CONCEPT MAP

GENERAL ORGANIC CHEMISTRY (Part-1)

Introduction :
- Vital-force theory- ("organic substances could originate only from living material) – by Berzelius.
- Urea (NH_2CONH_2) was the 1st organic compound synthesised in lab by heating NH_4CNO – by F. Wöhler

Organic Compounds

Classification

- Acyclic → Open-chain/Aliphatic
- Cyclic → Closed-chain/Ring
  - Homocyclic (Carbocyclic)
    - Alicyclic
    - Aromatic
      - Benzenoid
      - Non-benzenoid
  - Heterocyclic
    - Non-aromatic (Alicyclic)
    - Aromatic

Isomerism

Structural

(Same molecular formula but different structural formulae)

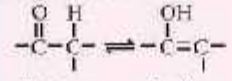
- **Chain (Nuclear/Skeleton) :** (Difference in the nature of the carbon chain). ➡ $CH_3CH_2CH_2CH_3$ (n-Butane) & $CH_3CH(CH_3)CH_3$ (Isobutane)
- **Position :** (Difference in the position of the substituent atom/group or an unsaturated linkage in the same C-chain). ➡ $CH_2=CH-CH_2-CH_3$ (But-1-ene) & $CH_3-CH=CH-CH_3$ (But-2-ene)
- **Ring-chain :** (Difference in mode of linkage of C-atoms). ➡ $CH_3-CH=CH_2$ (Prop-1-ene) & Cyclopropane (H_2C-CH_2, CH_2)
- **Functional :** (Difference in the nature of functional group). ➡ CH_3CH_2OH (Ethanol) & CH_3-O-CH_3 (Dimethyl ether)
- **Metamerism :** (Difference in the nature of alkyl groups attached on either side of the same functional group) ➡ $CH_3-O-C_3H_7$ (Methyl n-propyl ether) & $C_2H_5-O-C_2H_5$ (Diethyl ether)
- **Tautomerism (Desmotropism) :** (Isomers exist in dynamic equilibrium);

Dyad system : If the H-atom oscillates between two polyvalent atoms linked together;

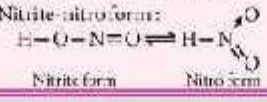
$H-C\equiv N \rightleftharpoons C=N-H$

Triad system : If the H-atom migrates from first polyvalent atom to third polyvalent atom within the same molecule in a chain.

– Keto-enol system :



– Nitrile-nitro form :



Stereoisomerism

Conformational

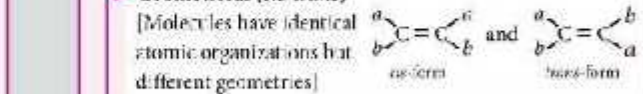
[Differ in the conformation]

Stability : staggered (anti) > skew or gauche > partially eclipsed > fully eclipsed

Configurational

Geometrical (*cis-trans*)

[Molecules have identical atomic organizations but different geometries]



Optical

[Rotate the plane polarised light]
[Contain an asymmetric (chiral) carbon atom]

Breaking of a covalent bond

depends upon the electronegativity

Homolytic fission
(Similar electronegativity)

$\geq C:X \rightarrow \dot{C} - \dot{X}$

free radicals

Heterolytic fission
(Different electronegativity)

$\geq C:X$

- $\geq C^+ + X^-$ [Carbocation] (Electronegativity, C < X)
- $\geq C^- + X^+$ [Carbanion] (Electronegativity, C > X)

Have A Look!

- A few compounds of carbon such as $CaCO_3$ and LiCN are considered to be inorganic compounds.
- Pairs of compounds always form functional isomers with each other :
  - Dienes (allenes) and alkynes
  - Aldehydes, ketones and unsaturated alcohols
  - 1°, 2° and 3° amides
  - Cyanides and isocyanides
  - Alcohols and ethers
  - Carboxylic acids and esters
  - Nitroalkanes and alkyl nitrites
  - Aromatic alcohols, phenols and ethers
- Tautomerism term was introduced by 'Laar'.
- Benzophenone oxime, $(C_6H_5)_2C=NOH$ having two similar aryl groups does not show geometrical isomerism.
- Quartz was the first substance to exhibit the phenomenon of optical activity.
- Malic acid (saturated hydroxy dicarboxylic acid) —shows→ optical isomerism.
- Maleic acid (unsaturated dicarboxylic acid) —shows→ geometrical isomerism.
- Conformational isomerism only found in alkanes, cycloalkanes and their derivatives.
- Anomers – Differ in configuration around C_1-atom.
- Enantiomers – Mirror images but not superimposable.
- Diastereomers – Not mirror images with each other.

Free radical	Carbocation	Carbanion	Carbene
• Electrically neutral, highly unstable, *e* deficient	• +ve charge on C, • Electrophilic, Lewis acid	• –ve charge on C, • Nucleophilic, Lewis base	• Neutral, divalent with 2-unshared electrons • Both nucleophilic and electrophilic
• sp^2, planar	• sp^2, planar	• sp^3 (Non-conjugated), pyramidal sp^2 (Conjugated), planar	• (i) sp^2 (singlet) : –C– (Planar); (ii) sp (triplet) : –C– (Linear)
• Paramagnetic	• Diamagnetic	• Diamagnetic	• (i) Diamagnetic (ii) Paramagnetic
• $Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > 3° > 2° > 1° > \dot{C}H_3 > CH_2=\dot{C}H$ • e.g. Wurtz reaction – Anti-Markownikoff's addition – Kolbe's electrolysis	• $Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2 > CH_2=CH-\overset{+}{C}H_2 > 3° > 2° > 1° > \overset{+}{C}H_3$ • e.g. Pinacol pinacolone rearrangement – Electrophilic addition reactions of alkenes, alkynes and alkadienes. – S_N1 reaction of *R*–*X* and diazonium salts	• $Ph_3C > Ph_2CH > PhCH_2 >$ Allyl $> CH_3 > 1° > 2° > 3°$ • e.g. Aldol condensation – Cannizzaro's reaction – Perkin's reaction – Knoevenagel reaction	• Stability : Triplet > Singlet • e.g. Carbylamine reaction – Reimer—Tiemann reaction – Wittig reaction – Wolff rearrangement