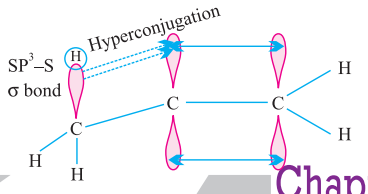


Chapter - 8

Organic Chemistry : Some Basic Principles and Techniques

FAST TRACK : QUICK REVISION

ORGANIC CHEMISTRY

It deals with the study of hydrocarbons (compounds of carbon and hydrogen elements) and their derivatives.

Some organic compounds may also contain nitrogen, oxygen, sulphur, phosphorus, halogens, etc.

Berzelius, proposed that a 'vital force' was responsible for the formation of organic compounds.

This was rejected by F. Wohler who synthesised first organic compound urea from an inorganic compound.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2CONH_2}$$

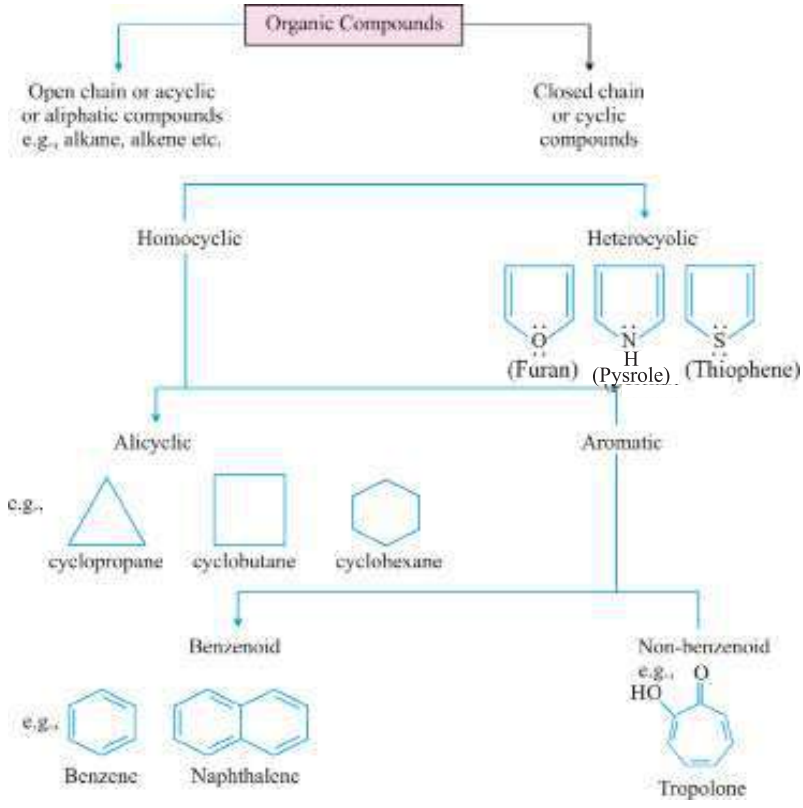
- Acetic acid was synthesised by Kolbe and methane by Berthelot.
- **Types of hybridisation of C-atom :**

Hybridisation	Structure	Bond angle	Examples
sp^3	Tetrahedral	109°28'	Ethane, Methane
sp^2	Trigonal	120°	Ethene, Propene
sp	Linear	180°	Ethyne, Propyne

- **Reasons for existence of large number of organic compounds:**
- **Catenation :** The property of atoms of an element to link with one another forming chains of identical atoms is called *catenation*. Carbon exhibits catenation to the maximum extent.
- **Isomerism :** It is the property by virtue of which two or more compounds have the same molecular formula but different physical or chemical properties.

- **Formation of multiple bonds :** Because of its small size carbon atom is capable of forming multiple bonds with other atoms and this gives a variety of compounds.

- **CLASSIFICATION OF ORGANIC COMPOUNDS**



- **CLASSIFICATION OF CARBON ATOMS**

  On the basis of number of C attached

  (i) **Primary carbon atom :** when carbon atom is attached with one other carbon atom only, it is called **primary or 1°** carbon atom.

  (ii) **Secondary carbon atom :** When carbon atom is attached with two other carbon atoms, it is called **secondary or 2°** carbon atom.

  (iii) **Tertiary carbon atom :** When carbon atom is attached with three other carbon atoms, it is called **tertiary or 3°** carbon atom.

  (iv) **Quaternary carbon atom :** When carbon atom is attached with four other carbon atoms, it is called **Quarternary or 4°** carbon atom.

- **Functional Group :** The atom *e.g.,* –Cl, –Br, etc., or group of atoms *e.g.,* –COOH, –CHO, which is responsible for the chemical properties of the molecule, is called **functional group**.

- **Homologous Series :** The series in which the molecular formula of adjacent members differ by a $-CH_2$ unit, is called homologous series and the individual members are called homologous, *e.g.,* The homologous series of alkene group is

$$\left.\begin{matrix} C_2H_4 \\ C_3H_6 \\ C_4H_8 \\ C_5H_{10} \end{matrix}\right\} \text{difference of} -CH_2 \text{ unit or 14 unit mass}$$

The general characteristics of this series are :

1. All the homologues contain same functional group. That's why their chemical properties are almost similar.
2. All the members of a series have same general formula, *e.g.,*

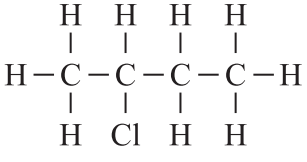
Series	General Formula
Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}
Alcohol and ether	$C_nH_{2n+2}O$
Aldehyde and ketone	$C_nH_{2n}O$
Acid and ester	$C_nH_{2n}O_2$

3. All the members can be prepared by almost similar methods.
4. With increase in the molecular weight of a series, the physical properties vary gradually.

- **Representation of Organic Compounds :**

Organic compounds can be represented by the following ways:

(i) **Complete Structural Formula :** All the bonds present between any two atoms are shown clearly. *e.g.*,

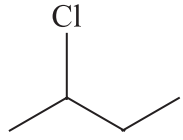


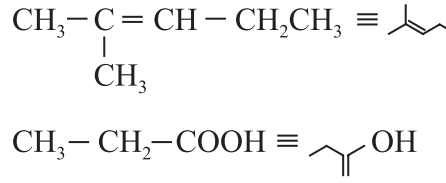
(ii) **Condensed Formula :** All the bonds are not shown clearly. *e.g.*,

$CH_3CHCH_2CH_3$
|
Cl

$CH_3CH(Cl)CH_2CH_3$

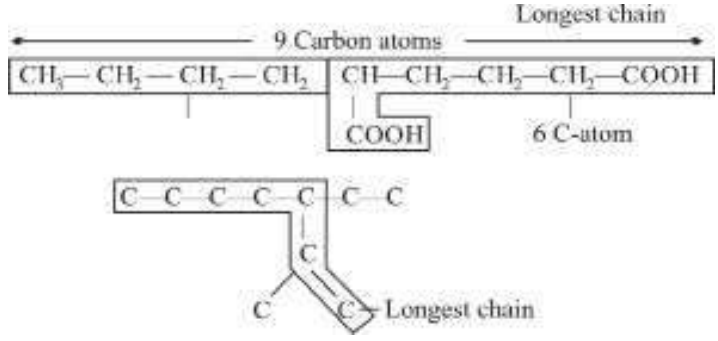
(iii) **Bond Line Formula :** Every fold and free terminal represents a carbon and lines represent the bond. *e.g.*,





- **IUPAC Nomenclature of Organic Compounds :** Following rules are used to write the IUPAC name of an organic compound.

Rule 1. : Longest chain rule : The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain.
In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain *e.g.*,



Word Root for Carbon Chain

Chain length	Word root	Chain length	Word root
C_1	Meth-	C_7	Hept
C_2	Eth-	C_8	Oct
C_3	Prop-	C_9	Non
C_4	But-	C_{10}	Dec
C_5	Pent-	C_{11}	Undec
C_6	Hex-	C_{12}	Dodec

Rule 2 : Lowest number rule : Numbering is done in such a way so that
(i) branching if present gets the lowest number.
(ii) the sum of numbers of side chain is lowest.
(iii) principal functional group gets the lowest number.

Select the principal functional group from the preference series :

$$-COOH > -SO_3H > \text{acid anhydride} > -COOR > -COX > -CONH_2 > -CN > -NC > -CHO > C=O > -OH > -SH > -NH_2 > = > \equiv > \text{substituents}$$

Functional group other than the principal functional group are called substituents.

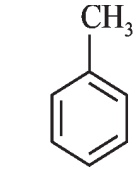
Rule 3: Naming the prefix and suffixes : Prefix represents the substituent and suffix is used for principal functional group.

Primary suffix are **ene, ane** or **yne** used for double, single and triple bonds respectively.

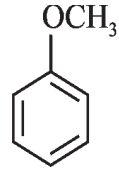
Secondary suffixes are tabulated below :

No.	Class	Formula	Prefix	Suffix
1.	Acid halides	$-\overset{\overset{O}{\|}}{C}-X$	halocarbonyl	—oyl halide —carbonyl halide
2.	Alcohols	—OH	hydroxy	—ol
3.	Aldehydes	—CHO	formyl	—al —carbaldehyde
4.	Ketones	$>C=O$	oxo (keto)	—one
5.	Amides	$-CONH_2$	carbamoyl	—amide
6.	Amine	$-NH_2$	amino	—amine
7.	Carboxylic acid	—COOH	carboxy	—carboxylic acid
8.	Ester	—COOR	alkoxy carbonyl	—alkyl alkan**oate**
9.	Nitriles	—CN	cyano	—nitrile
10.	Sulphonic acid	$-SO_2-OH$	sulpho	—sulphonic acid

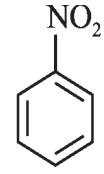
- **Nomenclature of substituted benzene compounds :**



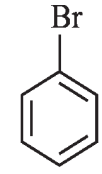
Methylbenzene



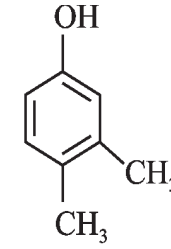
Methoxy benzene



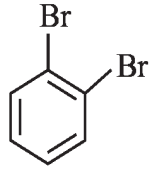
Nitrobenzene



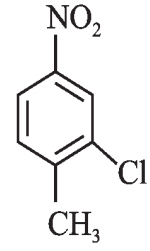
Bremobenzene



3, 4-Dimethyl phenol



1, 2-Dibromo benzene
In Trivial name
1, 2-ortho (o)
1, 3-meta (m)
1, 4-para (p)



2-Chloro-1-methyl 1-4-nitrobenzene

ISOMERISM

Structural isomerism

Same molecular formula but different structures

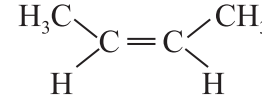
Types

1. **Chain Isomerism**
   e.g., Pentane and 2-Methylbutane
2. **Position Isomerism**
   e.g., But-1-ene
   But-2-ene
3. **Functional Isomerism**
   e.g., Propanal & Propanone
   Ethanol & Methoxymethane
4. **Metamerism**
   e.g., Pentan-2-one and Pentan-3-one

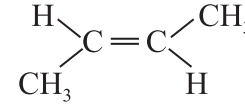
Stereo isomerism

Same molecular and structural formula but different configuration

e.g., Geometrical isomerism (cis-trans isomerism)



Cis.But-2-ene



Trans.But-2-ene

- **Fission of a Covalent Bond :**

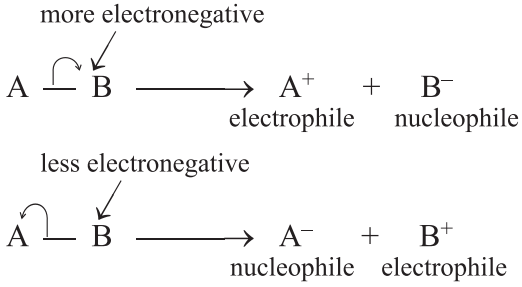
(i) **Homolytic Fission :** In this one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. The neutral chemical species thus formed, are called free radicals. Generally, homolytic fission takes place in non-polar covalent molecules in the presence of sunlight or high temperature.

$$A-B \xrightarrow{\text{Sunlight}} \underbrace{A^* + B^*}_{\text{free radicals}}$$

$$Cl_2 \xrightarrow{\text{Sunlight}} 2Cl^*$$

Free radicals are highly reactive, neutral and electron deficient species.

(ii) **Heterolytic Fission :** The covalent bond breaks in such a fashion that the shared pair of electrons goes with one of the fragments.



Heterolytic fission generally takes place in polar covalent molecules but in non-polar molecules, it takes place in the presence of catalyst like $AiCl_3$ (anhy.), $FeCl_3$ (anhy.) etc.

- **Attacking Reagents :**

These are of two types

(i) **Electrophiles or Electrophilic Reagents**

These are electron deficient species, i.e., behave as Lewis acids.

e.g., Cl^+, $\overset{+}{N}O_2$, CH_3CO^+ etc.

BF_3, $ZnCl_2$ (anhydrous), $FeCl_3$ (anhydrous), $AlCl_3$ (anhydrous)

(ii) **Nucleophiles or Nucleophilic Reagents**

These are negatively charged or neutral molecules with unshared electron pair.

e.g., $\overline{O}H$, CN^-, $R\overset{\circ\circ}{N}H_2$, $\overset{\circ\circ}{N}H_3$

- **Reaction Intermediates :**

(i) **Free radicals :** These are the product of homolysis and contain an odd electron. These are highly reactive planar species with sp^2 hybridisation.

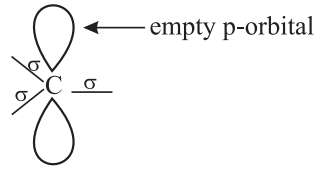
Their order of stability is

$(C_6H_5)_3\overset{\circ}{C} > (C_6H_5)_2\overset{\circ}{C}H > C_6H_5\overset{\circ}{C}H_2$

$> CH_2 = CH - \overset{\circ}{C}H_2 > 3° > 2° > 1° > CH_2 = \overset{\circ}{C}H$

(ii) **Carbocations :** These are the product of heterolysis and contain a carbon bearing positive charge. These are electron deficient species.

These are also polar chemical species i.e., sp^2 hybridised with an empty p-orbital.



Stability order of carbocation is

$(C_6H_5)_3C^+ > (C_6H_5)_2\overset{+}{C}H > 3° > C_6H_5\overset{\oplus}{C}H_2 > 2° > CH_2=CH_2-\overset{+}{C}H_2$

$> 1° > CH_2 = \overset{\oplus}{C}H$

(iii) **Carbanions :** These are the product of heterolysis and contain a carbon bearing negative charge and 8 electrons in its valence shell.

These have pyramidal shape with sp^3 hybridised carbon (having one lone pair) order of stability of carbanions is

$(C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > C_6H_5\bar{C}H_2$

$> \bar{C}H_3 > 1° > 2° > 3°$ carbanions

- **Electron Displacement in Covalent Bond**

1. **Inductive Effect :** If shared pair is more shifted towards more electronegative atom, the less electronegative atom acquires slight positive charge and more electronegative atom acquires partial negative charge,

e.g., $\overset{+\delta}{C}H_3 \rightarrow\!\!- \overset{-\delta}{C}l$

Permanent effect and propagates through carbon chain.

Atoms or groups having greater electron affinity than hydrogen are said to have electron attracting or negative inductive effect (–*I*) while that having, smaller electron affinity than hydrogen are said to have electron releasing or positive inductive effect (+*I*).

e.g., $\overset{+\delta\delta}{C}H_3 \rightarrow\!\!- \overset{+\delta}{C}H_2 \rightarrow\!\!- \overset{-\delta}{C}l$

$\overset{+\delta\delta\delta}{C}H_3 \rightarrow\!\!- \overset{+\delta\delta}{C}H_2 \rightarrow\!\!- \overset{+\delta}{C}H_2 \rightarrow\!\!- \overset{-\delta}{C}l$

1° alkyl halide

Cl has –I effect and alkyl group has +I effect.

Order of groups producing –I effect is

$R_3N > -NO_2 > -CN > -SO_3H > -CHO > -CO > -COOH > -F > -Cl > -Br > -I > -OH > -OR > -NH_2 > -C_6H_5 > -H$

Order of groups producing +I effect is

3° alkyl group > 2° alkyl group > 1° alkyl group > $-CH_3 > -H$

- **Applications of Inductive Effect**

(i) Presence of groups showing +I effect increases the stability of carbocation while presence of groups showing –I effect decreases their stability.

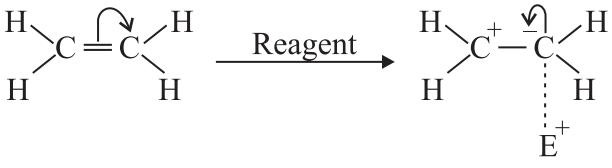
(ii) Strength of acid increases with the attachment of group showing –I effect and decreases with the attachment of group showing +I effect.

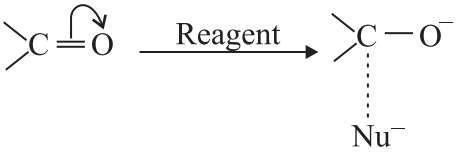
(iii) Presence of +I showing groups increases the basic strength of amines.

2. **Electromeric Effect :** Defined as the polarity produced in a multiple bonded compound as a reagent approaches it. In the presence of attacking reagent, the two π electrons are completely transferred to any of the one atom. This effect is temporary.

It may be of +E type (when displacement of electron pair is away from the atom of group) or of –E type (when displacement is towards the atom or group).

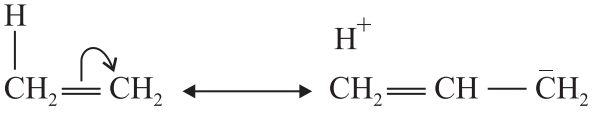
e.g.,





3. **Hyper-conjugation :** It involves delocalisation of σ electron of a C – H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital.

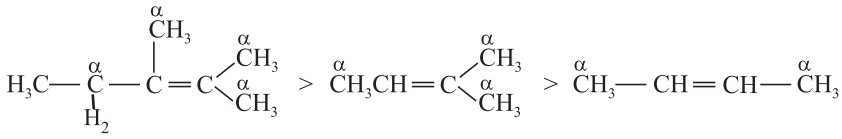
e.g.,



This effect is also called no bond resonance or Baker Nathan effect.

Applications of Hyper-conjugation

Stability of alkenes : More the number of α-hydrogen atoms, more stable is the alkene.



Stability of Carbocation : Greater the number of alkyl groups attached to positively charged carbon atom, the greater is the stability.

e.g., $(CH_3)_2\overset{+}{C}H > CH_3-\overset{+}{C}H > \overset{+}{C}H_3$

4. **Resonance Effect :** When the properties of a molecule cannot be shown by a single structure and two or more structures are required to show all the properties of that molecule, then the structures are called resonating structures or canonical forms and the molecule is referred as resonance hybrid. This phenomenon is called resonance.

Conditions for resonance

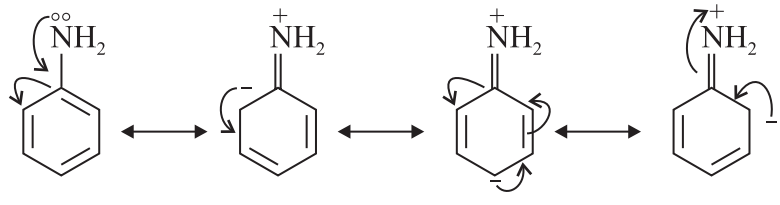
(i) The arrangement of atoms must be identical in all the formula.

(ii) The energy content of all the canonical forms must be nearly same.

(iii) Each canonical of π electrons. This effect may be of +R type or –R type.

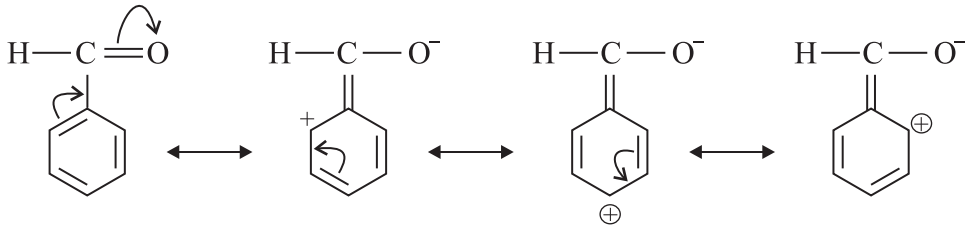
Positive Resonance Effect (+R)

Electron donating groups with respect to conjugated system show +R effect. Central atom of functional groups should be more electronegative than the surrounding atoms or groups to show +R effect. *e.g.*, halogens, –OH, –OR, $–NH_2$, NHCOR, etc.



Negative Resonance Effect (–R)

Electron withdrawing groups with respect to conjugate system show –R effect. Central atom of functional groups should be less electronegative than surrounding atoms or groups to show –R effect. *e.g.*, halogens, –COOH, –COOR, CHO, –CN, $–NO_2$, etc.



Methods of Purification of Organic Compounds

Method	Principle	Applications
Crystallization	Different solubilities of a given organic compound and its impurities in the same solvent.	• Crystallization of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348K (sugar dissolves whereas common salt remains insoluble).
Sublimation	Some solid substances change from solid to vapour state without passing through liquid state. Sublimable compounds get separated from non-sublimable impurities.	• Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride). • Camphor, naphtalene, anthracence, benzoic Acid, etc. are purified.
Distillation	It is used to separate • Volatile liquids from non-volatile impurities. • Liquids having sufficient difference in their boiling points.	• Hexane (b.p. 342K) and toluene (b.p. 384K) • Chloroform (b.p. 334K) and aniline (b.p. 457K)
– Fractional Distillation	If the difference in boiling points of two liquids is not much, this method is used.	• Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.
– Steam Distillation	This method is used to separate substances which are (i) steam volatile, (ii) immiscible with water, (iii) posses a vapour pressure of 10-15 mm Hg and (iv) contain non-volatile impurities.	• Aniline is separated from aniline water mixture. • Essential oils, turpentine oil, o-nitrophenol, bromobenzene nitrobenenze, etc. can be purified.
Differential Extraction	By shaking an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.	• Benzoic acid can be extracted from its water solution using benzene.

Chromatography	Differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.	• Widely used for separation purification, identification and characterization of the components of a mixture, whether coloured or colourless.
– Adsorption Chromatography	Differential adsorption of the various components of a mixture on a suitable adsorbent such as silica get or alumina.	
– Column Chromatography	The mixture is passed through adsorbent packed in glass tube.	• Mixture of naphthalene and benzophenone.
– Thin Layer Chromatography	The mixture is passed over adsorbent on a thin glass plate.	• Amino acids can be detected by spraying the plate with ninhydrin solution.
– Partition Chromatography	Differential partitioning of components of a mixture between stationary and mobile phases.	
– Paper Chromatography	A special quality paper known as chromatography paper is used. It contains water trapped in it, which acts as the stationary phase.	• For separation of sugars and amino acids.

Types of Chromatography	Mobile / Stationary Phase
Column Chromatography	Liquid / Solid
Thin Layer Chromatography	Liquid / Solid
High Performance Liquid Chromatography (HPLC)	Liquid / Solid
Gas Liquid Chromatography (GLC)	Gas / Solid
Partition or Paper Chromatography	Liquid / Solid

Element	Detection	Confirmatory Test	Reactions
Carbon	$2CuO + C \xrightarrow{\Delta} 2Cu + CO_2$	CO_2 gas turns lime water milky.	$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_3\downarrow} + H_2O$ (Lime water)
Hydrogen	$CuO + 2H \xrightarrow{\Delta} Cu + H_2O$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous $CuSO_4$ blue.	$\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaCN}$	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl. Gives blue or green colour.	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

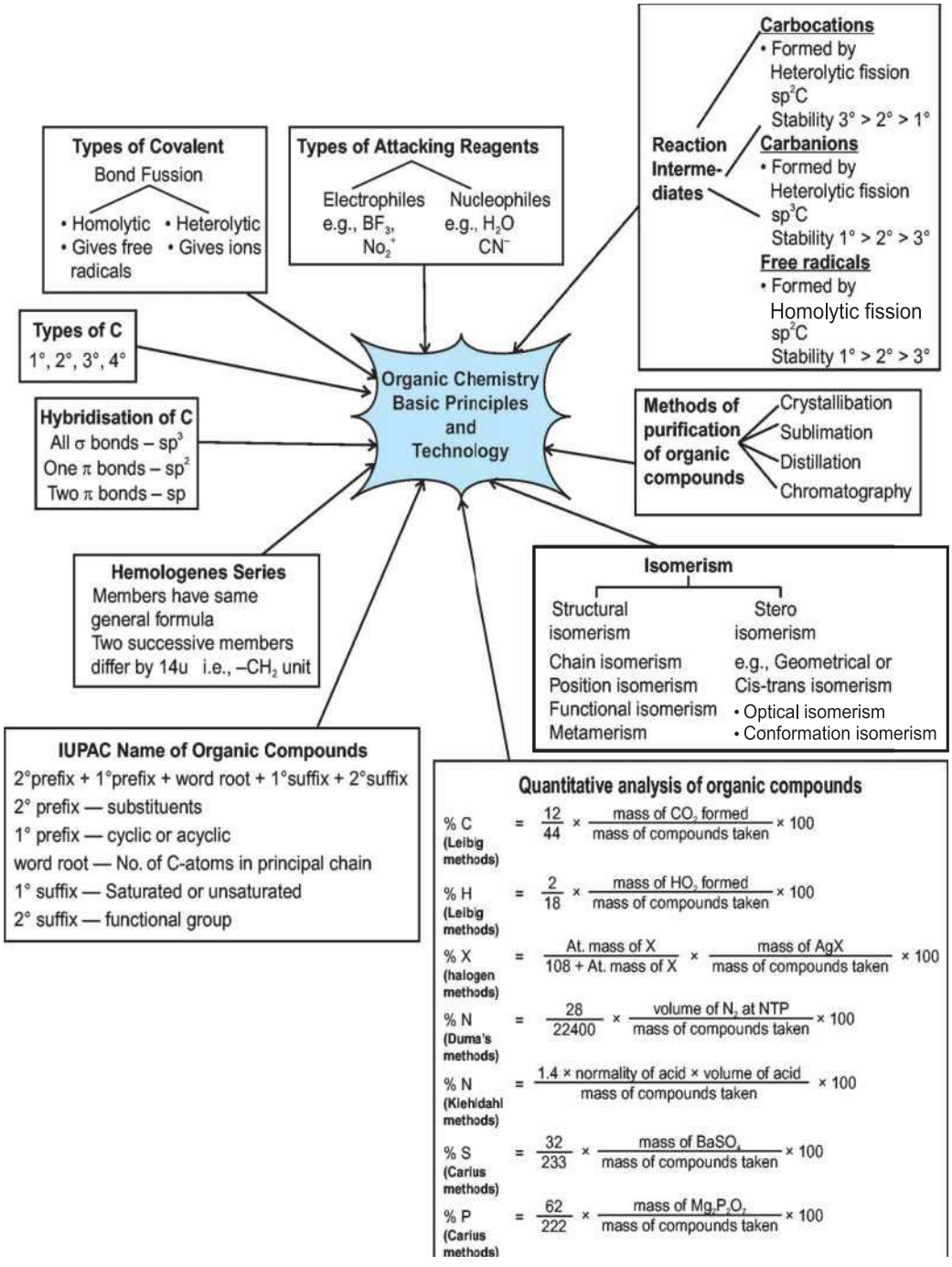
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	– L.E. + sodium nitroprusside A deep violet colour. – L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow$ Sodium nitroprusside $Na_4[Fe(CN)_5NOS]$ Deep violet $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH}$ $Pbs\downarrow + 2CH_3COONa$ Black ppt.
Halogens	$Na + X \xrightarrow{\Delta} NaX$ (L.E.)	L.E. + HNO_3 + $AgNO_3$ – White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. – Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. – Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow$ ppt. $AgCl + 2NH_{3(aq.)} \longrightarrow [Ag(NH_3)_2]Cl$ White ppt. Soluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta}$ NaSCN Sodium thiocyanate (L.E.)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$NaSCN + FeCl_3 \longrightarrow$ $[Fe(SCN)Cl_2 + NaCl$ Blood red colour
Phospho-rus	$P \xrightarrow{Na_2O_2, \text{boil}} Na_3PO_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate $(NH_4)_2MoO_4$. Formation of yellow ppt. indicates presence of phosphate (hence, phosphorus) in organic compound.	$Na_3PO_4 + 3HNO \longrightarrow H_3PO_4 + 3NaNo_3$ $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$ $\longrightarrow (NH_4)_3PO_4.12MoO_3$ Ammonium phosphomolybalate (yellow ppt.) $+ 21NH_4NO_3 + 12H_2O$

- **Quantitative analysis of organic compounds :** The percentage composition of elements presence an organic compound is determined by the methods based on the following principles :

Elements	Method
Carbon and Hydrogen	**Liebig's Combustion method :** A known mass of an organic compound is burnt in the presence of excess of O_2 and CuO. $$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$ CO_2 evolved is absorbed by conc. solution of KOH or ascarite (NaOH + CaO).H_2O produced is absorbed by anhydrous $CaCl_2$ or $Mg(ClO_4)_2$. Increase in masses of these absorbing compounds gives the masses of CO_2 and H_2O produced. $$\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of compound taken}} 100;$$ $$\% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of } H_2O \text{ formed}}{\text{mass of compound taken}} 100$$
Halogens	**Carius method :** Halogen in organic compound is precipitated as silver halide by boiling with conc. NHO_3 and then adding $AgNO_3$. $$X \xrightarrow[AgNO_3]{HNO_3, \Delta} AgX\downarrow$$ $$\% \text{ of X} = \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times \frac{\text{mass of AgX formed}}{\text{mass of compound taken}} \times 100$$
Nitrogen	**Dumas method :** Nitrogen containing organic compound is heated with CuO in an atmosphere of CO_2. $$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CO_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O + N_2 + \left(2x + \frac{y}{2}\right)Cu$$ N_2 evolved gets collected over conc. KOH solution which absorbs all other gases. $$\% \text{ of N} = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$$ **Kjeldahl's method :** Organic compound + $H_2SO_{4\,(conc.)} \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 +$ $2NH_3 + 2H_2O + 2NH_3 + H_2SO_4 \longrightarrow (Na_4)_2SO_4$ $$\% \text{ of N} = \frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$$

Sulphur	**Carius method :** Sulphur in organic compound is converted into H_2SO_4 by boiling with Na_2O_2 or conc. HNO_3 and is precipitated as $BaSO_4$ by adding excess of $BaCl_2$ solution in water. $S \xrightarrow[(ii)\ BaCl_2]{(i)\ HNO_3,\ \Delta} \underset{\text{white ppt.}}{BaSO_4\downarrow}$ $\%\ \text{of S} = \frac{32}{233} \times \frac{\text{mass of } BaSO_4 \text{ formed}}{\text{mass of compound taken}} \times 100$
Phosphorus	**Ignition method :** $P \xrightarrow[\text{heat}]{HNO_3} H_3PO_4$ $H_3PO_4 + Mg^{2+} + NH_4CL \xrightarrow{\Delta} \underset{\substack{\text{Magnesium ammonium}\\ \text{phosphate (white ppt.)}}}{MgNH_4PO_4} + HCl$ $2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$ $\%\ \text{of P} = \frac{62}{222} \times \frac{\text{mass of Mg } P_2O_7 \text{ formed}}{\text{mass of compound taken}} \times 100$

MIND MAP : ORGANIC CHEMISTRY

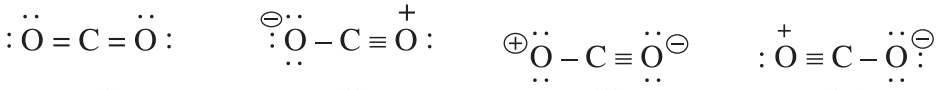


CASE BASED STUDY - QUESTIONS

PASSAGE -I

The resonance effect is defined as the polarity produced in the molecule by the interaction of two π bonds as between a π bond and lone pair of electrons present an on adjacent atom. The effect is transmitted through the chain. In positive resonance effect the transfer of electrons is away from on atom or subsitituent group attached to the conjugated system. The electron displacement makes certain positions in the molecule of high electron densities. In negative resonance effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

1. Draw resonance structure of carboxylate ion
2. What do you understand by +R and –R effect.
3. Write resonance structures of CH_2=CH–CHO indicate relative stability of the contributing structures.
4. Draw the resonating structures of (a) phenol (b) Benzoic acid
5. Out of the resonating structures of CO_2 which structures is not correct for CO_2?



(i) (ii) (iii) (iv)

PASSAGE -II

The Lassaigne's extract is usually alkaline because excess of sodium reacts with water to form sodium hydroxide. If not it may be made alkaline by the addition of a few drops of a dilute solution of sodium hydroxide. To a part of the extract a small amount of a freshly prepared ferrous sulphate solution is added and the content are warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with dilute hydrochloric acid the appearance of a bluish green colour due to the formation of ferric ferrocyanide confirm the presence of nitrogen in the organic compound.

1. In sodium fusion test of organic compound the nitrogen in an organic compound is converted into which compound.
2. In the Lassaigne's test for the detection of sulphure the purple colour is due to the formation of which complex.
3. What is the name of the Prussian blue colour compound formed in Lassaigne's test for nitrogen in an organic compound.
4. Why do we boil Lassaigne's extract with conc. HNO_3 while detecting halogens in an organic compound.
5. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphure and halogens.

MULTIPLE CHOICE QUESTIONS (MCQ)

1. Homolytic fission of C-C bond in ethane gives an intermediate in which carbon is:
   a. sp^3 hybridised
   b. sp^2 hybridised
   c. sp-hybridised
   d. sp^3d- hybridized

2. The kind of delocalization involving sigma bond in conjugation with pi electrons is called:
   a. Inductive effect
   b. Hyperconjugation effect
   c. Electromeric effect
   d. Mesomeric effect

3. Which organic species has only one type of hybridized carbon?
   a. $CH_2=C=CH_2$
   b. $CH_3-\overset{\oplus}{C}H-CH_3$
   c. $CH_3-C\equiv CH$
   d. $CH_2=CH-\overset{\oplus}{C}H_2$

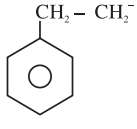
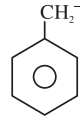
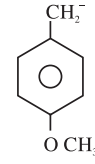
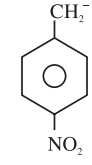
4. Which of the following can act as an electrophile?
   a. CN^-
   b. OH^-
   c. H_2O
   d. BF_3

5. Which of the following is correct about the species: $(CH_3)_3-C^+$
   a. It is planar
   b. Its C+ is sp^2 hybridised
   c. A nucleophile can attack on its C^+
   d. All of these

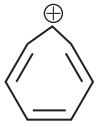
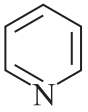
6. Which of the following has all the effects namely Inductive, Mesomeric and Hyperconjugative ?
   a. CH_3Cl
   b. $CH_3CH=CH_2$
   c. $CH_3CH=CHCOCH_2Cl$
   d. $CH_2=CH-CH=CH_2$

7. The most stable free radical among the following is:
   a. $C_6H_5\dot{C}H_2CH_2$
   b. $C_6H_5\dot{C}HCH_3$
   c. $CH_3\dot{C}H_2$
   d. $CH_3\dot{C}HCH_3$

8. Isomers of a compound must have :
   a. Same physical properties
   b. Same chemical properties
   c. Same structural properties
   d. Same molecular weight

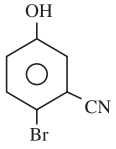
9. Most stable carbanion among the following is
   a. 
   b. 
   c. 
   d. 

10. Which of the following species have six π conjugated electrons?

a.  b. $CH_2=CH-CH=CH-CH_2^-$ c.  d. All of these

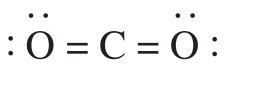
11. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is:
    a. $-COOH$, $-SO_3H$, $-CONH_2$, $-CHO$
    b. $-SO_3H$, $-COOH$, $-CONH_2$, $-CHO$
    c. $-CHO$, $-COOH$, $-SO_3H$, $-CONH_2$
    d. $-CONH_2$, $-CHO$, $-SO_3H$, $-COOH$

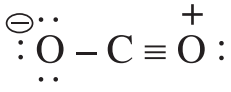
12. The IUPAC name of $CH_3-CH=CH-C\equiv CH$ is:
    a. pent-3-en-1-yne
    b. pent-3-en-4-yne
    c. pent-2-en-4-yne
    d. pent-2-en-3-yne

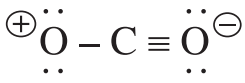
13. The IUPAC name of the following compound is 

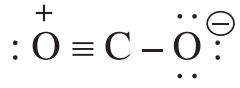
    a. 4–Bromo –3– cyanophenol
    b. 2–Bromo–5–hydroxy benzonitrile
    c. 2–cyano–4–hydroxybromo benzene
    d. 6–Bromo–3–hydroxy benzonitrile

14. The order of the stability of the following of carbocations is :









    a. III > I > II
    b. III > II > I
    c. II > III > I
    d. I > II > III

15. Quantitative measurement of nitrogen in an organic compound is done by the method:
    a. Berthelot method
    b. Lassaigne method
    c. Carius method
    d. Kjehldahl method

ANSWERS

1. a 2. b 3. d 4. d 5. d 6. c 7. b 8. d 9. d 10. d
11. a 12. a 13. b 14. a 15. d

FILL IN THE BLANKS

1. A triple bond between two carbon atoms is composed of one _____ and _____ bonds.
2. An organic compound which decomposes below its boiling point can be purified by _____.
3. Electrophiles are the species which attack the regions of ___ electron density.
4. Hyperconjugation effect is also known as _____ resonance.
5. In Duma's method, the nitrogen present in an organic compound is set free as _____.

ANSWERS

1. σ , two π 2. Vacuum distillation 3. high 4. No-bond 5. Nitrogen

TRUE AND FALSE TYPE QUESTIONS

1. Ethanol and methoxymethane are position isomers.
2. A free radical is a species with an unpaired valence electron.
3. Inductive effect is observed in π bond in presence of attacking reagent.
4. The percentage of carbon and hydrogen are estimated simultaneously in an organic compound by Liebig method.
5. Chromatography is the method used to separate and purify compounds when present in small amounts.

ANSWERS

1. F 2. T 3. F 4. T 5. T

ASSERTION REASON TYPE QUESTIONS

The questions given below are Assertion (A) and Reason (R). Use the following key to select the correct answer.

(a) If both assertion and reason are correct and reason is correct explanation for assertion.
(b) If both assertion and reason are correct but reason is not correct explanation for assertion.
(c) If reason is correct but assertion is incorrect.
(d) If both assertion and reason are incorrect.

1. Assertion: But-1-ene and 2-Methylprop-1-ene are position isomers.
   Reason: Position isomers have same molecular formula but different arrangement of carbon atoms.

2. Assertion: Duma's method is more applicable to nitrogen containing organic compounds than the Kjeldahl's method.
   Reason: Kjeldahl's method does not give satisfactory result in which nitrogen atom is directly attached to oxygen atom.
3. Assertion: Alkanes having more than three carbon atoms exhibit chain isomerism.
   Reason: All carbon atoms in alkanes are sp-hybridised.
4. Assertion: In $CH_2=C=CH_2$, all the carbon atoms are sp^2 hybridised.
   Reason: All the hydrogen atoms lie in one plane.
5. Assertion: Butane and 2-Methylbutane are homologues.
   Reason: Butane is a straight chain alkane while 2-Methylbutane is branched chain alkane.
6. Assertion: Tertiary carbocations are generally formed more easily than primary carbocations.
   Reason: Hyperconjugation as well as inductive effect due to additional alkyl groups stabilize tertiary carbocations.
7. Assertion: Alkyl carbanions like ammonia have pyramidal shape.
   Reason: The carbon atom carrying negative charge has an octet of electrons
8. Assertion: Carbocations are planar in nature.
   Reason: Carbocations are sp^2 Hybridised.
9. Assertion: IUPAC name of compound $CH_3CH=CH-CHO$ is But-2-enal.
   Reason: Functional group gets preference over multiple in IUPAC name of a compound.
10. Assertion: Glycerol is purified by distillation under reduce pressure.
    Reason: Organic compounds in liquid state are purified by distillation.

ANSWERS

1. d 2. c 3. c 4. d 5. b 6. a 7 . b 8. a 9. a 10. c

MATCH THE COLUMNS

Match the statements (a,b,c,d) in column I with the statements (I,ii,iii,iv) in column II.

1.

Column I	Column II	Column II
a. Leibig method	i. N_2	e) Aniline
b. Dumas method	ii. AgX	f) Halogens
c. Kjehldahl method	iii. CO_2 and H_2O	g) Schiff's Nitrometer
d. Carius method	iv. NH_3	h) $CaCl_2$ tube

2.

Column I	Column II
a. Nonbenzenoid aromatic compound	i. 50% s character
b. Catenation	ii. Species containing single unpaired nonbonding electrons
c. Free radical	iii. Chain-forming property of an element
d. sp-hybridised carbon atom	iv. Tropolone

ANSWERS

1. a. iiii, h b. i, g c. iv, e d. ii, f
2. a. iv b. iii c. ii d. i

ONE WORD ANSWER TYPE QUESTIONS

1 Name one common adsorbent in column chromatography.

2. Mention the hybridisation of underlined carbon in $CH_3\underline{C}\equiv N$.
3. What type of isomerism is shown by Pentane and 2-Methylbutane?
4. Nucleophiles are Lewis acids or Lewis bases?
5. What type of bond fission results in the formation of free radicals?
6. What is the number of electrons present in the outermost shell of carbon in the methyl radical?
7. What is the other name for no-bond resonance?
8. What is the name of the Prussian blue coloured compound formed in Lassaigne's test for nitrogen in an organic compound?
9. SO_3 is an electrophile or nucleophile in sulphonation reaction of benzene?
10. Name suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

1-MARK QUESTIONS

1. Which unique property of carbon is responsible for the large number of carbon compounds?
2. Which has the longest C—C bond length among ethane, ethene and ethyne.
3. How many secondary carbon atoms are present in 2-Methylpentane?
4. Draw structure of 3-Isopropyl-2-methylhexane.

5. Draw bond line structure of $CH_3(CH_2)_6CH{=}CH(CH_2)_2{-}COOH$
6. What are the bond angles in sp^3, sp^2 and sp hybrid orbitals?.
7. Write the correct of priority of the following functional groups:

   $-C{\equiv}N$, $>C{=}O$, $-OH$, $-COOH$, $-CONH_2$
8. Write IUPAC name of :

   (i) $CH_3{-}CH_2{-}CN$

   (ii) $CH_2{=}CHCH_2OH$

   (iii) $CH_3CH_2CH(CH_3){-}CO{-}CH_2CH_3$

   (iv) $CH_3CH_2{-}O{-}CH_2CH(CH_3)CH_3$

   (v) $Cl{-}CH_2{-}C{\equiv}CH$
9. What type of isomerism is exhibited by Propanal and Propanone?
10. Classify the following into electrophiles and nucleophiles:

    $H+$, NH_3, $AlCl_3$, NO_2^+, CN^- , H_2O, ROH, RNH_2, Carbocation
11. What type of attacking reagents are produced by heterolytic cleavage of covalent bond?
12. Name each of the following species and indicate which member of each pair is more stable:

    (i) CH_3^+, $CH_3CH_2^+$

    (ii) $C_6H_5\overset{+}{C}HCH_3$, $CH_3\overset{+}{C}HCH_3$

    (iii) $CH_2{=}CH{-}\dot{C}H_2$, $\dot{C}H{=}CH{-}CH_3$

    (iv) $CH_3{-}\bar{C}H_2$, $CH_3{-}\bar{C}H{-}CH_3$
13. Identify electrophilic centre in CH_3CHO.
14. What is state oh hybridization of positively charged carbon atom in carbocation?
15. What is the effect of introducing an alkyl group on the stability of carbocation?
16. Out of Benzyl and ethyl carbocation which is more stable and why?
17. Arrange the following in increasing order of acidic strength:

    $ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$
18. Name two solvents which are commonly used to dissolve organic solids.

19. Name the technique that can be used for purification of iodine that contains traces of NaCl.
20. A liquid (10 mL) has three components A, B, C. which technique is suitable to sparate A,B, C from such a small amount of mixture?
21. Under what condition do we use fractional distillation?
22. A liquid compound starts decomposing well before its boiling point under normal pressure. How will you purify it?
23. For which type of compounds Kjehldahl's method is not useful?
24. How do you precipitate sulphur in Carius method?
25. Which method is used to estimate carbon and hydrogen?
26. What do we notice in Lassaigne's test if the compound contains both nitrogen and sulphur?

2-MARKS QUESTION

1. How will you account for the presence of large number of organic compounds?
2. Draw the structural formulae of the following compounds:
   (i) Ethoxypropane
   (ii) But-1-en-3-yne
   (iii) 3,4,4,-Trimethylhex-1-yne
   (iv) sec-butyl alcohol
   (v) But-2-enoic acid
3. Give IUPAC name of the following compounds:
   (i) $C_6H_5\,CH_2\,CH_2OH$
   (ii) $(CH_3)_2\,CH_2\,CH_2\,CHO$
   (iii) $CH_2{=}CH{-}C{\equiv}N$
   (iv) $CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$
   (v) $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH{=}\underset{\displaystyle OCH_3}{\underset{|}{C}}{-}CH_2{-}COOH$
4. Indicate sigma (σ) and pi (p) bonds in the following molecules
   (i) CH_2Cl_2 (ii) $HCONH.CH_3$

5. Write bond line formulas for: (i) isopropyl alcohol (ii) heptane-4-one
6. Which is suspected to more stable:

   $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ and why?
7. What is the effect of introducing an alkyl group on the stability of a free radical?
8. Give two examples each of the groups exerting –I and + I effect when attached to a chain of carbon atoms.
9. A tertiary butyl carbocation is is more stable than isobutyl carbocation. Justify.
10. All electrophiles are Lewis acids while nucleophile are Lewis bases. Explain.
11. What is the purpose of filtration through hot water funnel?
12. What precautions are necessary while purifying an organic solid with the help of crystallization process?
13. Discuss the principle of steam distillation.
14. Discuss the role of fractionating column in fractional distillation.
15. How will you prepare Lassaigne's extract? Name the elements which can be detected from this extract?

3-MARKS QUESTIONS

1. Why stability of carbocations follows the order: tertiary>secondary>primary?
2. What are the various conditions essential for resonance?
3. Write resonance structures of $CH_2=CH-CHO$. Indicate relative stability of the contributing structures.
4. Inductive effect is of permanent nature while electromeric effect is only temporary. Explain.
5. What is chromatography? Name different types of chromatographic processes.
6. You are given a mixture of methanol and acetone. Discuss the process which you will employ to separate them.

5-MARK QUESTIONS

1. Classify the following reactions in one of the reaction type studies in this unit:

   (i) $CH_3CH_2Br \longrightarrow CH_3CH_2SH + Br^-$

   (ii) $(CH_3)_2C = CH_2 + HCl \longrightarrow (CH_3)_2C(Cl)CH_3$

   (iii) $(CH_3)_3CCH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3$

   (iv) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O + Br^-$

   (d) $CH_3CH_2Cl + \underset{aq}{KOH} \longrightarrow CH_3CH_2OH + KCl$

2. (a) An organic compound contains 69% carbon and 4.8% hydrogen the remainder being oxygen. Calculate the masses of carbon dioxide and water produce when 0.20 g of this compound is subjected to complete combustion.

   (b) 0.3780 of an organic compound gave 0.574 g of silver chloride in carious estimation. Calculate the percentage of chlorine in the compound.

3. Arrange the following in the order of property indicated against each set:

   (i) $-C_6H_5$, $-NO_2$, $-COOH$, $-I$, $-F$, $-CH_3$, $-C_2H_5$ (In the increasing order of –I effect)

   (ii) $CH_3CH_2CH_2CH_2^+$, $(CH_3)_3C^+$, $CH_3CH_2CH_2\overset{+}{C}HCH_3$ (In the order of increasing stability)

   (iii) $-Cl$, $-CONH_2$, $-CHO$ (In the increasing priority order if present in same molecule)

4. Draw the resonance structures for the following compounds. Show the electron shift using curved arrow notation.

   (i) $C_6H_5NO_2$

   (ii) $CH_3CH{=}CHCHO$

   (iii) C_6H_5OH

   (iv) $C_6H_5CH_2^+$

   (v) $CH_3CH{=}CHCH_2^+$

5. Suggest a method to separate the constituents from the following mixture:

   (i) Mixture of two miscible liquids

   (ii) A mixture of oil and water

   (iii) A mixture of plant pigments

   (iv) A mixture of solid benzoic acid and sodium chloride

   (v) o-Nitrophenol and p-Nitrophenol present in the mixture.

6. 0.378g of an organic compound containing carbon and hydrogen was subjected to combustion by Leibig's method, the CO_2 and H_2O formed were passed through potash bulbs and anhydrous $CaCl_2$ tube. At the end of the experiment, the increase in the respective weights were 0.264g and 0.162g. Calculate the percentage of carbon and hydrogen.

   (**Ans:** C = 19.05% , H = 4.76%)

UNIT TEST-I

Time Allowed: 1 Hr. **Maximum Marks : 20**

General Instructions:

(i) All questions are compulsory.

(ii) Maximum marks carried by each question are indicated against it.

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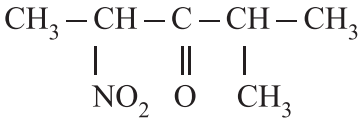
1. Write bond line formula for the following compound: [1]

   $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)COOH$

2. Write IUPAC name of the following compound: [1]



3. The central atom of compound $CH_2=C=CH_2$ is _____ hybridized. [1]

In the following questions a statement of Assertion (A) followed by Reason (R) is given. Use the following key to select correct answer :

(a) Both Assertion and Reason are correct but Reason is the correct explanation of Assertion.

(b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.

(c) Both Assertion and Reason are incorrect.

(d) Assertion is not correct but Reason is correct.

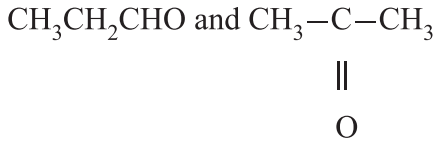
4. Assertion : Carbocations are planar in nature. [1]

   Reason : Carbocations are sp^2 Hybridized.

5. Assertion : All the carbon atoms of But-2-ene lie in are plane.

   Reason : All the carbon atoms in But-2-ene are sp^2 hybridized.

6. (i) What type of isomerism is exhibited by the following pair of compounds? [1]



   (ii) Give one example each of nucleophile and electrophile.

7. (i) Arrange the following in increasing order of stability:

$(CH_3)_3C^-$, $CH_3-\overline{C}H-CH_3$, $CH_3CH_2^-$

(ii) Differentiate between inductive and electromeric effect.

8. (i) When do we use hot water funnel for filtration?

(ii) How will you separate a mixture of two organic compounds which have different solubilities in the same solvent?

(iii) An organic liquid decomposes below its boiling point. How will you purify it?

9. Draw the resonating structures of (a) Phenol (b) Benzaldehyde.

10. Arrange the following in the order of property indicated against each set:

(i) $-C_6H_5$, $-NO_2$, $-COOH$, $-I$, $-F$, $-CH_3$, $-C_2H_5$

(In the increasing order of –I effect)

(ii) $CH_3CH_2CH_2CH_2^+$, $(CH_3)_3C^+$, $CH_3CH_2CH_2\overset{+}{C}HCH_3$

(In the order of increasing stability)

(iii) $-COOH$, $-CONH_2$, $-CHO$

(In the increasing priority order if present in same molecule)

(iv) $HCOOH$, CH_3COOH, $ClCH_2COOH$

(Increasing order of acidic strength)

(v) $O_2NCH_2CH_2O^-$, $CH_3CH_2O^-$

(species having greater stability)

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UNIT TEST-II

Time Allowed: 1 Hr. **Maximum Marks : 20**

General Instructions:

(i) All questions are compulsory.

(ii) Maximum marks carried by each question are indicated against it.

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1. Which of the following can act as an electropliile? [1]

   (a) CN^- (b) OH^- (c) H_2O (d) BF_3

2. The most stable free radical among the following is : [1]

   (a) $C_6H_5\,CH_2\,CH_2$ (b) $C_6H_5\,CH\,CH_3$

   (c) $CH_3\,CH_2$ (d) $CH_3\,CH\,CH_3$

3. What is the other name for no band resonance? [1]

In the following questions a statement of Assertion (A) followed by Reason (R) is given. Use the following key to select correct answer :

(a) Both Assertion and Reason are correct but Reason is the correct explanation of Assertion.

(b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.

(c) Both Assertion and Reason are incorrect.

(d) Assertion is not correct but Reason is correct.

4. Assertion : In $CH_2 = C = CH_2$ all the carbon atoms are sp^2 hybridized. [1]

   Reason : All the hydrogen atoms lie in one plane.

5. Assertion : Glycerol is purified by distillation under reduce pressure.

   Reason : Organic compound in liquid state are purified by distillation.

6. Give IUPAC name of the following compounds : [2]

   (a) $C_6H_5\,CH_2\,CH_2OH$

   (b) $CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$

7. Discuss the principle of steam distillation. [2]

8. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen sulphur and halogens. [2]

9. What are the various conditions essential for resonance? [3]

10. Suggest a method to separate the constituents from the following mixture : [5]

    (a) Mixture of two miscible liquids.

    (b) A mixture of oil and water.

    (c) A mixture of plant pigments.

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