Organic Chemistry - Some Basics Principles and Techniques



DESIGNED

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COMPOUNDS: They are of mainly two types

- Inorganic: Obtained from Mineral.
- Organic: Obtained from plants and animal.

Organic compounds: They play a vital role in our life. They constitute our body, our diet, our medicine etc. Almost 95% of organic compound are manmade (prepared in laboratory).

• "Organic Chemistry is study of Hydrocarbon & their derivatives".

Unique properties of carbon

• **TETRAVALENCY**: It is a characteristic property of Carbon atom by virtue of which it can form four covalent bonds.

Atomic Number = 6, Valency = +4 or -4 Therefre It mainly forms covalent compounds.

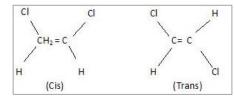
• CATENATION: "The property of forming bonds with atoms of same element and give rise to long chains, branched or un-branched chains."

the maximum catenation is shown by carbon as it forms strong bond with atom of its own kind.

Important feature of π bonds

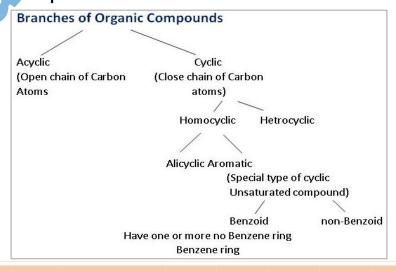
- 1. In C_2H_4 , the two un-hybridized orbital forming bond are parallel to each other. So, they restrict the molecule in planar shape.
- 2. Because of sidewise overlapping, rotation of one CH_2 group with respect to other is hindered, as rotation will break bond. Therefore, only 2 forms are possible.

For example: C2H2Cl2



(pi) bonds are more reactive sites, as they are placed above and below the plane of bonding atoms. So, more exposed to attacking agent.

Branches of Organic Compounds:



Functional groups: They are atom or group of atoms, that determine the characteristic properties of organic compound.

Example: -OH, -CHO, -COOH etc.

Homologous series: It is defined as series of similarly, constituent compounds having same functional group and same chemical properties, and they differ by CH_2 group and atomic mass by 14 a.m.u.

IUPAC system: According to this name of compound consist of 3 parts that is:

Prefix WordRoot Suffix

Word root: indicate no. of carbon atoms in parent chain

1. Meth 6. Hex 2. Eth 7. Hept 3. Prop 8. Oct 4. But 9. Non 5. Pent 10.Dec

Suffix: Suffix two types:- 1. Primary (Indicates the bond)

2. Secondary (Indicates the functional group)

Primary Suffix: Indicate the type of bond between Carbon atoms like:

- Single Bond(ane)
- Double Bond(ene)
- Triple Bond(yne)
- If two or three double or triple bond are present so, they are named as di, tri, tert etc.

Secondary suffix: Indicate the functional group

- ➤ Alcohol OH(ol)
- > Aldehyde CHO (al)
- Ketone RCOR(one)
- Ester RCOOR (oate)
- Acid chloride CoCl (oylchloride)
- Acid amide CoNH2 (amide)
- Nitrite RCN (nitrile)
- ➤ Amine RNH₂ (amine)

Prefix: Indicate substituent present in compound. They can be

- Alkyl group's (which have one Hydrogen less than alkane). Example:- CH_3 methyl , C_2H_5 Ethyl
- Functional group If more than two functional groups are present, than one is treated as main functional group and other as substituent. The prefix used for functional groups are: F = Fluoro

$$Cl = Chloro$$
, $Br = Bromo$, $I = Iodo$, $NH_2^- = Amino$, $NO = Nitro$, $OCH_3 = Methoxy$, $OH = Hydroxy$

Different Type of Organic Compounds:

- 1. Hydrocarbon: They are of two types:
 - A. Saturated: They are called as Alkanes (paraffins) with general formula C_nH_{2n+2}
 - B. Unsaturated: They are also called as olefins. They may be -
 - Alkenes (general formula C_nH_{2n}).
 - Alkynes (general formula C_nH_{2n-2.}).
- 2. Alkyl halides (Haloalkanes)Like in CH_4 the one Hydrogen atom is replaced by Halogen. So, it becomes CH_3CI . The general name of it is Haloalkane. Formula:- $C_nH_{2n+1}(RX)$
- 3. Alcohols C_nH_{2n+1}OH'

Example:

CH3 CH2 OH ethanol

4. Aldehyde (Alkanals) C_nH_{2n+1} CHO

HCHO Methanal

5. Ketone : C_nH_{2n+1}CO C_nH_{2n+1}

CH3-CO-CH3 Propanaone

6. Carboxylic acid: - C_nH_{2n+1}COOH

HCOOH = Methanoic Acid

7. Amines: - $C_nH_{2n+1}NH_2$

CH₃NH₂ MethylAmine

RULES FOR IUPAC

- Select the longest continuous carbon chain.
- Numbering is done in such way that substituent gets the lowest number.
- If the same subsequent appears twice or thrice then di, tri, or is used.
- If different substituent is present, than alphabetical order is followed.
- If double or triple bond is present in addition to substituent then double or triple bond gets the lowest number.
- If both double and triple bond are present, than lowest number is given to double bond.
- In IUPAC: Name is written in order-

Prefix... Word Root.... Primary Suffix.... Seconadry Suffix

Write IUPAC:-

1. 6 5 4 3 2 1 CH₂ = CH-CH = CH-CH = CH₂

 $CH_2 = CH-CH = CH-CH = Hex 1, 3, 5 triene$

Pent - 2 - en - 4 yne

2. 1 2 3 4 5 CH₃ - C = CH - C - (CH₃)₂ CH₃ CH₃

2, 4, 4 tri methyl pent -2- ene

3. 1 2 3 4 5 CH = C - CH = CH - CH₃ 4. 1 2 3 4 CH = C - CH = CH₂ Hex -1- 3diene NOMANCLATURE OF AROMATIC COMPOUNDS: Aromatic compounds are those which contain at least one benzene ring.

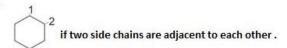
BENZENE - Hexagon of Carbon atoms with 3 alternate double Bonds.



Benzene

Three different forms in figure are:

1. Ortho form



2. Meta form



if two side chains are alternate to each other.

3. Para form



if two side chains are present digonally

Aryl group: - radicals obtained by removal of one or more H atom of

Some common Aromatic compound:



Phenol







- 1









Rules

- 1. When benzene ring is used as substituent, it is named as phenyl (ph).
- 2. Numbering can be done from any side.
- 3. Substituents are written in alphabetical order.



1,3 dimethyl benzene



1, 3, 5 trinitrobenzene



2 Chloro phenol

3,4-dimethyl phenol

ISOMERISM: It is existence of compounds in two or more forms, having same molecular formula but different physical and chemical properties.

It is basically of two types:

- a. Structural isomerism: Differ in arrangement of atoms within molecule.
- b. Stereoisomerism: Differ in arrangement of atom in space.

The structural isomerism type:

1) Chain isomerism- The compounds that have same molecular formula ,but different arrangement of atoms within the chain.

Example: $CH_3 - CH_2 - CH_3 - CH_3 - CH_3 - CH_4 - CH_5$ normal – Butane iso-butane

2) **Position isomerism**: The compounds with same molecular formula, but differ in position of substituent, side chain or functional groups.

 $CH_3 - CH - CH_2CH_2 - CH_3$ $CH_3 - CH_2 - CH - CH_2CH_3$ CH_3 $CH_$

3) Functional isomerism: The compounds with same molecular formula but differ in type of functional group and also in physical and chemical properties.

 $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO} & \text{CH}_3-\text{C}\text{ O}-\text{CH}_2-\text{CH}_3 \\ & \text{(Aldehyde)} & \text{(Ketone)} \end{array}$

4) **Metamerism**: The compounds that have same molecular formula ,but differ in number of carbon atoms around functional group.

It is shown by functional groups like ether, esters, ketones.

Stereo Isomerism: In it the compounds have same molecular formula, but different arrangement of atoms in three-dimensional space.

The different types of stereoisomerism are:

- Geometrical
- Optical

ELECTRON DISPLACEMENT IN COVALENT BONDS: Whenever any reaction occurs, old bonds break and new bonds are formed. This formation is due to shifting of electrons.

types of electron displacements:

1. **Inductive effect**: It is a permanent effect that arises when some electron releasing or withdrawing group is attached to chain of alkane.

Example:- C-C-C-C-C1-X

• It is of two types

-I effect -It is shown when electron withdrawing group is attached to the carbon chain.

- Please note: More is the electron withdrawing, more is the -I effect.
- Order of groups in increasing strength towards -I effect:

+I effect - It is shown when electron releasing group is attached to carbon chain.

Example - Alkyl groups.

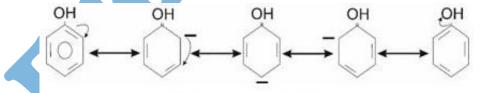
- "More the number of alkyl groups, more is the +I effect."
- Order of strength: 3°> 2°> 1°



- 2. Electrometric effect: It is a temporary effect that is shown in the presence of attacking agent.
 - \circ It is shown by multiple bonded systems like C=C , C=O
 - o It is of two 2 types:
 - +E effect: It is that effect when electron of π bond is transferred to atoms to which attacking agent attaches itself.
 - -E effect: "It is that effect when π electrons are transferred to atom other than the atom, to which attacking agent finally attaches itself."
- 3. Resonance: It occurs due to delocalisation of π electron cloud so as to get best structure as compared to other structure. Example: Structure of CO_2 : O = C = O:

Resonance is best seen in Benzene: It is also called as Mesomeric effect .It arises due to polarity developed in Benzene ring due to delocalisation of π electron.

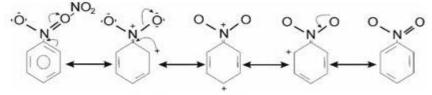
+ R effect: It is shown when electron donating group is attached to benzene ring. Like



Resonating structures of Phenol

If any positively charged group approaches it attacks at Ortho and Para positions.

-R effect - Shown by electron withdrawing group when attached to benzene ring. Example:



Resonating structures of Nitrobenzene

HYPER CONJUGATION: It is like resonance but the difference is that there is no bond present from where the electrons are shifted. The Condition required as it arises when = and - bond is at adjacent position.

Example: -
$$H \rightarrow CH_2 = CH \rightarrow CH_2 = CH \rightarrow CH_2 \rightarrow H \rightarrow CH_2 = CH \rightarrow CH_2 \rightarrow H \rightarrow CH_2 \rightarrow H \rightarrow CH_2 \rightarrow$$

- "More the terminal Hydrogen, more is the Hyper-conjugated structure."
- We can define it as interaction between π electrons and adjacent bond of substituent group attached to it.
- It can explain stability of Alkylated alkenes.

2,3 dimethyl but-2-ene

2-methyl but-2-ene

But-2-ene

ethene

Fundamental concepts of organic reactions: Whenever a chemical reaction takes place the old bonds break and new bonds of products is formed.

- Breaking of bond --- fission.
- Formation of bonds --- products formed.

Bond fission is of 2 types:

- 1) Homolytic fission: The bond breaks in such a way that each electron of shared pair is taken equally by each atom.
- 2) Heterolytic fission: The bond break in such a way, that one species takes both the electrons of shared pair and other remain deficient of shared pair.

REACTION INTERMEDIATES: Reaction intermediates are free carbocation and carbon anion.

- Free Radical: It formed as a result of homolytic fission. Due to this extra electron, they are quite reactive.
- Carbocation: It is formed as a result of hydrolytic fission. It is the Carbon with six electron and a positive charge.
- Carboanion: They are Carbon with 8 e⁻, electron rich Act as Lewis base, They are Formed as a result of heterolytic fission.

Attacking agents: When the reaction occurs, attacking agent attacks and the product is formed.

Type of attacking agents: They can be

- Free radical: With unpaired electron
- Nucleophile: With extra electrons. They also act as Lewis base and does Nucleus love. They are either:

Neutral with Lone pair: H_2O , NH_3 , NH_2 , R-O-H, R-O-R

Negatively Charged: CN⁻, X⁻, OH⁻

• Electrophile: With Positive charge has less electrons and act as Lewis acids. They are either:

Neutral: BF3 , BCl3 , AlCl3 etc .

Positively charged: NH_4^+ , NO_2^+ , H_3 O^+ etc.

Types of organic reactions: The organic reactions are of basic 4 types:

- 1) Substitution reaction
- 2) Addition Reaction
- 3) Elimination reaction
- 4) Rearrangement



- a) Sublimation
- b) Crystallisation
- c) Distillation
- d) Differential extraction
- e) Chromatography

Sublimation: It is the process in which solid directly changes to gaseous form on heating and on cooling the gaseous state convert in to solid state.

• The idea behind using this technique is to separate substance, that show sublimation from substance that do not sublime.

Crystallisation: This method is based on the difference in the solubility of compound and the impurities in the suitable solvent.

- The impure compound in dissolved in a solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher temperature.
- The solution is concentrated to get saturated solution.

Distillation: This method is used to separate volatile liquids from non volatile impurities and also the liquids that have difference in their boiling points.

• The liquids with different boiling point vaporise at different temperatures . Then these vapours are cooled and the liquids formed are collected separately.

Like chloroform and aniline can be easily separated by this technique as both have different boiling points.

- a) Fractional distillation: This method is used for those liquids which have nearly same boiling points that is the difference in their boiling point is not much. Therefore, both liquids condense and formed at same time.
- b) **Distillation under reduced pressure**: This method is used to purify liquids having very high boiling points and those which decompose at or below their boiling points.
- c) **Steam distillation**: This technique is applied to separate substances which are steam volatile and are immiscible in water

Differential extraction: When the organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water.

• The organic solvent and the aqueous solution should be immiscible with each other .So, that they form two distinct layers which can be separated with separating funnel.

Chromatography: It is a technique used to separate mixtures in to their components, purify. Compounds which can be solid or liquid and also test the purity of compounds.

• In this technique the mixture of substances are applied on to a stationary phase . Then a pure solvent or a mixture of solvents is allowed to move slowly over stationary phase . The components of mixture gets gradually separated from one another . The moving phase is mobile phase .

The chromatography is classified into two categories:

- Adsorption chromatography
- Partition chromatography
- 1) Adsorption chromatography: It is based on the facts that different compounds are adsorbed on adsorbent at different degrees. The commonly used adsorbents are silica gel and alumina.

Depending upon differential adsorption the two types of techniques are:

- a) Column chromatography: It involves separation of mixture over a column of adsorbent packed in a glass tube.
- b) Thin layer chromatography: This is another type of adsorption which involves separation of substances of mixture over a thin layer of adsorbent coated on glass tube.
- 2) Partition chromatography: It is based on the continuous differential partitioning of components of a mixture between stationary and mobile phases.
 - Paper chromatography: Is a type of partition chromatography .In this a special paper called chromatography paper is used .It contains water trapped in it which acts as a stationary phase.

Detection of carbon and hydrogen: They are detected by heating the compound with copper oxide. Carbon present in the compound is oxidised to Carbon-dioxide (tested with Lime water) and Hydrogen to Water. $C + CuO \rightarrow Cu + Co_2$

$$H_2 + CuO \rightarrow Cu + H_2O$$

 $CO_2 + Ca (OH)_2 \rightarrow CaCO_3 + H_2O$
 $H_2O + CuSO_4 \rightarrow CuSO_4 \cdot 5H_2O$

Detection of other elements: Nitrogen ,Sulphur, Halogen ,Phosphorous presence in organic compound are detected by Lasagne's test .The elements present in the compound are converted into covalent form in to an ionic form by fusing the compound with Sodium metal .



$$[Fe(CN)_6]^4+Fe^{3+}\rightarrow Fe_4[Fe(CN)_6]_3.xH_2O$$

• Test for Sulphur: The Sodium fusion extract is acidified with Acetic acid with Lead acetate is added to it. A Black precipitate of Lead Sulphide indicates the presence of Sulphur.

On treating Sodium fusion extract with Sodium Nitro Prusside, the Violet colour appears that confirms Sulphur.

$$S^2+[Fe(CN)_5NO]^2 \rightarrow [Fe(CN)_5NOS]$$

- Test for halogens: The Sodium fusion extract is acidified with Nitric acid and then treated with Silver Nitrate.
 - A White precipitate soluble in Ammonium hydroxide shows the presence of Chlorine.
 - A Yellow precipitate soluble in Ammonium hydroxide shows the presence of Bromine.
 - A Yellow precipitate not soluble in Ammonium hydroxide shows the presence of Iodine.

$$X^- + Ag^+ --- AgX$$

• Test for phosphorous: The compound is heated with Sodium Peroxide. The Phosphorus gets oxidised to Phosphate. Then the solution is boiled with Nitric acid and then treated with Ammonium mol bate. A Yellow precipitate indicates phosphorous.

Quantitative analysis

• Carbon and hydrogen: Both of them are estimated in one experiment. A known mass of Organic compound is burnt in presence of excess of Oxygen and Copper (ii)oxide. Carbon and Hydrogen both are oxidised to form Carbon dioxide and Water.

$$C_xH_y+(x+y/4)O_2\rightarrow xCo_2+y/2H_2O$$

Let the mass of organic compound = mg

Mass of water = m1

Mass of carbodioxide =m2

% of $C = (12 \times m_2 \times 100)/(44 \times)m$

% of H = $(2 \times m_1 \times 100)/(18 \times)m$

- Nitrogen: There are two methods for estimation of Nitrogen:
 - i. Dumas method
 - ii. Kjeldahl's method

Dumas method: In this Nitrogen containing compound is heated with Copper oxide in an atmosphere of Carbon dioxide, yields free Nitrogen in addition to Carbon dioxide and water.

$$C_xH_vN_z+(2x+y/2)CuO \rightarrow xCo_z+y/2H_zO+z/2N_z+(2x+y/2)Cu$$

Volume of N at STP = $(P_1V_1 \times 273)/(760 \times T_1)$

Kjeldahl's method: The compound containing Nitrogen is heated with concentrated Sulphuric acid. The Nitrogen in the compound gets converted to Ammonium sulphate. The resulting acid mixture is then heated with excess Sodium hydroxide. The liberated Ammonia gas is absorbed in excess of standard solution of Sulphuric acid. The amount of Ammonia produced is determined by estimating the amount of Sulphuric acid consumed in the reaction.

$C_xH_xN_z+(2x+y/2)CuO \rightarrow xCo_z+y/2H_zO+z/2N_z+(2x+y/2)Cu$

Halogens: For them we have Carious method. A known mass of organic compound is heated with fuming
Nitric acid in the presence of Silver nitrate contained in a hard glass tube known as Carious tube in a
furnace.

Let the mass of organic compound = mg

Mass of $AqX = m_1 q$

1 mole of AgX contains 1 mole of X

% of Halogen = (Atomic mass of $X \times m_1 \times 100$)/(molecular mass of AgX) $\times m_1 \times 100$

• Sulphur: A known mass of organic compound is heated in Carious tube with Sodium peroxide or fuming Nitric acid. Sulphur present is oxidised to Sulphuric acid. It is precipitated with Barium sulphate by adding excess of Barium chloride solution in water. The precipitate is filtered, washed and dried and weighed.

Let the mass of organic compound = mg

Let the mass of ammonium phosphor molybate = m_1 q

% of Sulphur = $(32 \times m_1 \times 100)/(233) \times m$

• Phosphorous: A known mass of organic compound is heated with fuming Nitric acid. As a result Phosphorous gets oxidised to Phosphoric acid. It is then precipitated with Ammonium molybdate.

Let the mass of organic compound = mg

Let the mass of ammonium phosphor molybate = $m_1 g$

• Oxygen: A definite mass of organic compound is decomposed in stream of Nitrogen gas . The mixture of gaseous products containing oxygen is passed over red hot coke when all the oxygen present is converted into Carbon monoxide . Then this mixture is passed over Iodine pent oxide, when CO is oxidised to Carbon dioxide producing Iodine.

KHATAM

