variety of compounds. Therefore, **the modern definition of organic chemistry is the study of carbon compounds**.

Probably, the vital force can be explained by the fact that most of the life-giving and life-sustaining functions are performed by carbon compounds, for example, the human tissues and skin are formed by proteins, respiration is possible due to haemoglobin, the information in our genes is carried out in the form of DNA/RNA etc.

General Organic Chemistry is the detailed study of the basic concepts and factors that govern the progress and outcome of reactions. *Note...* The making and breaking of bonds usually occurs in several discrete steps before transforming transforming into products. The detailed sequential description of all the steps is called the **mechanism** of the reaction.

2.1 Sigma and Pi Bonds - Comparison



Sigma Bond

Pi Bond

Property	Sigma (σ) Bond	Pi (π) Bond
Overlap	Axial/Head-on	Parallel/Lateral/ Side-ways
Electron Cloud	Along the inter-nuclear axis	Perpendicular to the inter-nuclear axis
Bond Strength	Stronger	Weaker

2.2 Structural Formulas

Several kinds of formulas are used by organic chemists to represent organic compounds.

2.2.1 Complete Formulas >

Complete formulas are lewis structures which shows all bond pair of electrons as a dash (–). Lone pair of electrons are shown as a pair of dots.

2.2.2 Condensed Formulas

Condensed formulas are written without showing all the individual bonds. Each central atom is shown together with the atoms that are bonded to it.

2.2.3 Line-Angle Formulas

These are also called **skeletal structures** or a **stick figure**. Line-angle formulas are often used for cyclic compounds and occasionally for non-cyclic ones. Bonds are represented by lines, and carbon atoms are assumed to be present where two lines meet or a line begins or ends. Hydrogens are generally implicit in these drawings.

2.2.4 Tetrahedral Representation

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(away from the observer) and out of the plane (towards the observer) respectively. Bonds lying in the plane of paper are depicted by using a normal line (—).



2.3 Degrees of Carbon

It is defined as the number of carbons attached to carbon under observation.



Table : Hybridization of Common Molecules.

Molecule LP Hybridization Geometry Shape sp^3 *CH₄ 4 0 0 Tetrahedral Tetrahedral sp^3 *NH₂ 3 0 1 Tetrahedral **Trigonal Pyramidal** sp³ H₂O* 2 0 2 Tetrahedral V-shape or Bent sp² *CH2=CH2 3 1 0 **Trigonal Planar Trigonal Planar** 2 *CH=CH 2 0 Linear Linear sp

2.4 Hybridization

Hybridisation is a process in which two or more atomic orbitals of comparable energy of the valence-shell of an atom (**central atom** of the molecule or ion) either in its ground state or in its excited state mix together and give rise to the formation of new degenerate orbitals which are called **hybrid orbitals**.

2.5 Applications of Hybridization

Hybridization	% s-character
sp^3	25.0
sp^2	33.3
sp	50.0

2.5.1 Size of Hybrid Orbitals

As % s-character increases, size of hybrid orbital decreases. Therefore

Size of Hybrid Orbital : $sp^3 > sp^2 > sp$

2.5.2 Electronegativity of Hybrid Orbitals

As % s-character increases, electronegativity of hybrid orbital increases. Therefore

EN of Hybrid Orbital : $sp > sp^2 > sp^3$

2.6 Dienes

Dienes are organic compounds containing two double bonds. There are three types of dienes :

(a) Isolated (b) Conjugated (c) Cumulated

2.6.1 Isolated Diene

In this case, double bonds are separated by atleast one sp³ carbon.

$$\begin{array}{c} CH_2 = CH - CH_2 - CH = CH_2 \\ \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ sp^3 sp^2 sp^3 sp^2 sp^2 sp^2 \end{array}$$

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2.6.2 Conjugated Diene

Double bonds are separated by only one single bond (or 4 sp^2 carbons in a row).

$$\begin{array}{c} CH_2 = CH - CH = CH_2 \\ \uparrow \qquad \uparrow \qquad \uparrow \qquad \uparrow \\ sp^2 \qquad sp^2 \qquad sp^2 \qquad sp^2 \qquad sp^2 \end{array}$$

2.6.3 Cumulated Diene

Both sets of double bonds are at the same carbon.

$$CH_3$$
— CH = C = CH — CH

A substituted allene

An allene is CH₂=C=CH₂

2.6.4 Stability of Dienes

The relative stabilities of dienes follows the order Conjugated > Isolated > Cumulated

Important: Stability $\propto \frac{1}{\text{Energy Content of the molecule}}$

2.7 Commonly Occuring Forms of Carbon

The commonly occuring forms of carbon are

(a) Diamond	(b) Graphite	(c) Carbides
(d) Fullerenes	(e) Charcoal	
Diamond -	Each C is sp ³ . Tetra	hedral solid.

Graphite - Each C is sp^2 . Layered solid with weak van der Waal's forces between layers.

Calcium Carbide - Each C is sp.

Fullerene - Each C is sp^2 .

3. BREAKING OF BONDS

In organic chemistry, the bond that is important for the study of reactions is covalent bond. We, therefore, study ways in which a covalent bond can be broken.

(a) Homolytic Fission (b) Heterolytic Fission

3.1 Homolytic Fission or Homolytic Cleavage

In this kind of bond breaking, each atom separates with one electron, leading to the formation of highly reactive species known as radicals (or free radicals).

$A^{\bullet} + B^{\bullet}$

The bond breaking is shown by two half-headed or fishhook arrows. A half-headed arrow shows the movement of one electron.

Radicals are neutral and are odd electron species.

3.2 Heterolytic Fission or Heterolytic Cleavage

In this type of covalent bond breaking, the shared pair of electrons are transferred to the more electronegative part. Therefore, this fission leads to the formation of a cation and an anion (ion-pair).

$$A \xrightarrow{\frown} B \longrightarrow A^{\oplus} + B^{\Theta} \quad (if EN_B > EN_A)$$

$$A \xrightarrow{\frown} B \longrightarrow A^{\Theta} + B^{\oplus} \quad (if EN_A > EN_B)$$

The bond breaking is shown by a full-headed arrow. A full headed arrow shows the movement of a pair of electrons. In organic chemistry, the movement of electrons is always shown by curved arrows - half-headed or full-headed arrows.

4. INDUCTIVE EFFECT

When two unlike atoms form covalent bond, the electronpair forming the sigma bond is never shared equally between the two atoms but is shifted slightly towards the more electronegative species.



There are broadly three types of groups/atoms that may be attached to carbon as illustrated. Although C is more electronegative than H, the electronegativity difference is small and the bond is generally consider non-polar.

4.1 Nature of Inductive Effect

Inductive effect is a permanent effect and can be directly correlated to its dipole moment.

It is a weak effect as the shifting of electrons takes place only through sigma bonds.

4.2 Effect of branched carbon chain

An illustration has been marked for operation of inductive effect which is self-explanatory.



More the number of δ , lesser the effect





4.3 Electron Donating and Electron withdrawing Groups

Inductive effect may be due to single atom or a group of atoms. Relative inductive effects are measured with reference to hydrogen. Those which donate electrons to carbon chain are called electron-donating groups (EDG) or electron-releasing groups (ERG) and are said to exert +I effect. Those which withdraw electrons from carbon chain are called electron-withdrawing groups (EWG) and are said to exert -I effect.

Important :

- 1. I.E. of alkyl groups : $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_{3}$ -
- In general, greater is the number of carbons in an alkyl group, 2. greater is its +I effect.
- For problem-solving, we take electronegativity of sp-3. hybridized carbon to be more than sp³ hybridized nitrogen.

4.4 Applications of Inductive Effect

4.4.1 Effect on Acidic/Basic Strength

EWG increases acidic strength and decreases basic strength. ERG decreases acidic strength and increases basic strength.

Example - 1

Compare the acidic strength :

(III) CH₂—COOH Ė

Solution :

An alkyl group is donating only if no other EWG is present on it. Therefore, groups like -CH2Cl and -CH2F become electron withdrawing groups.

Series of +I and -I groups in order of their strength -I Series (EWG)

Ċ1 Order of acidic strength : II > III > IV > I



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Order of Acidic Strength : III > II > I

4.4.2 Effect of Distance

If the ERG/EWG moves away, the inductive effect diminishes.

Example - 2

Compare the acidic strength of : (a)

(I)
$$CH_3CH_2CH_2$$
—COOH
(II) CH_3CH_2CH —COOH
 $|$
Cl
(III) CH_3CH —CH₂—COOH
 $|$
Cl
(IV) $CH_2CH_2CH_2$ —COOH
 $|$
Cl

Solution :

(a) (I)
$$CH_3CH_2CH_2$$
—COOH
 \rightarrow
(II) CH_3CH_2CH —COOH
(II) CH_3CH_2CH —COOH
(III) CH_3CH — CH_2 —COOH
(IV) CH_2 — CH_2CH_2 —COOF

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4.4.3 Basicity of Amines

The order in gaseous or liquid phase is :

$$3^{\circ} > 2^{\circ} > 1^{\circ} > NH_{3}$$

To determine the basic strength of amines in **aqueous phase**. We have to consider **inductive effect**, **solvation effect and steric hinderance**. The order of basic strength is therefore experimental in aqueous state as we can't give priority to stability provided by any one factor. Two results are important for aqueous phase :

(a)
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

i.e. $2^\circ > 1^\circ > 3^\circ > NH_3$ (R = CH₃)
(b) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
i.e. $2^\circ > 3^\circ > 1^\circ > NH_3$ (R = C₃H₅)

5. RESONANCE

Molecules are generally represented by simple lewis structures but some molecules can not be represented by just one Lewis structure. This led to the discovery of resonance. Resonance refers to the delocalization of electrons (generally π -electrons).

5.1 Conjugated Systems

5.1.1 Pi alternate Pi

Example - 3







5.1.2 Pi alternate Positive Charge

Example - 4



5.1.3 Pi alternate Negative Charge

Example - 5

$$\overbrace{CH_2}^{\frown} CH \xrightarrow{CH_2}^{\ominus} CH_2 \longleftrightarrow \overrightarrow{CH_2} - CH = CH_2$$

5.1.4 Pi alternate Odd Electron

Example - 6

$$\dot{C}H_2$$
 $\dot{C}H_-\dot{C}H_2$ \longleftrightarrow $\dot{C}H_2$ $\dot{C}H_2$ $\dot{C}H_2$

5.1.5 Pi alternate Lone Pair

This case is similar to 'pi alternate negative charge' as lone pair and negative charge are treated similarly.

Example - 7

$$\overbrace{CH_2}^{\frown} CH \xrightarrow{\frown} \overset{\frown}{NH_2} \longleftrightarrow \overset{\ominus}{CH_2} - CH = \overset{\oplus}{NH_2}$$

$$CH_2 = CH \xrightarrow{O} OCH_3 \iff CH_2 - CH = OCH_3$$

5.1.6 Lone Pair and Positive Charge on Adjacent Atoms

Example - 8

$$\stackrel{\oplus}{\operatorname{CH}}_2 \stackrel{\frown}{\longrightarrow} \operatorname{CH}_2 \stackrel{\oplus}{\longrightarrow} \operatorname{CH}_2 \stackrel{\oplus}{\longrightarrow} \operatorname{CH}_2$$

5.2 Rules for Validity of Lewis Structures

Rule-1:

All the lewis structures must conform to lewis octet rule.

Rule-2:

Position of atoms in all resonating structures must be the same. Only the electrons move.





Rule-3:

All the resonating structures must have the same number of paired and unpaired electrons, i.e. sum of bond pairs and lone pairs must be constant.

Rule-4:

All the atoms participating in resonance in a molecule must be coplanar. This is required for the effective overlap of p orbitals and the delocalization of electrons, for eg, buta-1,3-diene.

5.3 Criteria for Major/Minor Contributors

Resonance forms can be compared using the following criteria in the following order :

- 1. As many octets as possible (a neutral molecule is always more stable in which its octet is complete).
- 2. As many π bonds as possible.
- 3. Negative charge on more electronegative atom is stable.
- 4. Charge separation.

(a) Similar charges - Keep them as FAR as possible to minimize repulsion and instability.

(b) Opposite charges - Keep them as NEAR as possible to maximize attraction and stability.

Example - 9

Which of the following structures is more stable ?

$$\overset{\oplus}{\operatorname{CH}}_{2} \overset{\longrightarrow}{\operatorname{NH}}_{2} \overset{\bigoplus}{\operatorname{CH}}_{2} \overset{\oplus}{\underset{\operatorname{II}}{\operatorname{NH}}} H_{2}$$

Solution :

II is more stable as all the octets are complete.

Example - 10

Which of the following is more stable in the following pairs ?

(a)
$$\overset{\oplus}{\mathrm{CH}}_2 - \overset{\odot}{\overset{\odot}{\operatorname{CH}}} - \mathrm{CH}_3 \longleftrightarrow \mathrm{CH}_2 = \overset{\oplus}{\overset{\oplus}{\underset{(\mathrm{I})}{\operatorname{CH}}}} - \mathrm{CH}_3$$

(I) (II)



Solution :

(a) In II, all octets are complete. Therefore, II is more stable.

(b) I and II are tied on octets and number of π bonds but negative charge is more stable on more electronegative atom. Hence, II is more stable.

Example - 11

Give the order of stability of following resonating structures

(I)
$$CH_2 = CH - CH = CH_2$$

(II) $CH_2 - CH - CH = CH_2$
(III) $CH_2 - CH - CH = CH_2$
(III) $CH_2 - CH - CH - CH_2$
(IV) $CH_2 - CH - CH - CH_2$
(V) $CH_2 - CH = CH - CH_2$

Solution :

In (I), there are maximum number of pi bonds. Therefore, it is most stable. In (II) and (V), the number of pi bonds is equal but charge separation is greater in (V). Therefore, (II) is more stable than (V). In (III) and (IV), there is maximum charge separation but (III) is highly unstable due to electrostatic repulsion. Hence, the order of stability is :

6. MESOMERIC EFFECT

The permanent polarization, due to a group conjugated with a π bond or a set of alternate π bonds, is transmitted through the π electrons of the system-resulting in a different distribution of electrons in the unsaturated chain.

This kind of electron redistribution in unsaturated compounds conjugated with electron-releasing or electron-withdrawing groups (or atoms) is called **Mesomeric Effect** or **Resonance Effect**.

This effect is **permanent** and is indicated by the dipole moment.

6.1 Electron-Releasing and Electron-Withdrawing Group

Groups which release or withdraw electrons by resonance are said to exert M or R effect.

The common thing about all the groups listed is that the atom connected with the conjugated system has a lone pair to donate. Therefore, a generic representation can be

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 $-\ddot{z}$

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6.1.2 Electron-Withdrawing Groups (–R or –M effect)

$$-NO_2$$
, $-CN$, $-CHO$, $-COR$, $-COOH$, $-SO_3H$, $-NR_3$, $-NH_3$

The common thing about all the groups listed is that the atom connected with the conjugated system has a π bond with another more electronegative atom which withdraws the electrons or directly has a positive charge on them. Therefore, a generic representation can be

 $-Y \equiv Z (EN_Z > EN_Y)$

6.1.3 Dual Behaviour

Groups such as -N = O are both electron-releasing and electron-withdrawing as illustrated.

Example - 12

As electron releasing group

$$\dot{c}_{H_2} \rightarrow c_{H_2} \dot{c}_{H_2} \rightarrow \ddot{c}_{H_2} - c_{H_2} \dot{e}_{H_2} \rightarrow c_{H_2} \dot{e}_{H_2} - c_{H_2} \dot{e}_{H_2} - c_{H_2} \dot{e}_{H_2} \dot{e}_{H_2} - c_{H_2} \dot{e}_{H_2} \dot{$$

As electron withdrawing group

$$CH_2 \xrightarrow{\bigcirc} CH \xrightarrow{\sim} N \xrightarrow{\bigcirc} O \longleftrightarrow \xrightarrow{\oplus} CH_2 \xrightarrow{\leftarrow} CH \xrightarrow{\cong} N \xrightarrow{\ominus} O$$

Which behaviour dominates and which is used in a particular context will be discussed later in **Electrophilic Aromatic Substitution** later.

Resonance Effect does NOT depend upon distance unlike inductive effect.

6.2 Applications of Mesomeric Effect

6.2.1 Effect on Acidic Strength of Carboxylic Acids and Phenoly

The resonating structure of carboxylic acid leads to chargeseparated structure which is less stable than the carboxylate ion in which charge is delocalized. Therefore, carboxylic acid readily loses proton (H^{\oplus}) to form a carboxylate ion.



Charge Separation (less effective resonance)

Bond Polarity Increases

Carboxylate Ion

Charge Delocalization (more effective resonance)

Similarly, in phenol, resonance leads to charge separation which increases the rate of ionization and forms phenoxide ion which is stabilized by charge delocalization.





6.2.2 Effect on Reactivity of Carboxylic Acid Derivatives

A typical nucleophilic reaction is represented as :



The stronger is the bond between C and Z, the difficult it is for a nucleophile to break a bond and therefore, lower reactivity.



Reactivity order of carboxylic acid derivatives towards nucleophilic acyl substitution is :

Acyl Chloride > Acid Anhydride > Ester > Amide

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(I) (II) NO₂ ĊH₃ **OCH**₃ C1 (I) (II) (III) (IV) (V) **Solution :** -I+I-I-I √ -MV $+M\sqrt{}$ +MNH₂ VH2 The order of acidic strength is : II > V > I > III > IVIn the previous example, let's also discuss the stability of phenoxide ions corresponding to (II) and (IV). NO₂ (I)(II) -I-M √ ⊖⊖ O⊖ 0 Positive Bond to (II) and (IV). Formation and Negative leads to Stability. Charge in Vicinity. **Attractive Forces STABLE**

6.2.3 Effect of ERG/EWG on Acidic/Basic Strength

EWG increases the acidic strength and decreases the basic strength.

ERG decreases the acidic strength and increases the acidic strength.

Example - 13

Arrange the following in the order of decreasing acidic strength :



Solution :



00 $0^{\overset{\circ}{\ominus}}$:ÖCH3 :OCH3 OCH

> Same Charges in Vicinity. **Repulsive Forces ÛNSTABLE**

Example - 14

Arrange the following in decreasing order of basic strength





Therefore, order of basic strength is : IV > III > I > V > IILet's also discuss the stability of anilinium ions corresponding







7. HYPERCONJUGATION

Hyperconjugation is the ability of the σ bond electrons of an α C—H bond to undergo conjugation with the adjacent π electrons. It is also known as **Baker-Nathan Effect**, **No-Bond Resonance** and σ - π Effect.

7.1 α -Carbon and α -Hydrogen

We have already discussed the α , β , γ nomenclature. Let's take an example :



 α -Carbon is the carbon attached to a functional group such as C=C. The hydrogen attached to α -carbon is called α -hydrogen. For an α C-H bond to be eligible for hyperconjugation, α C must be sp³ hybridized.

Example - 15

Mark the number of α -C and α -H in the given compounds (a) $(CH_3)_2C = C(CH_3)_2$ (b) $[((CH_3)_3C)_3C]_2C = C[C(C(CH_3)_3)_3]_2$ (c) $CH_2 = CH - CH = CH_2$ (d) $CH_2 = CH - CH_2 - CH - CH = CH_2$ \downarrow CH_3

Solution :

(a)
$$\overset{\alpha}{CH_3}$$
—C==C $\overset{\alpha}{-}\overset{CH_3}{\underset{CH_3}{CH_3}}$



$$\alpha C = 4, \alpha H = 0$$

(c)
$$CH_2 = CH - \ddot{C}H = CH_2$$

 $\alpha C = 1$, $\alpha H = 1$ but since αC is sp² hybridized, therefore, it won't participate in hyperconjugation. Therefore, $\alpha H = 0$ that will participate in hyperconjugation.

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

$$\alpha C = 2, \alpha H = 3$$

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>>

7.2 Mechanism of Electron Donation in Hyperconjugation

$$H \xrightarrow{C} C \xrightarrow{H} C \xrightarrow{H} H \xrightarrow{i} H \xrightarrow{i}$$

The hybrid formed by these resonating structures better known as hyperconjugating structures is :

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$$H \xrightarrow{\delta^{\bigoplus}} C \xrightarrow{H} \xrightarrow{\delta^{\bigoplus}} H \xrightarrow{\delta^{\bigoplus}} C \xrightarrow{H} H \xrightarrow{\delta^{\bigoplus}} Partial Single Bond$$
$$H H H H^{\delta^{\bigoplus}}$$

Now, greater the number of α -H, greater the number of hyperconjugating structures and more is the electron donation of alkyl group to π bond.

The order of electron-donation of alkyl groups based on hyperconjugation is :

$$\overset{\alpha}{\operatorname{CH}}_{3} \longrightarrow \operatorname{CH}_{3} \longrightarrow \overset{\alpha}{\operatorname{CH}}_{2} \longrightarrow \operatorname{CH}_{3} \longrightarrow \overset{\alpha}{\operatorname{CH}}_{2} \longrightarrow \operatorname{CH}_{3} \longrightarrow \overset{\alpha}{\operatorname{CH}}_{3} \longrightarrow \overset{\alpha}{\operatorname{CH}$$

 $Methyl > 1^{\circ} > 2^{\circ} > 3^{\circ}$

More is the number of α -H, more is the π bond delocalized. This implies that more will be the stability of alkene and less will be the heat of hydrogenation and more is the **no-bond resonance energy**.

7.3 Applications of Hyperconjugation

7.3.1 Stability of Alkenes

More is the number of α -hydrogen, more is the number of hyperconjugating structure and therefore more stability and greater no bond resonance.

Example - 16

Which alkene is more stable ?

$$(CH_3)_2C = CH - CH_3$$
 $(CH_3)_2CH - CH = CH_2$
(I) (II)

Solution :

$$\begin{array}{c} \overset{\alpha}{C}H_{3} \longrightarrow C \Longrightarrow C \longrightarrow \overset{\alpha}{C}H_{3} \qquad CH_{3} \longrightarrow \overset{\alpha}{C}H \longrightarrow C \Longrightarrow C \longrightarrow H \\ | & | & | & | \\ H_{3}C & H & CH_{3} \longrightarrow H & H \\ (I) & (II) \\ \alpha C = 3, \alpha H = 9 & \alpha C = 1, \alpha H = 1 \\ I \text{ is more stable than II.} \end{array}$$

7.3.2 Acidic Character of Alkenes

Hyperconjugation weakens the α C-H bond in hyperconjugation hybrid (partial single bond) and therefore α H can be lost easily.



7.3.3 Stability of Carbocations

$$\begin{bmatrix} H & H^{\oplus} \\ H \stackrel{\alpha}{\longrightarrow} C \stackrel{\oplus}{\longrightarrow} H \stackrel{C}{\longrightarrow} C \stackrel{C}{=} CH_2 \stackrel{\bullet}{\longleftrightarrow} 2 \text{ more} \\ | & | & hyperconjugating} \\ H & H & structures. \end{bmatrix}$$

The positive charge on C is delocalized over αH to give stability to the carbocation. More is the number of αH , more is the stability of carbocations.

Stability of Carbocations



8. ELECTROMERIC EFFECT

Electromeric effect is observed only in the presence of a reagent and is therefore, a temporary effect. When a reagent approaches a molecule, the multiple bond such as C = C or C = O is polarized by the complete transfer of π electrons.

When the multiple bond is between two unlike atoms, the shift of electrons takes place towards more electronegative atom.

$$-\underbrace{C}_{l} \underbrace{\bigcirc}_{\text{Reagent Added}} \underbrace{\frown}_{\text{Reagent Removed}} \underbrace{\frown}_{l} \underbrace{\frown}$$

9. COMPARISON OF INDUCTIVE, HYPERCONJUGATION AND RESONANCE EFFECTS

Inductive Effect is a σ - σ interaction and acts through strong sigma bonds.

Resonance/Mesomeric Effect is a π - π interaction and acts through weak pi bonds.

Hyperconjugation is a σ - π interaction and acts through a strong sigma and a weak pi bond.

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Therefore, the order of importance is :

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Resonance > Hyperconjugation > Inductive

10. STERIC INHIBITION OF RESONANCE (SIR)

When both the **ortho positions** of a **bulky functional group** are occupied by **bulky substituents**, all the three groups are out of plane of the benzene ring.



FG, S1, S2 - Bulky Groups

Example - 17

Mark the order of basic strength :



Solution :

In (II) and (III), the lone pair of N is in conjugation with the benzene ring and is not available for donation. (II) is less basic than (III) due to -I and -M of $-NO_2$ group. It may seem that (I) is least basic due to presence of $2 - NO_2$ groups but $-NO_2$ and $-N(CH_3)_2$ are all bulky groups. This is a case of steric inhibition of resonance due to which the lone pair of N is not in conjugation and is readily available for electron donation. Hence, the order of basic strength is :

(I) > (III) > (II)

Example - 18

Mark the order of bond lengths in the given molecule.



Solution :

-I, $-NO_2$ are bulky groups and is case of steric inhibition of resonance. Therefore, the $-NO_2$ groups ortho to -I are out of conjugation while the $-NO_2$ group para to -I will be in conjugation with the benzene ring. Therefore, bonds 'a' and 'b' will always have single bond character while 'c' has double bond character. Therefore :

c < a = b

11. CARBOCATION

11.1 Definition

Carbocation is the intermediate of carbon containing positive charge. It has six electrons in the valence shell.

11.2 Geometry and Hybridization

Hybridization of $C^{\oplus} = sp^2$ Geometry of $C^{\oplus} =$ Trigonal Planar



11.3 Classification of Carbocations

This classification will also be used for carbanions and carbon free radical and will be studied only in this section.

$$R-CH_2$$
 1° Primary Carbocation

$$R_2$$
— CH 2° Secondary Carbocation

$$R_3C\oplus$$
 3° Tertiary Carbocation



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11.4 Stability of Carbocations

There are three factors contributing to the stability of carbocations :

- (a) Inductive Effect
- (b) Hyperconjugation
- (c) Resonance
- Order of stability :





Example - 19

Rank the stability of carbocations in each case :



Solution :





- (a) Resonance Stabilization (Positive charge is delocalized over 4 atoms) and 6αH and +I.E.
- 9αH and +I.E.



Resonance Stabilization (Positive charge is delocalized over 7 atoms) and 3αH and +I.E.

Order of stability : III > I > II

11.5 Formation of Carbocations

11.5.1 Ionization of Carbon-Leaving Group Bond In this method :

- (a) Bond between carbon and leaving group ionizes.
- (b) Leaving group accepts the pair of electrons that were shared in the covalent bond.

Rate of formation of carbocation depends on :

- (a) The stability of carbocation formed.
- (b) The nature of the leaving group. Weaker the base better the leaving group. This is because weaker leaving group implies a stable compound and its formation will therefore be favoured.

11.5.2 Addition of Proton to a π bond

$$R-CH = CH_2 + H^{\oplus} \longrightarrow R - CH - CH_3$$

Rate of carbocation formation depends on :

- (a) Stability of carbocation formed.
- (b) Strength of the electrophile.

11.6 Reactions of Carbocations

There are three important reactions of carbocations :

- (a) Capture a Nucleophile
- (b) Lose a proton to form a π bond.
- (c) Rearrangement

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11.6.1 Capture a Nucleophile

 $R^{\oplus} + Nu^{\stackrel{\bullet \bullet}{\ominus}} \longrightarrow R - Nu$



11.6.2 Loose a proton to form a π bond

Example - 20

Form the products from the following reaction :

$$\begin{array}{c} \text{CH}_{3} \longrightarrow \text{CH}_{2} \longrightarrow \text{CH}_{2} \longrightarrow \text{CH}_{3} \xrightarrow{\text{conc. H}_{2}\text{SO}_{4}} \\ | \\ \text{OH} \end{array}$$

Solution :

Step-1 : Protonation



Step-2 : Formation of Carbocation

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

$$\oplus OH_{2}$$

$$\downarrow$$

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

$$CH_3 - CH - CH_2 - CH_3 +$$

Step-3 : Deprotonation



When carbocation deprotonation can lead to more than one product, all products are formed and the most stable product is the major product.

Major

11.6.3 Carbocation Rearrangement

Minor

A carbocation can become more stable by rearrangement. Bonding electrons of carbocation may shift between adjacent atoms to form more stable carbocation. There are two kinds of shifts that take place in order to gain stability.



In the above example, both hydride and methyl shifts are possible leading to more stable carbocation but only that shift is preferred which leads to more stable carbocation. In this example, hydride shift will take place. Important : The shift takes place in the form of

12. CARBANIONS

 H^{\ominus} or CH_{2}^{\ominus} .

12.1 Definition

Carbanion is the intermediate of carbon containing negative charge. It has eight electrons in the valence shell.

Hybridization of C^{Θ} : sp³

Geometry: Trigonal Pyramidal

Carbanion and ammonia are isoelectronic species having same structure





Carbanion

Ammonia

12.3 Stability

ERG will increase the electron density at carbon and will make it unstable. EWG will decrease the electro density at carbon and will make it stable.

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Order of Stability :

$$\begin{array}{c} & \stackrel{\leftrightarrow}{\oplus} \\ & \stackrel{\leftarrow}{\leftarrow} \\ & \stackrel{\leftarrow}{\leftarrow} \\ & \stackrel{\leftarrow}{\to} \\ & \stackrel{\to}{\to} \\$$



Example - 22

Give the order of stability of :

$$\begin{array}{cccc} \overset{\overleftrightarrow{}}{\overset{}_{\scriptstyle \leftarrow}} & CH_2 & CH_2 \overset{\overleftrightarrow{}_{\scriptstyle \leftarrow}}{\overset{\scriptstyle \leftarrow}} & CH \overset{\overleftrightarrow{}_{\scriptstyle \leftarrow}}{\overset{\scriptstyle \leftarrow}} \\ (I) & (II) & (III) \end{array}$$

Solution :

As s-character increases, electronegativity of C increases and therefore negative charge will become more stable. Therefore, order of stability is :

 $\mathrm{III} > \mathrm{II} > \mathrm{I}$



12.4 Formation of Carbanion

There are two methods for the formation of carbanion :

- (A) Partial formation via Grignard Reagent
- (B) Formation from Carbonyl Compounds

We will discuss these methods in the subsequent section

12.4.1 Formation via Grignard Reagent



$$\delta^{\Theta} \delta^{\Phi} R - MgX$$

Development of partial charges in polar covalent bond.

- 1. Carbanion is never formed as an intermediate that can be isolated in the case of Grignard Reagent. It directly participates in the reaction.
- 2. Dry ether is used in this formation as it is inert to Grignard reagent. For the formation of Grignard reagent from aryl halides, we use tetrahedrofuran (THF) as solvent.



12.4.2 Formation from Carbonyl Compounds



There are three reasons for the easy formation of carbanion from carbonyl compounds

- (a) Resonance stabilization of carbanion which is the conjugate base of carbonyl compound.
- (b) Hyperconjugation makes the α C-H bond acidic.
- (c) –I of increases the acidic strength of C–H bond.

12.5 Reactions of Carbanion

The reactions of carbanion are very fast as electropositive carbon carries negative charge.

12.5.1 Grignard Reagent as a Base

In this reaction it captures acidic hydrogen.



In (d), the reaction with terminal alkyne also takes place as sp-hydridized carbon is highly electronegative and therefore H attached to it is fairly acidic.

12.5.2 Grignard Reagent as a Nucleophile

Grignard Reagent reacts with carbonyl compounds to form alcohols. This is a very important method for the synthesis of alcohols.

Mechanism :



 H_3O^{\oplus} is never added along with the first step as Grignard

Reagent will react with H^{\oplus} to give R—H as in previous reaction.

12.5.3 Aldol Condensation

This reaction is shown by carbonyl compounds containing atleast one α H in presence of dilute base such as dilute NaOH.

$$\overset{\alpha}{\operatorname{CH}_{3}} \overset{\square}{\operatorname{C-R}} \xrightarrow{\operatorname{OH}^{\ominus}(10\%)}_{\text{or dil NaOH}} \text{Aldol Condensation Product}$$

Mechanism :

0





13. CARBON FREE RADICALS

13.1 Definition

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Carbon Free Radical is the intermediate of carbon having an odd electron. It is neutral and has seven electrons in the valence shell. It is highly reactive as it requires only one electron to complete its octet and therefore, is short-lived.



The hybridization of carbon free radical was proposed after experimental verification of structure of different radicals.

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It was proposed that when ERG are placed on C[•], it has sp² hybridization and when EWG are placed on C•, it has sp³ hybridization.

Molecule	Hybridization	Location of odd electron
•CH ₃	sp^2	р
•CF ₃	sp ³	sp ³

13.3 Stability

ERG increase stability while EWG decrease stability.

$$\begin{array}{c} *CH_{2} \\ \hline \\ R_{3}C* > R_{2}CH* > RCH_{2}* > CH_{3}* > \\ \hline \\ CH_{2} = CH - CH_{2} \\ Resonance Stabilized \\ Most Stable \\ \end{array}$$

13.4 Formation of Carbon Free Radical

Carbon Free Radicals are formed by homolytic cleavage of bonds. They are formed :

(a) at high temperature in the gas phase

- (b) in non-polar solvents
- (c) by ultraviolet light
- (d) by addition of other radicals

13.5 Reactions of Carbon Free Radical

The most common reactions in which free radical is involved are :

(a) Halogenation of alkanes.

(b) Addition of HBr in the presence of peroxides to alkenes. (Anti-Markonikov Rule)

(c) α -Halogenation of alkenes.

- (d) Wurtz Reaction
- (e) Decarboxylation reaction

13.5.1 Free Radical Halogenation of Alkanes

The typical reactions of free radical are chain reaction mechanisms. There are three steps in a chain reaction mechanism : initiation, propagation and termination.

$$CH_4 + X_2 \xrightarrow{hv} CH_3X + HX$$

Mechanism

(I) Chain Initiation

There are two choices :

$$H_3C H \rightarrow CH_3 + H$$

Hydrogen free radical
is highly unstable.

(b)
$$Cl-Cl \xrightarrow{hv} 2Cl$$

(I) (b) will take place as it is energetically feasible.(II) Chain Propagation

(a)

(

(a)

$$Cl_{*} + H - Cl_{*} + CH_{3} - V$$

$$Cl_{*} + H - Cl_{*} + CH_{3} - V$$

$$Cl_{*} + H - Cl_{*} + CH_{3} - V$$

Highly Unstable

b)
$$\cdot CH_3 + Cl \longrightarrow CH_3 - Cl + Cl$$

This will again participate in II(a) to propagate the reaction.

(III) Chain Termination

The various free radicals in the progress of reaction are : $CI_{3} \cdot CH_{3} \cdot .$ There are ways in which free radicals from different chains may combine to terminate the reaction.

$$CH_{3^{*}} + Cl^{*} \longrightarrow CH_{3} - Cl$$

$$CH_{3^{*}} + CH_{3^{*}} \longrightarrow CH_{3} - CH_{3}$$

$$Cl^{*} + Cl^{*} \longrightarrow Cl_{2}$$

There is a side-product CH_3 — CH_3 that is formed in this reaction. Besides these, a number of other side-products such as CH_2Cl_2 , $CHCl_3$ and CCl_4 have also been observed. These get formed since carbon free radical is highly reactive. It randomly reacts with other species that make it stabler.

GENERAL ORGANIC CHEMISTRY





14. NOMENCLACTURE-I

14.1 INTRODUCTION

In 1949, an organization was set up to formulate the rules for naming organic compounds. This organization is **IUPAC** - **International Union for Pure and Applied Chemistry**. Prior to this, the organic compounds were known by their **trivial/common names** which generally indicated their source. For example, formic acid gets its name from *formica (Latin, red ants)* and acetic acid gets its name from *acetum (Latin, vinegar)*.

Important : Systematic nomenclature is required in order to have unambigous names for all compounds.

14.2 CLASSIFICATION OF HYDROCARBONS



Important :

- 1. Aliphatic Compounds do not have rings and exist as a chain of carbon atoms.
- **2. Alicyclic Compounds** have similar properties as aliphatic compounds except that the carbon chain exists in the form of ring.
- **3.** Aromatic Compounds are based on the structure of benzene. These compounds are also called **arenes**.

14.3 HOMOLOGOUS SERIES

A homologous series (*Greek homos* = "the same as") is a family of compounds in which each member differs from the next by one **methylene** (CH_2) group. The members of the homologous series are called **homologues**. Example :

(a) Alkanes $C_n H_{2n+2}$ (b) Alkenes $C_n H_{2n}$ (c) Alkynes $C_n H_{2n-2}$





Name	No. of Carbon Atoms	Structure	Substituent Name
<u>Meth</u> ane	1	CH ₄	Methyl
<u>Eth</u> ane	2	CH ₃ CH ₃	Ethyl
<u>Prop</u> ane	3	CH ₃ CH ₂ CH ₃	Propyl
<u>But</u> ane	4	CH ₃ (CH ₂) ₂ CH ₃	Butyl
<u>Pent</u> ane	5	CH ₃ (CH ₂) ₃ CH ₃	Pentyl
<u>Hex</u> ane	6	CH ₃ (CH ₂) ₄ CH ₃	Hexyl
<u>Hept</u> ane	7	CH ₃ (CH ₂) ₅ CH ₃	Heptyl
<u>Oct</u> ane	8	CH ₃ (CH ₂) ₆ CH ₃	Octyl
<u>Non</u> ane	9	CH ₃ (CH ₂) ₇ CH ₃	Nonyl
<u>Dec</u> ane	10	CH ₃ (CH ₂) ₈ CH ₃	Decyl
<u>Undec</u> ane	11	CH ₃ (CH ₂) ₉ CH ₃	
<u>Dodec</u> ane	12	CH ₃ (CH ₂) ₁₀ CH ₃	
<u>Tridec</u> ane	13	CH ₃ (CH ₂) ₁₁ CH ₃	
<u>Tetradec</u> ane	14	CH ₃ (CH ₂) ₁₂ CH ₃	
<u>Pentadec</u> ane	15	CH ₃ (CH ₂) ₁₃ CH ₃	
<u>Eicos</u> ane	20	CH ₃ (CH ₂) ₁₈ CH ₃	

14.4 NOMENCLATURE OF UNBRANCHED ALKANES

Meth, Eth, Prop, But, etc. are called compound roots. Compound roots represent the number of carbon atoms.

14.5 IUPAC NAME TEMPLATE

Prefix	Compound Root		Suffix
Substituente	No. of C in the	Unsaturatio	n + Functional Group
Substituents	Parent Chain	Index	Suffix (optional)
eg. Methyl	eg. Meth	eg. ane	eg. ol
Ethyl	Eth	ene	al
Propyl	Prop	yne	oic acid
Bromo			

This template will be used to give the name for any organic compound.

14.6 RULES FOR NOMENCLATURE OF SIMPLE HYDROCARBONS

Rule-1:

Determine the **longest carbon chain in the molecule (parent chain).** Where a double/triple bond is present, choose the chain which includes these bonds. If there is a cyclic structure present, the longest chain starts and stops within the cyclic structure.

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EXAMPLE



(II) is the correct chain selection.

Rule-2:

Assign numbers to each carbon of the parent chain. Numbering is done to identify the parent alkane (compound root) and to locate the positions of the carbon atoms at which branching takes place. The numbering is done in such a way that **the branched atoms get the lowest possible number**.

EXAMPLE



If there is a tie for the first branch, then go to the second and so on until a difference is observed.

EXAMPLE

(I)
$$\stackrel{1}{C} \stackrel{2}{--} \stackrel{3}{C} \stackrel{4}{--} \stackrel{5}{C} \stackrel{6}{--} \stackrel{C}{C}$$

(I) $\stackrel{1}{C} \stackrel{2}{--} \stackrel{3}{C} \stackrel{4}{--} \stackrel{5}{--} \stackrel{6}{--} \stackrel{C}{C}$
(II) $\stackrel{6}{C} \stackrel{-}{--} \stackrel{5}{--} \stackrel{4}{--} \stackrel{3}{--} \stackrel{2}{--} \stackrel{-}{--} \stackrel{C}{--} \stackrel{C}{--}$

Rule-3:

Determine the compound root and the unsaturation index. **Compound root corresponds to the number of carbon atoms in parent chain.** Add prefix cyclo if the parent chain is cyclic.

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Unsaturation Index	Suffix
C—C	—ane
C=C	— ene
C=C	—yne

EXAMPLE



Rule-4 :

Determine the correct name for each branch for example, alkyl groups such as methyl, ethyl, etc. Attach the name of the branches alphabetically along with their positions to the parent chain as prefix. Separate numbers from letters with hyphens.

EXAMPLE



6-Ethyl-2-methylnonane

If two substituents are in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.



Rule-5:

When two or more branches are identical, use prefixes di-, tri-, tetra-, etc. Numbers are separated with commas and prefixes are ignored while determining alphabetical order.

EXAMPLE

(I)
$$\overset{9}{C} \overset{8}{-} \overset{7}{C} \overset{6}{-} \overset{5}{C} \overset{4}{-} \overset{3}{} \overset{2}{-} \overset{1}{C} \overset{1}{-} \overset{2}{C} \overset{1}{-} \overset{1}{C} \overset{2}{-} \overset{1}{C} \overset{1}{-} \overset{1}{C} \overset{2}{-} \overset{1}{C} \overset{1}{-} \overset{1}{-} \overset{1}{C} \overset{1}{-} \overset$$

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- 3, 3-Dimethyl-7-ethylnonane INCORRECT
 - 7-Ethyl-3, 3-dimethylnonane CORRECT



INCORRECT

This is an incorrect selection as lowest number rule is violated.

EXERCISE

Give the IUPAC names of :







Solution :





14.7 ALKYL SUBSTITUENTS - COMMON AND SYSTEMATIC NAMES

CH ₃	-	Methyl
CH_3CH_2	_	Ethyl

From three carbon onwards, alkyl substituents can be complicated for which common as well as systematic names are possible.

Rules for Systematic and Common Names

- **Rule-1 :** For systematic names, the carbon atom of the branch that attaches to the parent chain is numbered one.
- **Rule-2**: Substituents which have branching at the first carbon can be classified as secondary (*sec-*) or tertiary (*tert-*) depending upon the number of carbons attached to it. '*sec-*' and '*tert-* are italicized and can also be abbreviated as '*s-*' or '*t-*' respectively.
- **Rule-3**: Substituents which have a CH₃- group on second last carbon are called **iso** and which have two methyl groups on second last carbon are called **neo**.
- Rule-4: |S0 and neo are considered while determining alphabetical order of substituents. 'sec-' and 'tert-' are not considered.



	Alkyl Substituent	Systematic Name	Common Name
1.	$-CH_2CH_2CH_3$	propyl	propyl
2.	-CH-CH ₃	1-methyl ethyl	isopropyl (not s-propyl)

- ĊH₃
- 3. $-CH_2CH_2CH_2CH_3$
- 4. $-CH-CH_2CH_3$ | CH_3

5. —CH₂—CH—CH₃ | CH₃

- 7. $-CH_2CH_2CH_2CH_2CH_3$
- 8. $-CHCH_2CH_2CH_3$ | CH_3
- 9. $-CH_2$ $-CH_-CH_2CH_3$ | CH_3
- 10. $-CH_2-CH_2-CH-CH_3$
- 11. $-CH-CH_2CH_3$ | CH_2CH_3
- 12. $-CH-CH-CH_3$ | | | CH_3 CH_3



14.
$$-CH_2$$
 $-CH_3$ $|$
 CH_3 $-CH_3$ $-CH_3$ $|$
 CH_3 $-CH_3$

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15. NOMENCLATURE-II

15.1 ALKYL SUBSTITUENTS - COMMON AND SYSTEMATIC NAMES

EXERCISE

Give IUPAC names for :





Solution :

15.1.1 Corollory to Longest Chain Rule

If there happen to be two chains of equal length, then that chain is selected which contains more number of side chains

EXAMPLE



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IUPAC Name : 2,3,5-Trimethyl-4-propyloctane

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{2}\mathrm{-}\mathrm{CH}_{3}\\ |\\ \mathrm{CH}_{3}\mathrm{-}\mathrm{C}\mathrm{-}\mathrm{CH}_{3}\\ |\\ \mathrm{CH}_{3}\mathrm{-}\mathrm{C}\mathrm{H}_{3}\end{array}$$





15.2 FUNCTIONAL GROUPS

A functional group is an atom or a group of atoms which characterizes the chemical reactivity of a molecule. The longest chain of atoms containing the functional group is numbered in such a way that the carbon to which functional group is attached is assigned the lowest number. In case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is named treating other functional groups as substituents.

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Class	Formula	Prefix	Suffix
Acid Halide	— COX — (C)OX	Halocarbonyl –	– carbonyl halide – oyl halide
Alcohols	— ОН	Hydroxy	– ol
Aldehydes	— СНО	Formyl	– carbaldehyde
	(C)HO	Охо	– al
Amides	$_$ CONH ₂	Carbamoyl	– carboxamide
	(C)ONH ₂	-	– amide
Amines	- NH ₂	Amino	– amine
Carboxylates	$-coo^{\ominus}$	Carboxylato	– carboxylate
	$-(C)OO^{\ominus}$	-	– oate
Carboxylic Acid	СООН	Carboxy-	– carboxylic acid
	(С)ООН	-	– oic acid
Ethers	OR	Alkoxy–	-
Esters of	COOR	Alkoxy carbonyl	Alkyl carboxylate
Carboxylic Acid	(C)OOR	-	Alkyl oate
Ketones)c=o	Oxo-	– one
cyanides (Nitriles)	—C≡N	Cyano	– carbonitrile
	—(C)==N	-	– nitrile
Salts of Carboxylic	$-\mathrm{COO}^{\ominus}\mathrm{M}^{\oplus}$	-	Cation carboxylate
Acids	$-(C)OO^{\ominus}M^{\oplus}$	-	Cation oate
Sulphonic Acids	—SO ₂ —OH	Sulfo-	– sulfonic acid
Thiols	SH	Sulfanyl	– thiol

The order of decreasing priority for functional groups is :

$$-$$
COOH, $-$ SO₃H, $-$ COOR, $-$ COCl, $-$ CONH₂, $-$ CN, $-$ CHO, C=O, $-$ OH, $-$ SH, $-$ NH₂, C=C, $-$ C=C

Important :

- (a) The -R, $-C_6H_5$, halogens, nitro and alkoxy groups are always treated as substituents.
- (b) If more than one functional group of same type is present, its number is indicated by adding di-, tri- etc.
- (c) When C is marked in parenthesis, the carbon of the functional group is counted as part of the parent chain and the numbering will always begin from this carbon and its position need not be marked in the name.

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EXERCISE

Write IUPAC names of :

(a)
$$CH_3CH_2CH_2CH_2COOH$$
 (b) CH_3CH_2CH — CH_3 (c) COOH
COOH

EXERCISE

Give IUPAC names for : (a) $H - C - CH = CH - CH_3$ (b) $CH_3 - CH_2 - C - CH_2CH_3$ (c) $CH_3 - C - CH_2CH_2CH_3$ (d) $H - C - CH_2CH_2CH_2CH_3$ O

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(e)
$$CH_3 - C = C - CH_2CH_2 - OH$$
 (f) $CH_3 - C - CH = CH - CH_2OH$
Br
(g) $CH_3 - C - CH_2 - COOH$

Βr

Solution :





EXERCISE

Give IUPAC names for :



Solution:

Important : Pentane-1, 5-dioic acid is incorrect name. There is no need to give positions of COOH because if we include their carbons in the parent chain, they will always be present at the end of the chain.

EXERCISE

Give IUPAC names of :





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Solution :

15.3 PRIORITY BETWEEN ALKENE AND ALKYNE

When there is a choice between alkene and alkyne, alkene is given lower number.

EXERCISE

Give IUPAC names of :

(a)

(b)



Solution :

Important : 'e' of 'ene' is dropped as 'yne' sounds like starting from 'i' (vowel).

15.3.1 Common Alkenyl/Alkynyl Substituents

Structure	Common Name	Systematic Name		
СН ₂ =СН-	Vinyl	Ethenyl		
$CH_2 = CH - CH_2 - CH_2$	Allyl	Prop-2-enyl		
CH=C-	-	Ethynyl		
2.0 Obsig selection Dules for Alleges and Alleges Driegity				

15.3.2 Chain selection Rules for Alkene and Alkyne Priority

Rule-1:

Select that chain which contains maximum number of double and triple bonds.

Rule-2:

If two chains are competing for selection as the chain with maximum number of unsaturated bonds, then the choice goes to

- (a) The one with the greatest number of carbon atoms.
- (b) The number of carbon atoms being equal, the one containing maximum number of double bonds.

EXERCISE

Give IUPAC names for :

(a)



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Solution :

15.4 CYCLIC COMPOUNDS

Corollory to Longest Chain Rule

A ring is treated as a substituent only when the number of carbon atoms are less in the ring than in the chain.

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15. NOMENCLATURE-III

15.1 SUBSTITUENTS - ALKOXY, NITRO AND HALOGEN GROUPS

CH₃O-

Alkoxy, nitro and halogen groups are always treated as substituentsAlcoholAlkoxy GroupSubstituent Name

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

СH₃CH₂CH₂O— СH₃—СНО— | СН₃

CH₃CH₂O-

Ethoxy Propoxy Isopropoxy

Methoxy

Он



Phenoxy

EXAMPLE

OCH₃ CH₃CH₂CHCHCH₃

HCHCH₂

2-Methoxypentane

EXAMPLE

Give IUPAC names of :



(b)
$$CH_3$$
— CH — CH — CH — CH_3
| |
 Cl Br

Solution :



15.2 CARBOXYLIC ACID DERIVATIVES

Nomenclature of acid halides and amides is very straight forward. **EXAMPLE**



Esters nomenclature is done in the following manner :

$$\begin{array}{c} O \\ R_{1} - C - OR_{2} \\ Alkyl (R_{2}) \\ Alkanoate (R_{1} - C - O) \end{array}$$
(I)
$$\begin{array}{c} O \\ H - C - O - CH_{3} \end{array}$$
(II)
$$CH_{3} - CH_{2} - CH_{2} - CH_{2}CH_{3} \\ \end{array}$$



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Solution :

2-Methylpropyl-3-chlorobutanoate

Acid Anhydrides

$$\stackrel{O}{\overset{\parallel}{\overset{\parallel}{\underset{\scriptstyle}}}} \stackrel{O}{\overset{\scriptstyle}{\underset{\scriptstyle}}} \stackrel{O}{\overset{\scriptstyle}{\underset{\scriptstyle}}} \stackrel{O}{\underset{\scriptstyle}{\underset{\scriptstyle}}} R_2$$

Alkanoic (R_1) + alkanoic (R_2) anhydride

If $R_1 = R_2$, then name is Alkanoic anhydride

EXAMPLE :

(I)
$$CH_3 - C - O - C - CH_3$$

(II)
$$CH_3 - C - O - C - CH_2CH_3$$

Ethanoic anhydride

Ethanoic Propanoic anhydride









Cyanides/Nitriles

$R-(C)\equiv N$	Alkane nitrile (C is counted as part of parent chain)
$R-C\equiv N$	Alkane carbonitrile (C is not counted as part of parent chain)

EXAMPLE:

(I) $CH_3 - CH_2 - C \equiv N$ Propanenitrile



Cyclohexane Carbonitrile

EXERCISE :



15.3 N-SUBSTITUTED AMINES/AMIDES

The substituents on nitrogen atom is written as N-<substituent name>. Here, 'N(italic) indicates the position of substituent.

EXAMPLE

(I)
$$\overset{4}{C}H_3 \overset{3}{\longrightarrow} \overset{3}{C}H_2 \overset{2}{\longrightarrow} \overset{2}{C}H \overset{1}{\longrightarrow} \overset{1}{C}H_2 \overset{1}{\longrightarrow} NH \overset{1}{\longrightarrow} Br$$

(II)
$$\overset{4}{C}H_3 \overset{3}{\longrightarrow} \overset{2}{C}H_2 \overset{2}{\longrightarrow} \overset{2}{C}H \overset{1}{\longrightarrow} \overset{1}{C}H_2 \overset{2}{\longrightarrow} NH \overset{1}{\longrightarrow} CH_2 \overset{2}{\longrightarrow} H_2 \overset{2}{$$

(III)
$$H_2 \overset{3}{C} \overset{2}{=} \overset{0}{C} H \overset{-}{-} C \overset{-}{-} N H \overset{-}{-} C l$$

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15.4 NOMENCLATURE OF BENZENE DERIVATIVES



With respect to substituent X, we define three positions on the benzene ring as shown in the figure. Ortho, meta, para positions are used for writing common names of disubstituted benzenes. The positions are also abbreviated as o-, m-, p-.

(III)

para

EXAMPLE



o-Dibromobenzene 1,2-Dibromobenzene



(II)

m-Dibromobenzene 1,3-Dibromobenzene



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EXERCISE

Give the IUPAC and common name (o/m/p wherever possible).



Solution:

15.4.3 Benzene as substituent-Phenyl Group

When C_6H_5 - group is treated as substituent, it's called phenyl group.

Important :

(a) A saturated chain containing benzene ring is named as derivative of the larger structural unit. (Use corollory for longest chain selection for cyclic compounds).

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(b) If the chain is unsaturated, the compound is always named as a derivative of that chain.

EXAMPLE

(III)



There is another special group in which C_6H_5 - is present.

$$\bigcirc$$
 $-CH_2$ or $C_6H_5CH_2$ Benzyl

15.5 Alpha (α), Beta (β), Gamma (δ) Nomenclature

Prior to IUPAC, greek symbols were used to indicate positions of the substituents or functional groups. The carbons attached to the principal functional group are numbered as illustrated.

 $\overset{\delta}{C} \overset{\gamma}{\longrightarrow} \overset{\beta}{\longrightarrow} \overset{\alpha}{\longrightarrow} \overset{\Gamma}{\longrightarrow} \overset{\Gamma}{\to} \overset{\Gamma}$

EXAMPLE







EXERCISE

Draw the structure of

(a) α -chloroacetic acid

(b) α , α '-Dibromoacetone

(II) $\overset{\gamma}{C} \overset{\beta}{\longrightarrow} \overset{\alpha}{\longrightarrow} \overset{\alpha}{\longrightarrow} OH$ (IV) $\overset{\gamma}{C} \overset{\beta}{\longrightarrow} \overset{\alpha}{\longrightarrow} \overset{\alpha}{\longrightarrow} C \Longrightarrow N$

Solution :





16. COMMON NAMES IN ORGANIC CHEMISTRY

A. ALKANES

 CH_4 Methane (Marsh Gas)

CH-CH₂-CH₃ | CH₃ Isopentane

CH₃-CH₂-

 CH_3 CH-CH₃ CH₃ CH ĊH₃ ĊH₃ Isooctane (Used in octane rating)

CH₃--CH-CH₃ I CH₃ Isobutane

 CH_3 CH₂ CH₃ ĊH₃ Neopentane

B. ALKENES

CH₃-CH₂-CH=CH₂ α -Butylene

 $C = CH_3$ CH_3 -CH₃ Isobutylene

CH2=C=CH2 Allene

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

Isoprene (Monomer of Natural Rubber)

 $CH_2 = CH - C = CH$

Vinylacetylene

C. ALKYNES

CH≡CH

Acetylene

 CH_3CHCl_2

Ethylidene Chloride

(Gem Dihalide)

 $Cl_2C = CCl_2$

Perclean (Solvent for Dry Washing)

CHCl₃

Chloroform

(Solvent in Organic

Synthesis, Anaesthetic)

D. ALKYL HALIDES

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Ethylene Dichloride (Vicinal Dihalide)

 $CF_2 = CF_2$ Tetrafluoroethene (Monomer of Teflon)

 CH_2Cl_2 Dichloromethane (DCM) (Solvent in Organic Synthesis)

CH=CH₂ CH2=C· Chloroprene (Monomer of Synthetic Rubber)

 $CH_3 - C \equiv CH$ Allylene

CHCl₂

CHCl₂

Acetylene Tetrachloride

(Westron)

(Solvent)

CHCl

CHAsCl₂

Lewisite

(Poisonous Gas)

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CICH=CCl₂ Westrosol (Solvent for paints, oils, varnishes and rubber)

 $CCl_3 - NO_2$ Chloropicrin (Tear Gas)

CH₃-CH=CH-CH₃ β-Butylene

-CH—CH₂-

ĊH₃

Active Amyl Group

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E. ALCOHOL



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p-Xylene

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