Class : Chemistry
Class : XI

Kannada

Organic Chemistry- Some Basic Principles and Techniques

General Introduction

- Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds.
- In 1828 F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.
- $\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$

- **Tetravalence of Carbon: Shapes of Organic Compounds**
  The Shapes of Carbon Compounds:
- The fundamental concepts of hybridisation helps in predicting the shape of molecules.

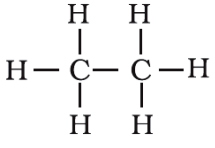
Hybridisation	**sp^3**	**sp^2**	**sp**
Angle	109°28′	120°	180°
Geometry Example	Tetrahedral Alkanes, cycloalkanes and in saturated part of all organic molecules	Trigonal Alkenes (C=C) and other compounds containing C=OC=N, or C-S double bond	Linear Alkynes and all other compounds containing triple bond,
Bond	Four- σ	Three- σ, One- π	Two- σ, Two- π
s%	25	33.3	50
p%	75	66.7	50
Electronegativity	2.48	2.75	3.25

Some Characteristic Features of π Bonds

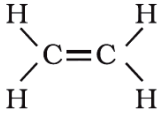
- π-bonds provide the most reactive centres in the molecules containing multiple bonds because it is present above and below the plane of bonding atoms which is easily available to attacking reagent.

Structural Representations of organic compounds

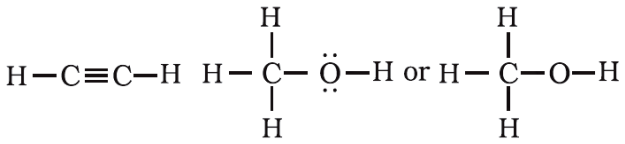
- **Condensed and Bond-line Structural Formulas**
- **Complete structure formulas**



Ethane



Ethene



Ethyne *Methanol*

- **Condensed structural formula.**

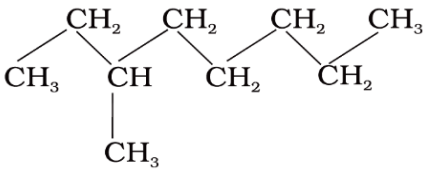
CH_3CH_3 $H_2C = CH_2$ $HC \equiv CH$

Ethane Ethane Ethyne

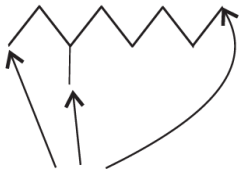
- **Bond-line structures** are the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. Examples 3-Methyloctane can be represented.

(a) $CH_3CH_2CHCH_2CH_2CH_2CH_2CH_3$ with CH_3 branch

(b)

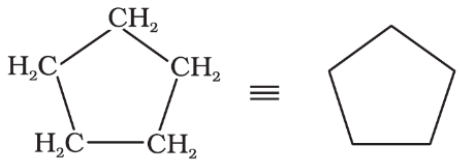


(c)



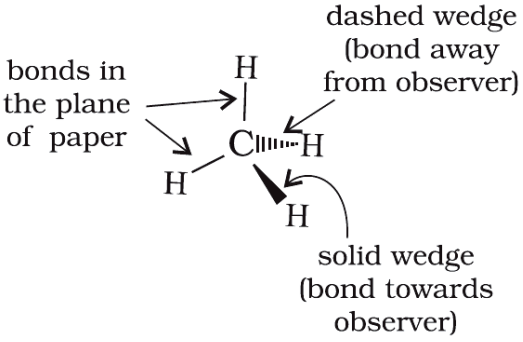
Terminals represent methyl group

- **Representation of Cyclic compounds**

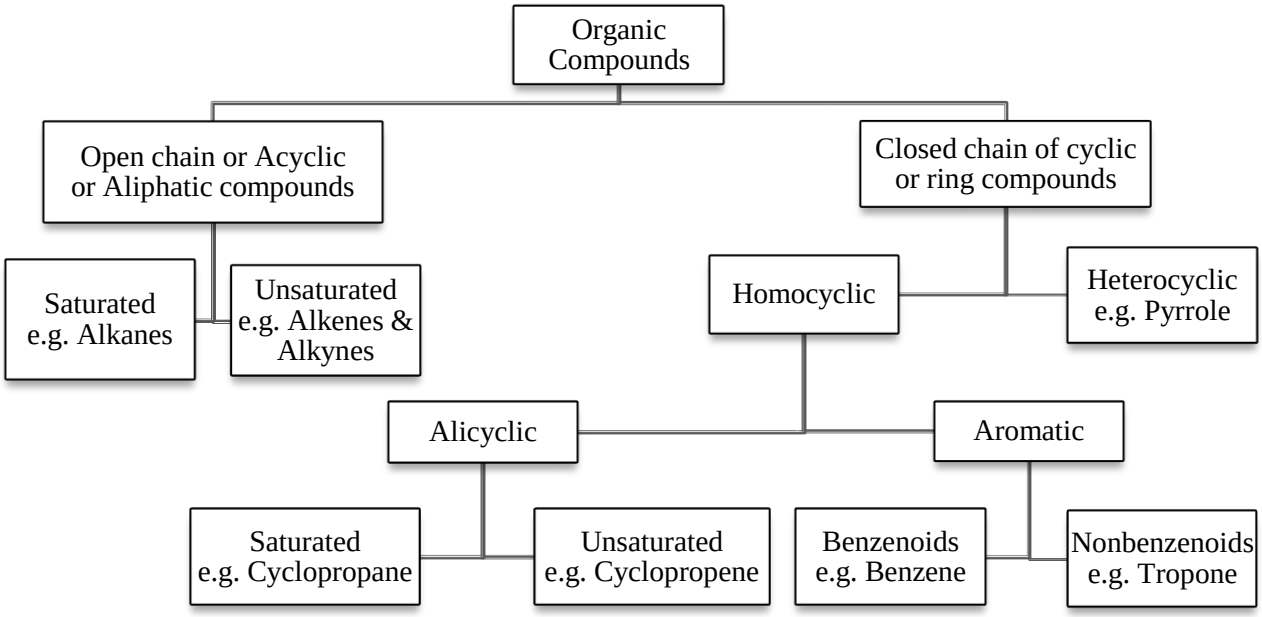


Cyclopentane

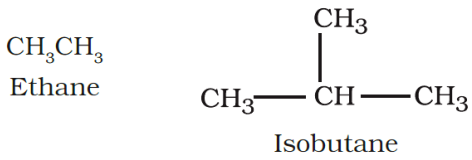
- **Three-Dimensional Representation of Organic Molecules**
- The three-dimensional (3-D) structure of organic molecules can bs represented on paper by using certain conventions.



Classification of Organic Compounds



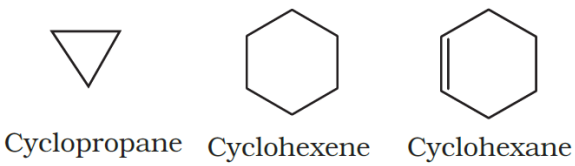
Acyclic or open chain compounds



Cyclic or closed chain or ring compounds

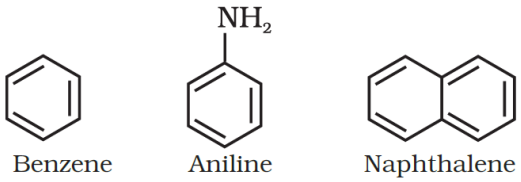
Home cyclic compounds

Alicyclic compounds



Aromatic compounds

Benzenoid compounds



Non benzenoid compounds



Tropone

Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Functional Group :

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

Homologous Series:

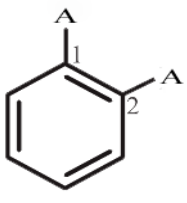
- A series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues.
- The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-\mathrm{CH_2}$ unit.

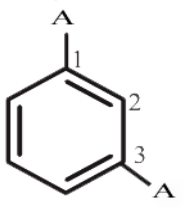
Nomenclature of Organic Compounds

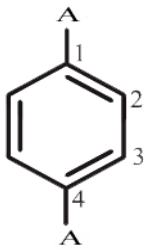
- Systematic method of naming has been developed and is known, Inion of Pure and Applied Chemistry**) IUPAC (International Union of Pure and Applied Chemistry)** System of nomenclature.
- **The IUPAC System of Nomenclature**
  i. Select longest C-chain in molecule
  ii. Branched carbon must have lowest number
  iii. Assign lowest number to substituent which comes first as alphabetical order.
  iv. Identical substituents are indicated by prefix such as di, tri, temp etc.
  v. If side chain is on the same C-atom than named as per alphabatical order.
  vi. If functional group is present than it must have possible low number based on order.

Nomenclature of Substituted Benzene Compounds

- For substituted benzene compounds, the substituents is placed as prefix to the word benzene. The substituents are given the lowest number possible while numbering the carbon atoms of the ring in disubstitute benzene ring.
- The prefix ortho $(o-)$ indicates $1,2-$, meta $(m-)$ indicates $1,3-$ and para $(p-)$ indicates 1,4-disubstituted benzene ring.





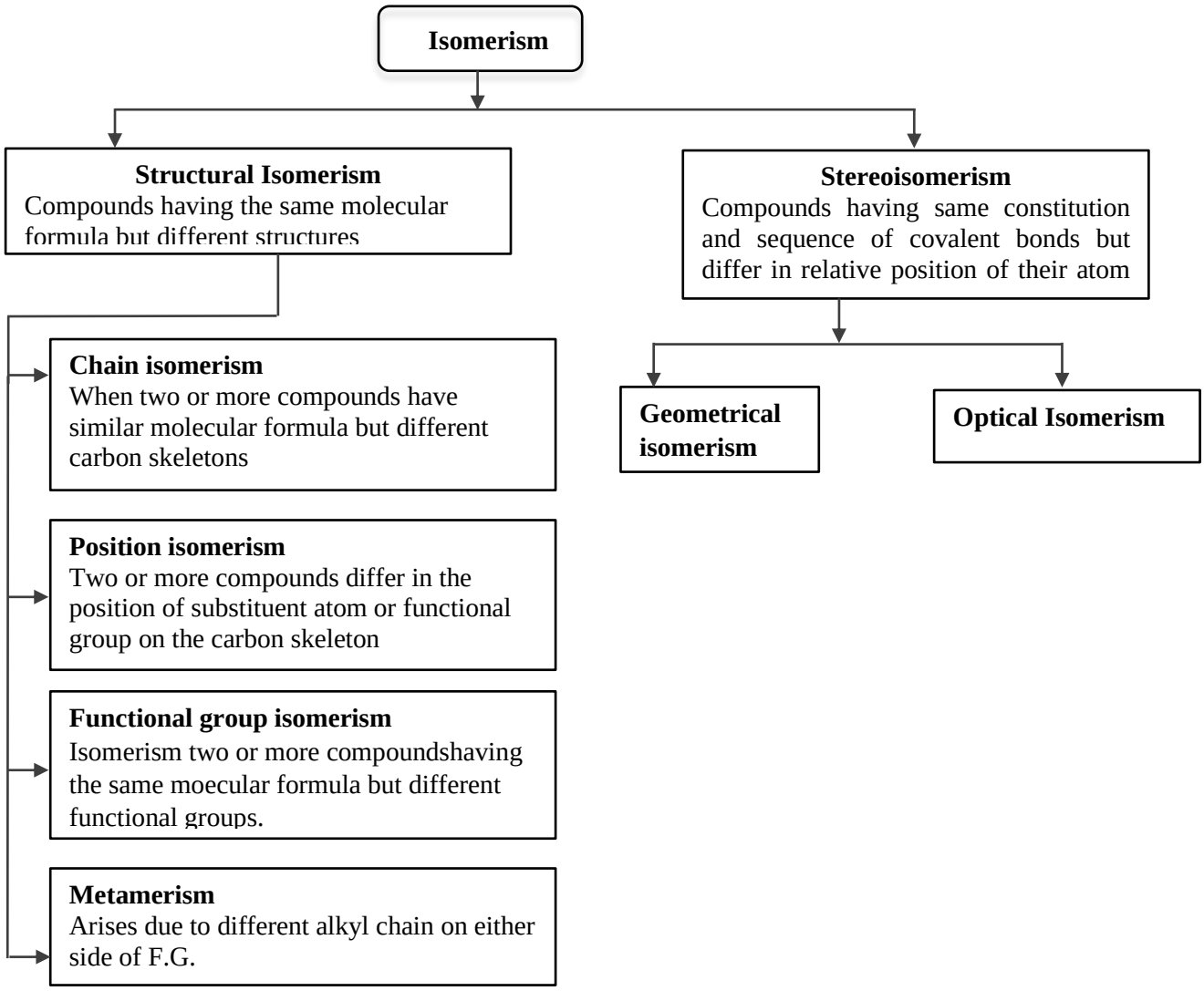


(1,2) ortho (1,3) meta (1,4) para

- In case of tri- or higher substituted benzene derivatives, common name of benzene derivatives taken as the base compound. Number 1 position is assigned to the substituent of the base compound and lowest locant rule is followed for other substituents.
- Benzene ring is considered as substituent [Phenyl, $-(C_6H_5)$] when it is attached to an alkane with a functional group.

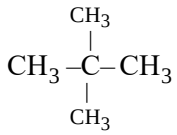
Isomerism

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



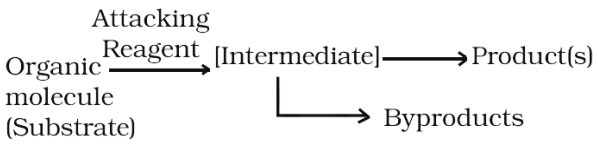
Organic Compounds

e.g.	**e.g.**	**e.g.**	**e.g.**
C_5H_{12}	C_3H_6O	C_3H_6O	$C_4H_{10}O$
$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2OH$	$CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$	$CH_3OC_3H_7$
$CH_3-\underset{\underset{CH_3}{\|}}{CH}-CH_2-CH_3$	$CH_3-\underset{\underset{OH}{\|}}{C}-CH_3$	$CH_3-CH_2-\overset{\overset{O}{\|\|}}{C}-H$	$C_2H_5OC_2H_5$



Fundamental Concepts in Organic Reaction Mechanism

- A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.
- The general reaction is depicted as follows :



- **Fission of a Covalent Bond**
- **Heterolytic cleavage:** In this, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.
  So one atom acquires positive charge and other acquires negative charge.



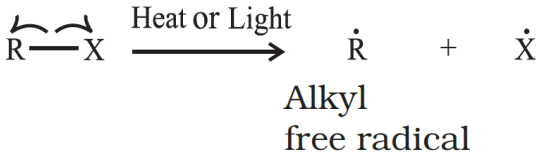
Carbocation

The heterolytic cleavage can also give a species in which the shared pair of electrons.



Carbanion

- **Homolytic cleavage:** In this, one of the electrons of the shared pair in, covalent bond goes with each of the bonded atoms.
- Such cleavage results in the formation of neutral species (atom a group) which contains an unpaired electron called free radicals,



- **Substrate and Reagent**

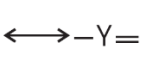
- A molecule whose carbon is involved in new bond formation is called substrate.
- The molecule or substance that reacts with the substrate is called reagent.
- A reagent which is nucleus seeking or nucleus loving are called nucleoptile and reactions are termed as nucleophilic.
- A reagent which is electron loving or electron seeking is called electrophile and reactions are termed as etectrophilic.
  Examples of nucleophiles:

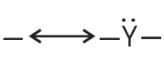
- $OH^-, HS^-, C_2H_5O^-, 2H_2\ N^-$

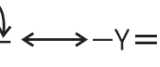
  Examples of electrophiles: carbocations (CH_3^+)carbonyl group ($> C = 0$)

- **Electron Movement in Organic Reactions**

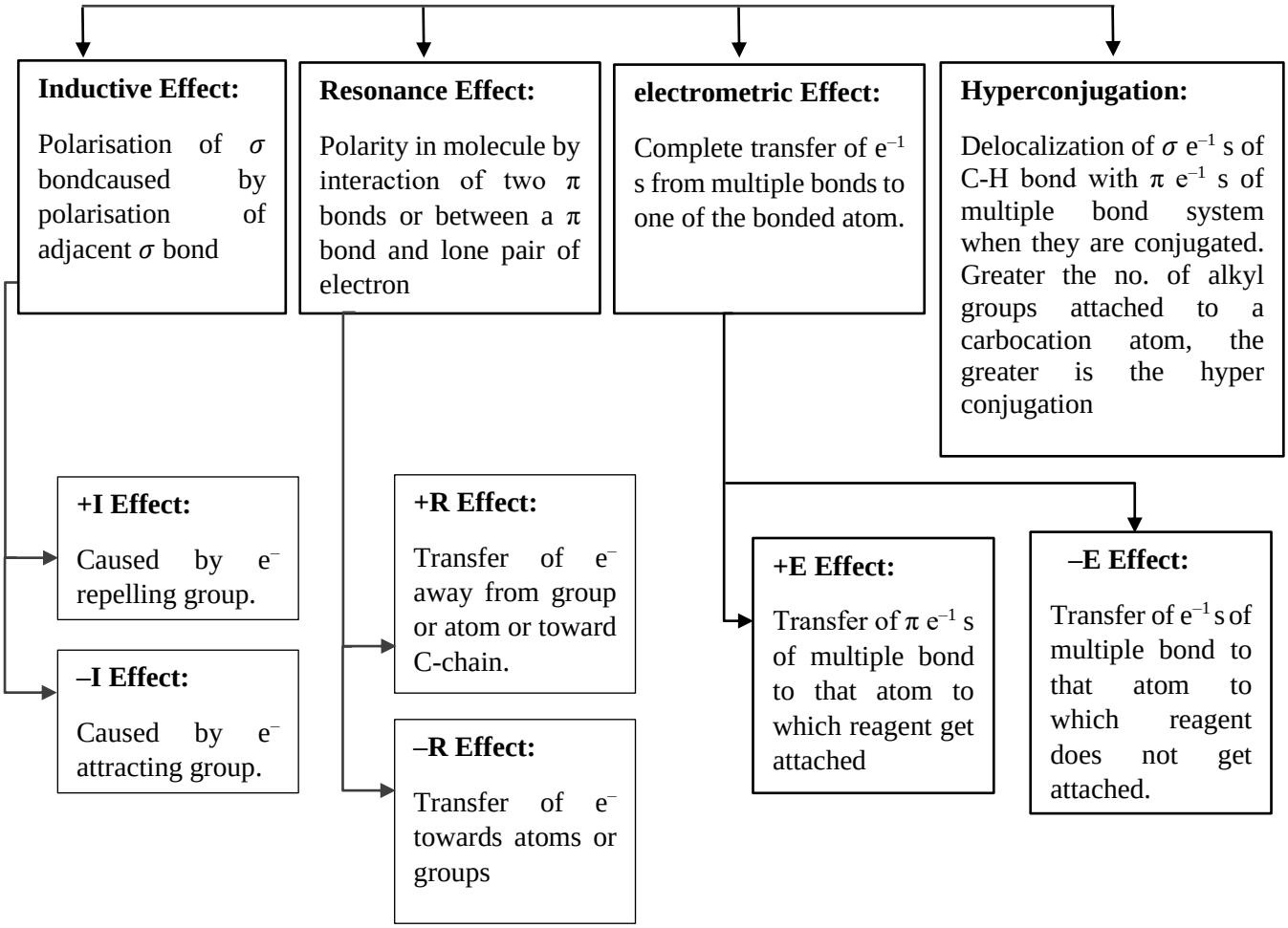
  Presentation of shifting of electron pair is given below :

  (i)  from π bond to adjacent bond position

  (ii)  from π bond to adjacent atom

  (iii)  from atom to adjacent bond position

Electron Displacement Effects in Covalent Bonds



Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

(i) Substitution reactions

(ii) Addition reactions

(iii) Elimination reactions

(iv) Rearrangement reactions

Methods of Purification of Organic Compound

	Method	Principle	Use
1	Sublimation	Sold vapour ⇌ Vapour without passing through liquid state.	Pure sublimable compounds from non sublimable impurities.
2	Crystallisation	Difference in the solubility of main compound and impurities in a suitable solvent and then cooling,	Used for purification of solid organic compound.
3	Simple Distillation	Liquids having sufficiently boiling points vaporises at different temperature. These vapour at coded and collected separately this method is called simple distillation.	Separation of chloroform (334 K) and aniline (457).
4	Fractional distillation	In this technique vapours of a liquid mixture are passed through a fractionating column before condensation. Vapours of the liquid with higher boiling point condense before the other liquid with lower b.pt.	This method is used. If the difference in boiling points of two liquids is not much. Separation of fraction of crude oil.
5	Distillation under reduced pressure	A liquid boils at its atmospheric or external pressure. If this pressure is reduced, liquid will boil before its boiling point.	This method is used to purify liquids having very high b.pt. or those liquid which decomposes on heating e.g. Glycerol can be separated from spent lye in soap industry.
6	Steam Distillation	If any organic matter to be distilled is mixed with steam then the liquid boils when the sum of vapour pressures (P_T) due to water (P_1) and due to organic liquid (P_2) becomes equal to atmospheric pressure. Hence, the mixture of two liquids boils at lower temperature than b. pt. of either liquid.	It is used to separate substance which are steam volatile and are immiscible with water.
7	Differential Extraction	Two immiscible liquids have different solubility in a solvent forms different layer. Hence they can be separated using a separating funnel organic solvent is removed by evaporation.	This method is used to separate two immiscible liquid mixture.
8	Chromatography (i) Adsorption Chromatography (ii) Partition Chromatography	Different compounds are adsorbed on an adsorbent to different categories. There are two phase stationary phase : solid (Alumina silica gel MgO etc.) Mobile phase: liquid (liquid solid). It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Stationary phase : Liquid Mobile phase: Liquid	Two main types of chromatographic technique based on the principle of different adsorption. (a) Column chromatography (b) Thin layer chromatography It mainly includes paper chromatography in which a strip of chromatographic paper is spotted with the solution mixture is suspended in a suitable solvent or a mixture solvent which acts as mobile phase.

Detection of Carbon and Hydrogen:

- These elements are detected by heating the compounds with copper (II) oxide

$$C+2CuO \xrightarrow{\Delta} 2Cu+CO_2$$
$$2H+CuO \xrightarrow{\Delta} Cu+H_2O$$
$$CO_2+Ca(PH)_2 \longrightarrow CaCO_3\downarrow+H_2O$$
$$5H_2O+CuSO_4 \text{ (white)} \longrightarrow CuSO_4 \cdot 5H_2O \text{ (Blue)}$$

Qualitative Analysis:

Element	Sodium Effect	Procedure	Reaction
Nitrogen	Na + C N → NaCN(S.E)	SE + $FeSO_4$ + NaOH then boil and cool + $FeCl_2$ + conc. HCl → Blue or green colour	$FeSO_4 + 2NaCN \rightarrow Fe(CN)_2 + Na_2SO_4$ $Fe(CN)_2 + 6NaCN \rightarrow Na_4[Pe_e(Cl_{(a)}$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_2 + 12NaCl$
Sulphur	2Na + S → Na_2S(S.E)	- S.E + Sodium nitro prusside → A deep violet colour. - SE + CH_3COOH + $(CH_3COO)_2$ Pb → Black ppt.	$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5(NO_5)]$ $Na_2S + (CH_3COO)_2Pb \rightarrow PbS + 2CH_3COONa$
Halogen	Na + Cl → NaCl(S.E)	- White ppt. soluble in aq. NH_3 confirms Cl. - Pale yellow ppt. partially soluble in excess aq. NH_3 confirms Br. - Yellow ppt. insoluble in aq. NH_3 confirms I.	$NaX + AgNO_3 \rightarrow AgX$ $AgCl + 2NH_3$ (aq.) → $[Ag(NH_3)_2]Cl$ White ppt. $AgBr + 2NH_3$ (aq.) → $[Ag(NH_3)_2]Br$ Yellow ppt. $AgI + NH_3$ (aq.) → Insoluble
Nitrogen & Sulphur	Na + Cl +N+S → NaCNS(S.E)	As in test for nitrogen; instead of green or blue colour, blood red coloration confirms presence of N and S both.	$NaCNS + FeCl_3$ → [Fe(CNS)+3Nacl

Quantitative Analysis
Liebig's Method

$$\% \text{ of carbon } = \frac{12 \times \text{ Mass of } CO_2 \times 100}{44 \times m}$$

$$\text{of hydrogen} = \frac{2 \times \text{Mass of } H_2O \times 100}{18 \times m}$$

m = mass of organic compound

Dumas Method:

N containing compound is heated with CuO

$$C_xH_y\ N_2 + \left(\frac{2x+y}{2}\right) CuO \rightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}\ N_2 + \left(\frac{2x+y}{2}\right) Cu$$

Some Basic Principles & technique

$$\% \text{ of Nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Kjeldahil's Method:

Organic compound $+H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \overset{2NaOH}{\rightarrow} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$\% \text{ of nitrogen} = \frac{1.4 \times M \times 2(V - V_1/2)}{m}$$

V and V_1 are volume (mL) of H_2SO_4 and volume (mL) of NaOH respectively.

(Carius method)

$$\% \text{ of halogen} = \frac{\text{At. mass of X} \times \text{ mass of AgX} \times 100}{\text{mol. mass of AgX} \times \text{m}}$$

Test for sulphur:

- Organic compound contain S in carius tube $\xrightarrow{Na_2O_2 + \text{ or } HNO_3} H_2SO_4 \xrightarrow{\text{excess of } BaCl2} BaSO_4$

$$\% \text{ of sulphur} = \frac{32 \times \text{ Mass of } BaSO_4 \times 100}{233 \times \text{m}}$$

Test for phosphorus:

- The compound is heated with an oxidising agent like Na_2O_2. The phosphorus present in the compound is oxidised to phosphate.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$
$$H_3PO_3 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$$

Ammonium molybdate

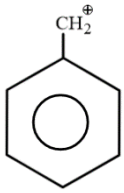
$$\% \text{ of phosphorus} = \frac{62 \times \text{ Mass of } Mg_2P_2O_7 \times 100}{222 \times \text{m}}$$

Past Years ONE-LINERS
NEET/JEE Main/Board

- $Fe_2[Fe(CN)_6]_3 =$ Prussian blue
  $Fe_3[Fe(CN)_6]_2 =$ Turnbull's blue
  $[Fe(CN)_5NOS^{1-} =$ Purple
  $NaSCN =$ Colourless
  $[Fe(SCN)]^{2+} =$ Blood - red
- Metamerism is a type of structural isomerism in which compounds having same molecular formula but different alkyl group on either side of functional $grop_p$,
- Paper chromatography is a type of partition chromatography which involves paper sheets or strips as the adsorbent being the stationary phase and solvent or mixture of solvent (mobile phase) which flows through the stationary phase.

- $AlCl_3 + Cl - Cl \longrightarrow [Al - Cl_4]^- + Cl^+$
  Cl^+acts as an electrophile.
- -1 effect increases on increasing electronegativity of atom.
- As o-nitrophenol has intramolecular H-bonding while nitrophenol has intermolecular H-bonding due to which B.pt. of o-nitrophenol is less than p-nitrophenol and it is steam volatile.
- In $CH_3 - C \equiv C^-$terminal C^-has 1σ bond and 2π bonds 1 lone pair. Its hybridisation is sp.

  Stable due to resonance



$> CH_3 - \overset{\oplus}{C}H_2 > CH_2 = \overset{\oplus}{C}H > CH \equiv \overset{\oplus}{C}$

- +ve charge on $sp^3 - C$
- +ve charge on $sp^2 - C$
- +ve charge on $sp - C$
- $-COOCH_3$ groups has more -1 and $-M$ effect and acidic strength $\propto -I, -M$ effect.
- Higher the basically of a base, stronger will be its nucleophilic character. Further a stronger base has a weaker conjugate acid.
- In column chromatography the component which is firmly attached to column or stationary phase will move slowly and cover little distance (R_f will less).
- More the stability of carbocation, higher will be the reactivity of alkyl halides towords S_N1 route. Among the following carbocation the order of stability is :

$$\underset{1^\circ \text{ carbocation}}{CH_1 - CH_2 - \overset{+}{C}H_2} < \underset{2^\circ \text{ carbocation}}{CH_3 - \overset{+}{C}H - CH_2 - CH_3} < \underset{\substack{\text{Max. stable due to } +M \text{ effect} \\ \text{of } -OCH_3 \text{ group}}}{P - H_3CO - C_6H_4 - CH_2^+}$$

- Glycerol and spent-lye are separated by distillation under reduced pressure in which a liquid boils at low temp. and will not reach upto its temp. of decomposition. Glycerol boils at $290^\circ C$ with decomposition, while under reduced pressure it boils at $180^\circ C$ without decomposition.

Tips/Tricks/Techniques ONE-LINERS
(Exam Special)

- Tautomerism: A type of isomerism which involves transfer of proton from one atom to another in an intramolecular manner. e.g. ketoenol tautomerism.

$$\underset{\substack{| \\ OH}}{CH_3–C=CH_2} \rightarrow \underset{\substack{|| \\ O}}{CH_3–C–CH_3}$$

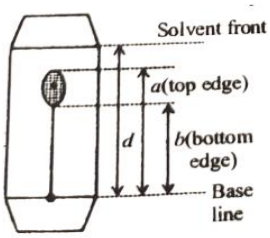
- Metamerism is a rare type of isomerism and is limited to molecules having a divalent atom like O or S and alkyl group around it. It is also observed in compounds containing four and more than four carbon atoms. In order to find the number of hyper conjugations, following formula is used No. of hyper conjugation structure = No. of alpha hydrogen +1
- If resonance, mesomeric, hyperconjugation, inductive effect and aromatic effect is asked in a single problems, then their predomination becomes important. So always remember the following order
- Aromatic > Resonance > Mesomeric > hyper conjugation > Inductive
- The retardation factor (R_f) value is defiend as the ratio of the distance moved by the solute and the distance moved by the solvent along the chromaplate, where both distances are measured from the common origin or baseline. The

diagram explains what are the distances to be taken to calculate these $R_f s$. By definition the actual R_f is that of the centre (b). Generally, R_f values are always between zero and one.

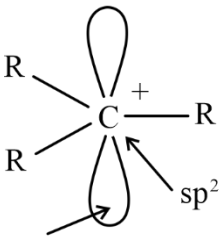
R_f top $= R_f(a) = \frac{a}{d}$

R_f bottom $= R_f(b) = \frac{b}{d}$

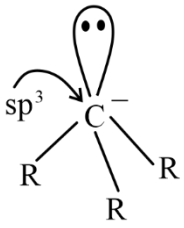
R_f centre $= R_f(c) = \frac{\left[\frac{a+b}{2}\right]}{d}$



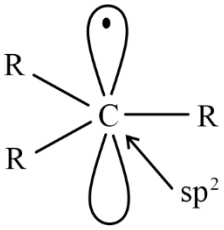
Reactive Intermediates:



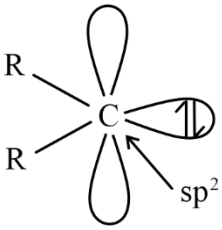
vacant p-orbital (planar)



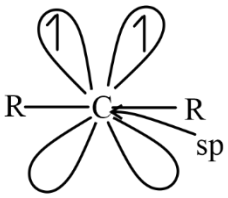
(Pyramidal)



(Planar, paramagnetic)



(Bent, Diamagnetic)



(Linear, paramagnetic)

- Stability order of carbocations:
- $(CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3 > CH_2 = \overset{+}{C}H > HC \equiv \overset{+}{C} > \overset{+}{C}6H_5$
- Stability order of carbanions:
- $HC \equiv \bar{C} > (C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > CH_2 = \bar{C}H >$
- $-\bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$
- Stability order of free radicals:
- $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (CH_3)_3\dot{C} > C_6H_5\dot{C}H_2 >$
- $CH_2 = CH - \dot{C}H_2 > (CH_3)_2\dot{C}H > \dot{C}H_3 > HC \equiv \dot{C}$
- Kjeldahl method is not applicable to compounds containing nitrogen in nitro, azo groups and nitrogen present in rings (e.g.,) pyridine, quinoline, isoquinoline) as nitrogen of these compounds does not convert to $(NH_4)_3SO_4$ under the conditions of this method.
- **Lassaigne's test :**
- NaCNS is formed only when N and S both are present together in an O.C.
- Ambiphiles: The species that behave like an electrophile and nucleophile. e.g. $H_3\overset{+}{O}$, RÖH

*****



PW Web/App - https://smart.link/7wwosivoicgd4

Library- https://smart.link/sdfez8ejd80if