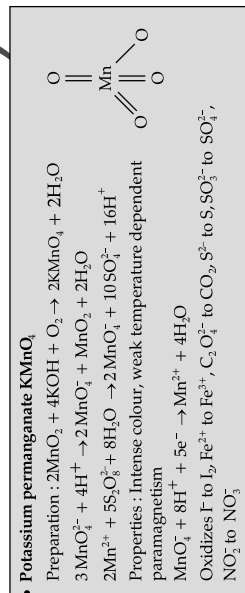
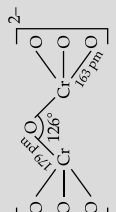
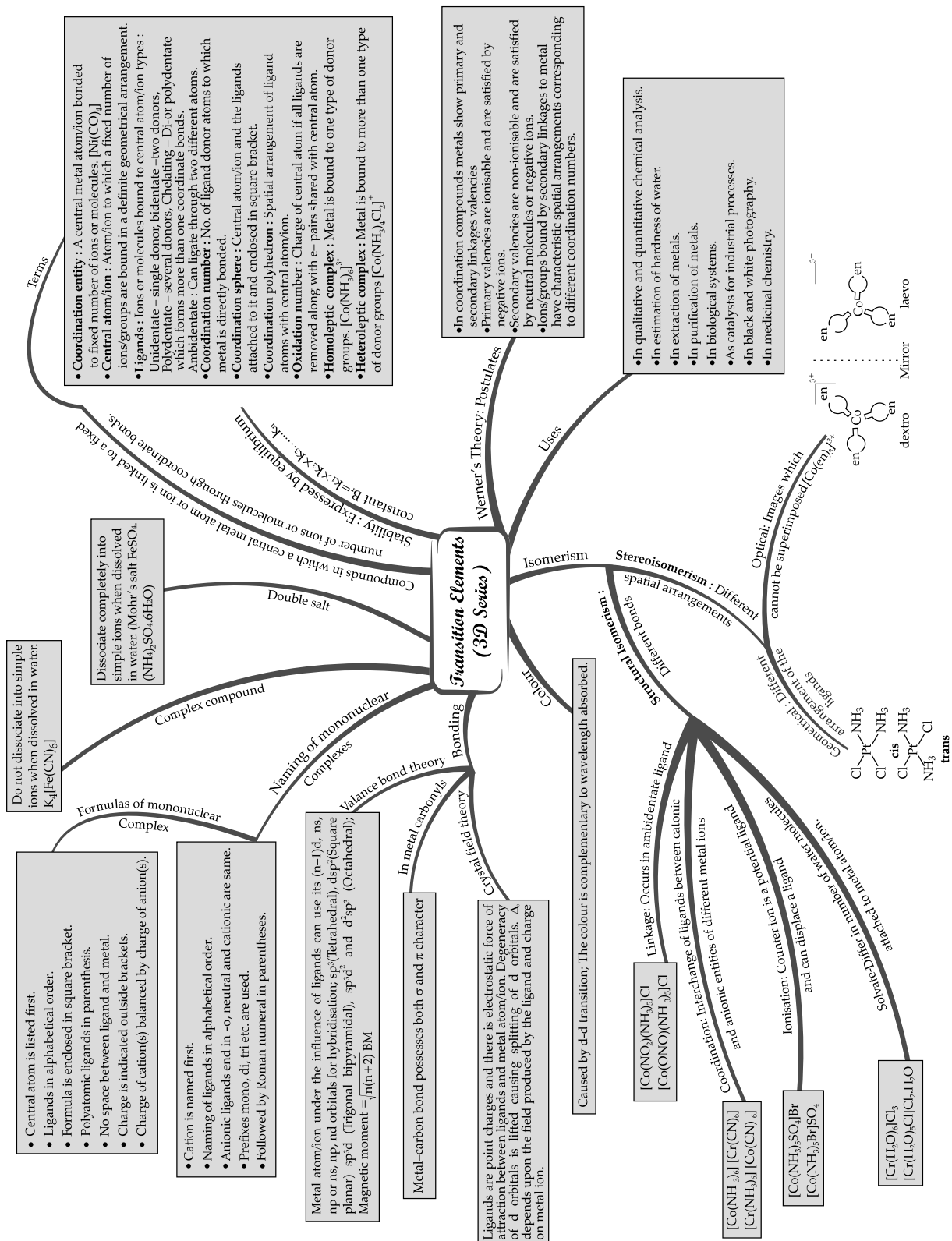
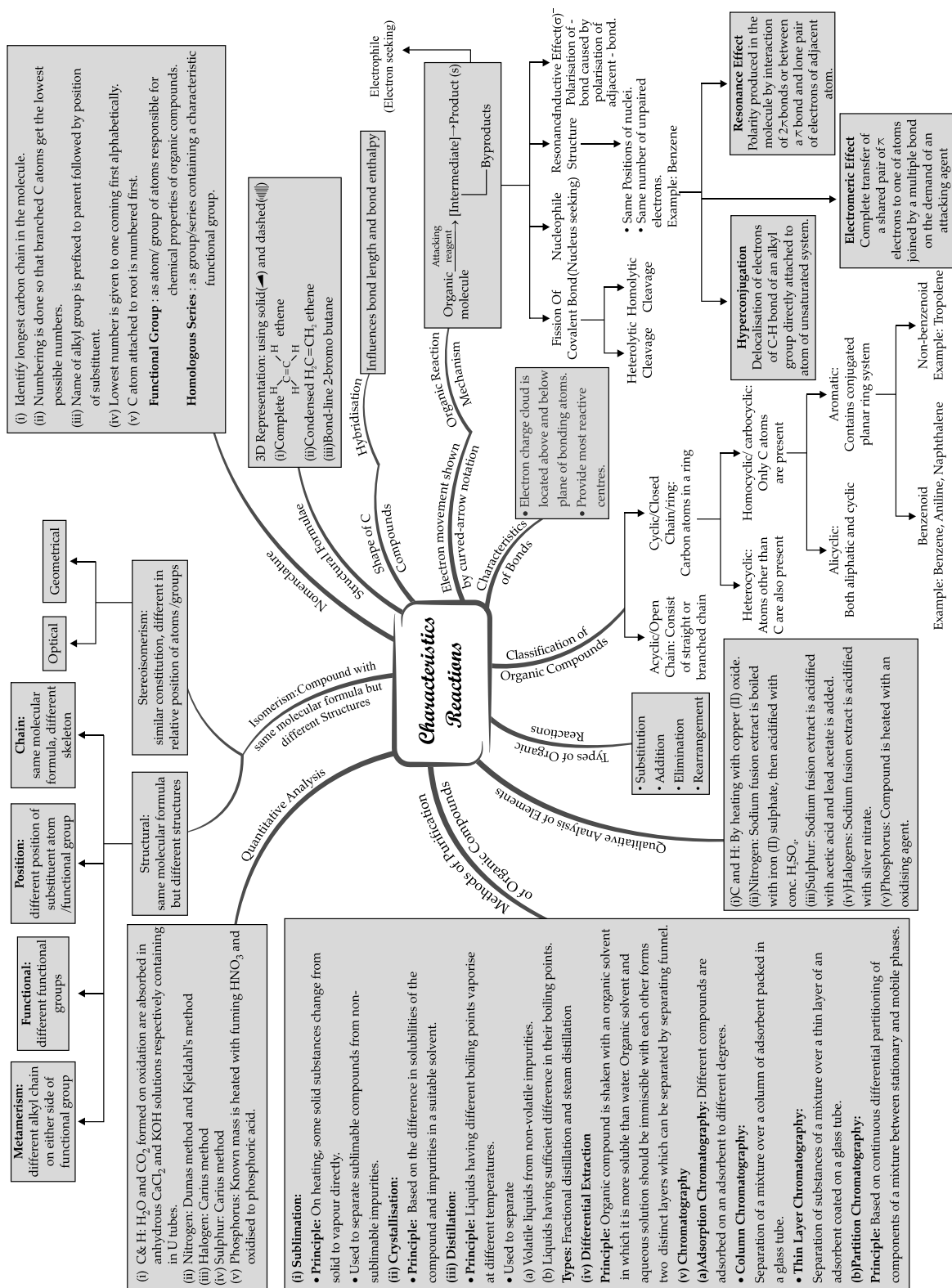


- Position : Between s- and p-blocks.
- General Electronic configuration : (n-1)d<sup>1-10</sup> ns<sup>1-2</sup>
- Physical properties : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization.
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to imperfect shielding of one e<sup>-</sup> by another in same set of orbitals.
- Ionisation enthalpies : Increases from left to right.
- Oxidation states : Variable; higher ON stable.
- Trends in M<sup>2+</sup>/M : E<sup>o</sup> for Mn, Ni and Zn are more negative than expected.
- Trends in M<sup>2+</sup>/M<sup>3+</sup> E<sup>o</sup> : Variable.
- Chemical reactivity and E<sup>o</sup> values : Variable; Ti<sup>2+</sup>, V<sup>2+</sup> and Cr<sup>2+</sup> are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions : Form coloured compounds due to d-d transitions.
- Formation of complex compounds : Form a large number of complex compounds.
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Form interstitial compounds : Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.







# Hydrocarbons

**Compounds of Carbon and Hydrogen**

**Aromatic Hydrocarbon**

**Mechanism of Electrophilic Substitution reactions**

**Alkynes (C<sub>n</sub>H<sub>2n-2</sub>)**

**Alkenes (C<sub>n</sub>H<sub>2n</sub>)**

**Alkanes (C<sub>n</sub>H<sub>2n+2</sub>)**

**Physical Properties**

**Chemical Properties**

**Classification**

**Saturated: Contain C-C and C-H single bonds, (alkanes)**

**Unsaturated: Contain C-C multiple bonds (alkenes, alkynes)**

**Aromatic: Contain cyclic compounds**

**Types: Benzenoids** – contain benzene ring, Non-benzenoids – does not contain benzene ring.

- Isomerism: Ortho (o-), Meta (m-), Para (p-)
- Structure:

**Aromaticity:** Planarity, complete delocalisation of the π-electrons in the ring, presence of (4n + 2) π electrons in the ring where n is an integer (n = 0, 1, 2, ..... ) (Hückel rule)

**Preparation:**

- Cyclic polymerisation of ethyne
- C<sub>6</sub>H<sub>5</sub>COONa + NaOH  $\xrightarrow{\Delta}$  CaO, H<sub>6</sub> + Na<sub>2</sub>CO<sub>3</sub>
- C<sub>6</sub>H<sub>5</sub>OH + Zn  $\xrightarrow{\Delta}$  C<sub>6</sub>H<sub>6</sub> + ZnO

**Physical Properties**

- Non-polar, usually colourless liquids or solids with characteristic aroma.
- Immiscible with water but miscible with organic solvents.
- Burns with sooty flame.

**Chemical Properties:**

- + conc. HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub>  $\xrightarrow{323-333K}$  + H<sub>2</sub>O
- + Cl<sub>2</sub>  $\xrightarrow{\text{Anhyd. AlCl}_3}$  + HCl; + H<sub>2</sub>SO<sub>4</sub>  $\xrightarrow{\Delta}$  + H<sub>2</sub>O
- + CH<sub>3</sub>Cl  $\xrightarrow{\text{Anhyd. AlCl}_3}$  + HCl
- + CH<sub>3</sub>COCl  $\xrightarrow{\text{Anhyd. AlCl}_3}$  + HCl

**Preparation:**

- Wurtz reaction: CH<sub>2</sub> = CH<sub>2</sub> + H<sub>2</sub>  $\xrightarrow{\text{pd/pf/Ni}}$  CH<sub>3</sub> - CH<sub>3</sub>
- Wurtz-Fittig reaction: CH<sub>3</sub>Br + 2Na + BrCH<sub>3</sub>  $\xrightarrow{\text{Dry ether}}$  CH<sub>3</sub> - CH<sub>3</sub> + 2NaBr
- CH<sub>3</sub>COONa + NaOH  $\xrightarrow{\text{CO}}$  CH<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub>
- 2CH<sub>3</sub>COONa + 2H<sub>2</sub>O  $\xrightarrow{\Delta}$  C<sub>2</sub>H<sub>6</sub> + 2CO<sub>2</sub> + H<sub>2</sub> + 2NaOH

**Physical Properties:**

- Non-polar, weak van der Waals forces, colourless, odourless.
- B.P. increases with increases in molecular size.

**Chemical Properties:**

- CH<sub>4</sub>  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>3</sub>Cl  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>2</sub>Cl<sub>2</sub>  $\xrightarrow{\text{hv/hv}^+}$  CHCl<sub>3</sub>  $\xrightarrow{\text{hv/hv}^+}$  CCl<sub>4</sub>
- C<sub>n</sub>H<sub>2n+2</sub> +  $\left(\frac{3n+1}{2}\right)$  O<sub>2</sub>  $\longrightarrow$  nCO<sub>2</sub> + (n+1)H<sub>2</sub>O
- 2CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Cu}/523K/100\text{atm}}$  2CH<sub>3</sub>OH
- CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Mn}_2\text{O}_7}$  HCHO + H<sub>2</sub>O
- CH<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>  $\xrightarrow{\text{Anhyd. AlCl}_3/\text{HCl}}$  CH<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>-CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- CH<sub>4</sub> + H<sub>2</sub>O  $\xrightarrow{\text{Ni}}$  CO + 3H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>6</sub>H<sub>12</sub> + H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>4</sub>H<sub>8</sub> + C<sub>2</sub>H<sub>6</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> + CH<sub>4</sub>

**Shows structural and geometrical isomerism**

**Preparation:**

- RC≡CR' + H<sub>2</sub>  $\xrightarrow{\text{Pd/C}}$
- RC≡CR' + H<sub>2</sub>  $\xrightarrow{\text{Na/Liquid NH}_3}$
- H<sub>3</sub>C-CH<sub>2</sub>X  $\xrightarrow{\text{Alc. KOH}}$  H<sub>2</sub>C=CH<sub>2</sub>
- CH<sub>3</sub>Br - CH<sub>2</sub>Br + Zn  $\longrightarrow$  CH<sub>2</sub>=CH<sub>2</sub> + ZnBr<sub>2</sub>
- CH<sub>3</sub>CH<sub>2</sub>OH  $\xrightarrow{\text{conc. H}_2\text{SO}_4}$  CH<sub>2</sub>=CH<sub>2</sub> + H<sub>2</sub>O

**Physical Properties:**

- Ethene is a colourless gas with faint sweet smell.
- All others are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents.
- Increase in b.p. with increase in molecular size.

**Chemical Properties:**

- CH<sub>2</sub>=CH<sub>2</sub> + Br<sub>2</sub>  $\xrightarrow{\text{CCl}_4}$  BrCH<sub>2</sub>-CH<sub>2</sub>Br
- CH<sub>2</sub>=CH<sub>2</sub> + HBr  $\longrightarrow$  CH<sub>3</sub>-CH<sub>2</sub>Br
- CH<sub>3</sub>-CH=CH<sub>2</sub> + HBr  $\xrightarrow{\text{Markovnikov rule}}$
- H<sub>3</sub>C-C=CH<sub>2</sub> + H<sub>2</sub>O  $\xrightarrow{\text{H}^+}$
- CH<sub>3</sub>-CH=CH-CH<sub>3</sub>  $\xrightarrow{\text{KMnO}_4/\text{H}^+}$  2CH<sub>3</sub>COOH
- n(CH<sub>2</sub>=CH<sub>2</sub>)  $\xrightarrow{\text{High Temp/Pressure Catalyst}}$  -(CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-
- n(CH<sub>2</sub>-CH=CH<sub>2</sub>)  $\xrightarrow{\text{High Temp/Pressure Catalyst}}$  -(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-

**Shows structural and geometrical isomerism**

- H-C-H bond angles – 190.5, C-C and C-H bond lengths are 154 pm and 112 pm respectively.
- Shows structural and chain isomerism.

**Preparation:**

- CH<sub>2</sub> = CH<sub>2</sub> + H<sub>2</sub>  $\xrightarrow{\text{pd/pf/Ni}}$  CH<sub>3</sub> - CH<sub>3</sub>

**Wurtz reaction:**

- CH<sub>3</sub>Br + 2Na + BrCH<sub>3</sub>  $\xrightarrow{\text{Dry ether}}$  CH<sub>3</sub> - CH<sub>3</sub> + 2NaBr
- CH<sub>3</sub>COONa + NaOH  $\xrightarrow{\text{CO}}$  CH<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub>
- 2CH<sub>3</sub>COONa + 2H<sub>2</sub>O  $\xrightarrow{\Delta}$  C<sub>2</sub>H<sub>6</sub> + 2CO<sub>2</sub> + H<sub>2</sub> + 2NaOH

**Physical Properties:**

- Non-polar, weak van der Waals forces, colourless, odourless.
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**Chemical Properties:**

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- C<sub>n</sub>H<sub>2n+2</sub> +  $\left(\frac{3n+1}{2}\right)$  O<sub>2</sub>  $\longrightarrow$  nCO<sub>2</sub> + (n+1)H<sub>2</sub>O
- 2CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Cu}/523K/100\text{atm}}$  2CH<sub>3</sub>OH
- CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Mn}_2\text{O}_7}$  HCHO + H<sub>2</sub>O
- CH<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>  $\xrightarrow{\text{Anhyd. AlCl}_3/\text{HCl}}$  CH<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>-CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- CH<sub>4</sub> + H<sub>2</sub>O  $\xrightarrow{\text{Ni}}$  CO + 3H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>6</sub>H<sub>12</sub> + H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>4</sub>H<sub>8</sub> + C<sub>2</sub>H<sub>6</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> + CH<sub>4</sub>

**Physical Properties**

- First three members are gases, next eight are liquids and higher ones are solids.
- Colourless, ethyne has characteristic odour and other are odourless.
- Lighter than water, immiscible with water but soluble in organic solvents.
- M.p, b.p. and density increase with increase in molar mass.

**Chemical Properties:**

- HC≡CH + Na  $\longrightarrow$  HC≡CNa + 1/2H<sub>2</sub>
- HC≡CH + H<sub>2</sub>  $\xrightarrow{\text{Pd/Pf/Ni}}$  [H<sub>2</sub>C=CH<sub>2</sub>]  $\xrightarrow{\text{H}^+}$  CH<sub>3</sub>-CH<sub>3</sub>
- CH<sub>3</sub>-C≡CH + Br<sub>2</sub>  $\longrightarrow$  [CH<sub>3</sub>CBr=CHBr]  $\xrightarrow{\text{Br}_2}$
- HC≡C-H + HBr  $\longrightarrow$  [CH<sub>2</sub>=CH-Br]  $\xrightarrow{\text{HBr}}$  CH<sub>3</sub>-CH<sub>2</sub>Br
- HC≡CH + H<sub>2</sub>O  $\xrightarrow{\text{Hg}^{2+}/\text{H}^+}$   $\xrightarrow{333K}$  [CH<sub>2</sub>=C(H)-OH]  $\xrightarrow{\text{Isomerisation}}$  CH<sub>3</sub>-C(=O)-H

**Polymerisation:**

- $\xrightarrow{\text{Red hot iron tube}}$
- $\xrightarrow{873K}$

**(i) Generation of Electrophile**

**(ii) Formation of carbocation intermediate**

**(iii) Removal of proton**

**IUPAC name:** replacing 'ane' by the suffix 'yne'.

**Shows position and chain isomerism**

- CaCO<sub>3</sub>  $\xrightarrow{\Delta}$  CaO + CO<sub>2</sub>
- CaO + 3C  $\longrightarrow$  CaC<sub>2</sub> + CO
- CaC<sub>2</sub> + 2H<sub>2</sub>O  $\longrightarrow$  Ca(OH)<sub>2</sub> + C<sub>2</sub>H<sub>2</sub>
- CH<sub>3</sub>Br - CH<sub>2</sub>Br + KOH  $\xrightarrow{\text{alcohol}}$  H<sub>3</sub>C=CHBr  $\xrightarrow[\text{-NH}_3]{\text{NaNH}_2/\text{-H}_2\text{O}}$  CH≡CH

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- HC≡CH + H<sub>2</sub>  $\xrightarrow{\text{Pd/Pf/Ni}}$  [H<sub>2</sub>C=CH<sub>2</sub>]  $\xrightarrow{\text{H}^+}$  CH<sub>3</sub>-CH<sub>3</sub>
- CH<sub>3</sub>-C≡CH + Br<sub>2</sub>  $\longrightarrow$  [CH<sub>3</sub>CBr=CHBr]  $\xrightarrow{\text{Br}_2}$
- HC≡C-H + HBr  $\longrightarrow$  [CH<sub>2</sub>=CH-Br]  $\xrightarrow{\text{HBr}}$  CH<sub>3</sub>-CH<sub>2</sub>Br
- HC≡CH + H<sub>2</sub>O  $\xrightarrow{\text{Hg}^{2+}/\text{H}^+}$   $\xrightarrow{333K}$  [CH<sub>2</sub>=C(H)-OH]  $\xrightarrow{\text{Isomerisation}}$  CH<sub>3</sub>-C(=O)-H

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- CH<sub>4</sub> + H<sub>2</sub>O  $\xrightarrow{\text{Ni}}$  CO + 3H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>6</sub>H<sub>12</sub> + H<sub>2</sub>
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- 2CH<sub>3</sub>COONa + 2H<sub>2</sub>O  $\xrightarrow{\Delta}$  C<sub>2</sub>H<sub>6</sub> + 2CO<sub>2</sub> + H<sub>2</sub> + 2NaOH

**Physical Properties:**

- Non-polar, weak van der Waals forces, colourless, odourless.
- B.P. increases with increases in molecular size.

**Chemical Properties:**

- CH<sub>4</sub>  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>3</sub>Cl  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>2</sub>Cl<sub>2</sub>  $\xrightarrow{\text{hv/hv}^+}$  CHCl<sub>3</sub>  $\xrightarrow{\text{hv/hv}^+}$  CCl<sub>4</sub>
- C<sub>n</sub>H<sub>2n+2</sub> +  $\left(\frac{3n+1}{2}\right)$  O<sub>2</sub>  $\longrightarrow$  nCO<sub>2</sub> + (n+1)H<sub>2</sub>O
- 2CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Cu}/523K/100\text{atm}}$  2CH<sub>3</sub>OH
- CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Mn}_2\text{O}_7}$  HCHO + H<sub>2</sub>O
- CH<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>  $\xrightarrow{\text{Anhyd. AlCl}_3/\text{HCl}}$  CH<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>-CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- CH<sub>4</sub> + H<sub>2</sub>O  $\xrightarrow{\text{Ni}}$  CO + 3H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>6</sub>H<sub>12</sub> + H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>4</sub>H<sub>8</sub> + C<sub>2</sub>H<sub>6</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> + CH<sub>4</sub>

**Physical Properties**

- First three members are gases, next eight are liquids and higher ones are solids.
- Colourless, ethyne has characteristic odour and other are odourless.
- Lighter than water, immiscible with water but soluble in organic solvents.
- M.p, b.p. and density increase with increase in molar mass.

**Chemical Properties:**

- HC≡CH + Na  $\longrightarrow$  HC≡CNa + 1/2H<sub>2</sub>
- HC≡CH + H<sub>2</sub>  $\xrightarrow{\text{Pd/Pf/Ni}}$  [H<sub>2</sub>C=CH<sub>2</sub>]  $\xrightarrow{\text{H}^+}$  CH<sub>3</sub>-CH<sub>3</sub>
- CH<sub>3</sub>-C≡CH + Br<sub>2</sub>  $\longrightarrow$  [CH<sub>3</sub>CBr=CHBr]  $\xrightarrow{\text{Br}_2}$
- HC≡C-H + HBr  $\longrightarrow$  [CH<sub>2</sub>=CH-Br]  $\xrightarrow{\text{HBr}}$  CH<sub>3</sub>-CH<sub>2</sub>Br
- HC≡CH + H<sub>2</sub>O  $\xrightarrow{\text{Hg}^{2+}/\text{H}^+}$   $\xrightarrow{333K}$  [CH<sub>2</sub>=C(H)-OH]  $\xrightarrow{\text{Isomerisation}}$  CH<sub>3</sub>-C(=O)-H

**Polymerisation:**

- $\xrightarrow{\text{Red hot iron tube}}$
- $\xrightarrow{873K}$

**Physical Properties**

- Non-polar, weak van der Waals forces, colourless, odourless.
- B.P. increases with increases in molecular size.

**Chemical Properties:**

- CH<sub>4</sub>  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>3</sub>Cl  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>2</sub>Cl<sub>2</sub>  $\xrightarrow{\text{hv/hv}^+}$  CHCl<sub>3</sub>  $\xrightarrow{\text{hv/hv}^+}$  CCl<sub>4</sub>
- C<sub>n</sub>H<sub>2n+2</sub> +  $\left(\frac{3n+1}{2}\right)$  O<sub>2</sub>  $\longrightarrow$  nCO<sub>2</sub> + (n+1)H<sub>2</sub>O
- 2CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Cu}/523K/100\text{atm}}$  2CH<sub>3</sub>OH
- CH<sub>4</sub> + O<sub>2</sub>  $\xrightarrow{\text{Mn}_2\text{O}_7}$  HCHO + H<sub>2</sub>O
- CH<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>  $\xrightarrow{\text{Anhyd. AlCl}_3/\text{HCl}}$  CH<sub>3</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>-CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>
- CH<sub>4</sub> + H<sub>2</sub>O  $\xrightarrow{\text{Ni}}$  CO + 3H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>6</sub>H<sub>12</sub> + H<sub>2</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>4</sub>H<sub>8</sub> + C<sub>2</sub>H<sub>6</sub>
- C<sub>6</sub>H<sub>14</sub>  $\xrightarrow{733K}$  C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> + CH<sub>4</sub>

**Shows structural and geometrical isomerism**

- H-C-H bond angles – 190.5, C-C and C-H bond lengths are 154 pm and 112 pm respectively.
- Shows structural and chain isomerism.

**Preparation:**

- CH<sub>2</sub> = CH<sub>2</sub> + H<sub>2</sub>  $\xrightarrow{\text{pd/pf/Ni}}$  CH<sub>3</sub> - CH<sub>3</sub>

**Wurtz reaction:**

- CH<sub>3</sub>Br + 2Na + BrCH<sub>3</sub>  $\xrightarrow{\text{Dry ether}}$  CH<sub>3</sub> - CH<sub>3</sub> + 2NaBr
- CH<sub>3</sub>COONa + NaOH  $\xrightarrow{\text{CO}}$  CH<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub>
- 2CH<sub>3</sub>COONa + 2H<sub>2</sub>O  $\xrightarrow{\Delta}$  C<sub>2</sub>H<sub>6</sub> + 2CO<sub>2</sub> + H<sub>2</sub> + 2NaOH

**Physical Properties:**

- Non-polar, weak van der Waals forces, colourless, odourless.
- B.P. increases with increases in molecular size.

**Chemical Properties:**

- CH<sub>4</sub>  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>3</sub>Cl  $\xrightarrow{\text{hv/hv}^+}$  CH<sub>2</sub>Cl<sub>2</sub>  $\xrightarrow{\text{hv/hv}^+}$  CHCl<sub>3</sub>  $\xrightarrow{\text{hv/hv}^+}$  CCl<sub>4</sub>
- C<sub>n</sub>H<sub>2n+2</sub> +  $\left(\frac{3n+1}{2}\right)$  O<sub>2</sub>  $\longrightarrow</$

**Chloroform**

- Solvent for fats, alkaloids, I etc.
- Production of freon.

**Iodoform**

- Antiseptic

**Carbon tetrachloride**

- For aerosol propellants, refrigeration and air conditioning purposes.
- Cleaning fluid.

**DDT**

- As insecticide

**Dichloromethane**

- Paint remover.
- Propellant in aerosols.
- Metal cleaning and finishing solvent.

**Haloalkanes and Haloarenes**

**Polyhalogen compounds**

- Chiral: Objects which are non-superimposable.
- Achiral: Objects which are superimposable.

**Racemisation  $S_N1$**

**$S_N2$  Stereoinversion**

**Haloalkanes**

- (a) Dextro (+/d)
- (b) Laevo (-/l)

**Reactions:**

(a) Nucleophilic substitution

(i) Resonance effect

(ii) Hybridization of C-X bond in: Haloalkane -sp; Haloarene -sp<sup>2</sup>

(iii) Phenyl cation stabilised by resonance

(i) NaOH, 623K, 300atm

(ii) H<sup>+</sup>

(i) NaOH, 443K

(ii) H<sup>+</sup>

(b) Electrophilic substitution

Anhyd. FeCl<sub>3</sub>

HNO<sub>3</sub> / conc. H<sub>2</sub>SO<sub>4</sub>

conc. H<sub>2</sub>SO<sub>4</sub> / Δ

Friedel-Crafts reaction

+ CH<sub>3</sub>Cl

Anhyd. AlCl<sub>3</sub>

+ H<sub>3</sub>C-C-Cl

Anhyd. AlCl<sub>3</sub>

(c) Reaction with metals

Wurtz - Fitting reaction

X + 2Na + RX Ether → R + 2NaX

Fittig reaction

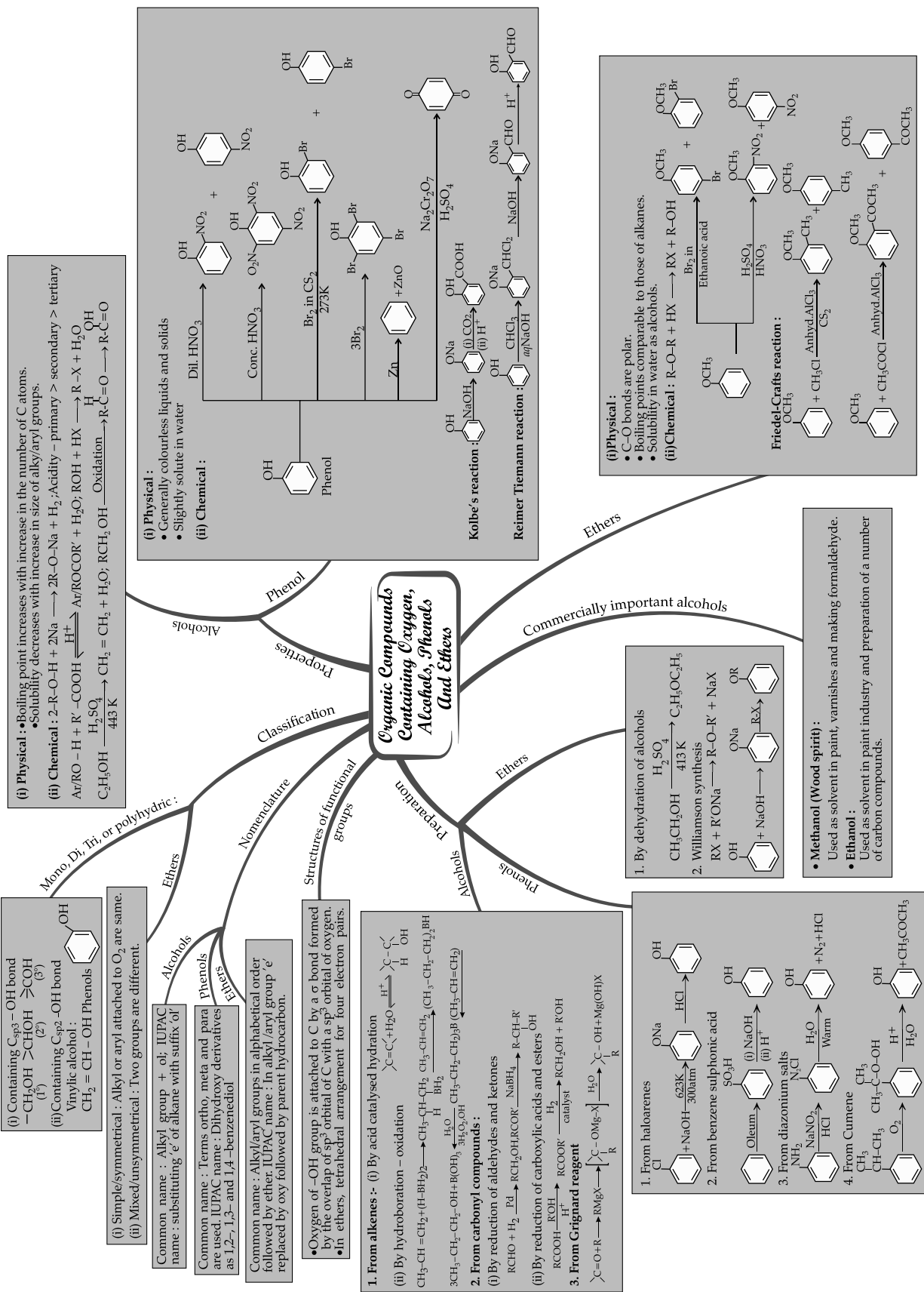
2 X + 2Na Ether → R + 2NaX

**Classification**

- No. of halogen atoms
- C<sub>2</sub>H<sub>5</sub>X
- Monohaloalkane
- CH<sub>2</sub>X
- Dihaloalkane
- Trihaloalkane
- Monohaloarene
- Dihaloarene
- Trihaloarene
- Compounds containing sp<sup>3</sup> C-X bond
- (a) Alkyl halides
- (b) Allylic halides
- (c) Benzylic halides
- Compounds containing sp<sup>2</sup> C-X bond
- (a) Vinylic halides
- (b) Aryl halides
- Nomenclature
- Common name: Alkyl group followed by halides. Dihalogen derivatives, prefixes o-, m-, p- are used.
- IUPAC name: Numerals are used.
- Nature of C-X bond
- Carbon-halogen bond is polarized.

**Preparation**

- From alcohol: ZnCl<sub>2</sub> → R-Cl + H<sub>2</sub>O
- 3R-OH + PX<sub>3</sub> → 3R-X + H<sub>3</sub>PO<sub>3</sub>
- ROH + PCl<sub>5</sub> → R-Cl + POCl<sub>3</sub> + HCl
- From hydrocarbons:
  - By free radical halogenation: CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  $\xrightarrow{Cl_2/UV}$  CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl + CH<sub>3</sub>CH<sub>2</sub>CH(Cl)CH<sub>3</sub>
  - By electrophilic substitution:
    - CH<sub>3</sub> + X<sub>2</sub>  $\xrightarrow{Fe, Dark}$  CH<sub>3</sub>X + X
    - Sandmeyer's reaction: Nc1ccccc1  $\xrightarrow{273-278K}$  Nc1ccccc1X + N<sub>2</sub>
  - From alkenes:
    - H<sub>2</sub>C=CH<sub>2</sub> + Br<sub>2</sub>  $\xrightarrow{CCl_4}$  BrCH<sub>2</sub>-CH<sub>2</sub>Br
    - Halogen exchange: R-X + NaI → R-I + NaX
- Properties:
  - Physical: Colourless, volatile, sweet smell.
  - Lower members are gases at room temperature while higher are solids.
  - B.P: RI > RBr > RCl > RF.
  - M.P: Para isomers have high m.p. than ortho and meta - isomers.
  - Density: Increases with increase in number of C/X atoms and atomic masses of the X atoms.
  - Solubility: Very slightly soluble in water.
- Chemical:
  - (a) Nucleophilic substitution: Nu<sup>-</sup> +  $\overset{\delta+}{C}-\overset{\delta-}{X} \rightarrow \overset{\delta+}{C}-Nu + X^-$
  - For S<sub>N</sub>2 reaction: Tertiary, Secondary, Primary
  - For S<sub>N</sub>1 reaction: (a) Elimination reaction: B:  $\overset{\delta+}{C}-\overset{\delta-}{X} \rightarrow C=C + B-H + X^-$
  - B = Base; X = Leaving group
  - (c) Reaction with metals: CH<sub>3</sub>CH<sub>2</sub>Br + Mg → CH<sub>3</sub>CH<sub>2</sub>MgBr
  - Wurtz reaction: 2RX + 2Na → RR + 2NaX



**Aldehydes and Ketones:**

(i) **Physical:** Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

(ii) **Chemical: Nucleophilic addition reactions:** Aldehydes are more reactive than ketones due to steric and electronic reasons.

$$\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{C}=\text{O} \\ | \\ \text{R} \end{array} + \text{OH}^- \rightleftharpoons \begin{array}{c} \delta^- \\ \text{C} \\ | \\ \text{R} \end{array} + \text{H}_2\text{O}; \begin{array}{c} \delta^+ \\ \text{C} \\ | \\ \text{R} \end{array} + \text{CN}^- \rightleftharpoons \begin{array}{c} \text{C} \\ | \\ \text{R} \end{array} + \text{CN}^-$$

**Reduction:** (a) To alcohols – aldehydes and ketones reduce to primary and secondary alcohols respectively by  $\text{NaBH}_4$  or  $\text{LiAlH}_4$ .

$$\text{C}=\text{O} \xrightarrow{\text{Zn-Hg}} \text{CH}_2 + \text{H}_2\text{O} \text{ (Clemmensen Reduction)}$$

$$\text{C}=\text{O} \xrightarrow[\text{-H}_2\text{O}]{\text{NH}_2, \text{NH}_3} \text{C}=\text{NNH}_2 \xrightarrow[\text{Heat}]{\text{KOH/Ethylene glycol}} \text{CH}_2 + \text{N}_2 \text{ (Wolf-Kishner)}$$

**Oxidation:**  $\text{RCHO} \xrightarrow{[\text{O}]} \text{R-COOH}$

**Tollen's test:**  $\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH}^- \rightarrow \text{RCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$

**Fehling's test:**  $\text{RCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$

**Haloforn reaction:**

$$\text{R-C-CH}_3 \xrightarrow{\text{NaOX}} \text{R-C-ONa} + \text{CH}_3\text{X}$$

**Reactions due to  $\alpha$ -hydrogen:**

$$2\text{CH}_3\text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{-CH}=\text{CH-CHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{-CH}=\text{CH-CHO}$$

$$2\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Ba(OH)}_2} \text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)\text{-CH}_2\text{-COCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)\text{-CH}_2\text{-CO-CH}_3$$

$$\text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{CH}_3\text{-CH}=\text{CH-CHO} + \text{CH}_3\text{-CH}_2\text{-CH}=\text{C}(\text{OH})\text{CHO}$$

**Cannizzaro reaction:**  $2\text{HCHO} + \text{conc. KOH} \xrightarrow{\Delta} \text{CH}_3\text{OH} + \text{HCOOK}$

**Electrophilic substitution reaction:**

$$\text{CHO} \xrightarrow[\text{273-283 K}]{\text{HNO}_3/\text{H}_2\text{SO}_4} \text{NO}_2\text{CHO}$$

**Carboxylic acids:**

(i) **Physical:** Higher boiling points than aldehydes, ketones or alcohols. Solubility decreases with increasing number of C atoms

(ii) **Chemical:**  $2\text{RCOOH} + 2\text{Na} \rightarrow 2\text{RCOONa} + \text{H}_2$

Forms corresponding anhydride on heating with mineral acids

$$\text{RCOOH} + \text{R'OH} \xrightarrow{\text{H}^+} \text{RCOOR}' + \text{H}_2\text{O}$$

$$\text{RCOOH} + \text{PCl}_5 \rightarrow \text{RCOCl} + \text{POCl}_3 + \text{HCl}$$

$$\text{CH}_3\text{COOH} + \text{NH}_3 \xrightarrow{\text{Heat}} \text{CH}_3\text{COONH}_4 \xrightarrow[\text{-H}_2\text{O}]{\Delta} \text{CH}_3\text{CONH}_2$$

$$\text{RCOOH} \xrightarrow[\text{H}_3\text{O}^+]{\text{B}_2\text{H}_6} \text{RCH}_2\text{OH}$$

$$\text{RCOONa} \xrightarrow[\text{NaOH \& CO}_2]{\text{Heat}} \text{R-H} + \text{Na}_2\text{CO}_3$$

$$\text{RCH}_2\text{COOH} \xrightarrow[\text{H}_2\text{O}]{\text{X/Red P}} \text{R-CH}_2\text{-COOH (HVZ reaction)}$$

**Aldehydes:**

- From acyl chloride
 
$$\text{R-COCl} \xrightarrow{\text{H}_2, \text{Pd-BaSO}_4} \text{R-CHO}$$
- From nitriles and esters: Stephen reaction
 
$$\text{RCN} + \text{SnCl}_2 + \text{HCl} \rightarrow \text{RCH}=\text{NH} \xrightarrow{\text{H}_3\text{O}^+} \text{R-CHO}$$
- From hydrocarbons: Etard reaction
 
$$\text{CH}(\text{OC}_2\text{H}_5)_2 \xrightarrow{\text{H}_3\text{O}^+} \text{R-CHO}$$

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{CrO}_2\text{Cl}_2 \xrightarrow{\text{CS}_2} \text{C}_6\text{H}_5\text{CHO}$$

$$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{Cl}_2/\text{hv}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{H}_2\text{O}, 373\text{K}} \text{C}_6\text{H}_5\text{CHO}$$
- Gratterman – Koch reaction
 
$$\text{C}_6\text{H}_6 \xrightarrow[\text{Anhyd. AlCl}_3]{\text{CO, HCl}} \text{C}_6\text{H}_5\text{CHO}$$

**4. Ketones:**

- From acyl chloride
 
$$2\text{R}'\text{-C-Cl} \xrightarrow{\text{O}} \text{R}'\text{-C-R}' + \text{CdCl}_2$$
- From nitriles
 
$$\text{CH}_3\text{CH}_2\text{CN} + \text{C}_6\text{H}_5\text{MgBr} \xrightarrow{\text{Ether}} \text{CH}_3\text{CH}_2\text{-C}(\text{C}_6\text{H}_5)_2 \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)\text{C}_6\text{H}_5$$
- From benzene or substituted benzenes (Friedel Crafts Acylation)
 
$$\text{C}_6\text{H}_6 + \text{Ar/R-C-Cl} \xrightarrow{\text{Anhyd. AlCl}_3} \text{C}_6\text{H}_5\text{-C(=O)-Ar/R}$$

**Carboxylic Acids:**

- From primary alcohols and aldehydes  $\text{RCH}_2\text{OH} \xrightarrow{\text{alk. KMnO}_4, \text{H}_3\text{O}^+} \text{RCOOH}$
- From alkylbenzenes
 
$$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{KMnO}_4/\text{KOH}} \text{C}_6\text{H}_5\text{COOH}$$
- From nitriles and amides  $\text{R-CN} \xrightarrow[\text{-H}_2\text{O}]{\text{H}^+/\text{OH}^-} \text{R-C(=O)-NH}_2 \xrightarrow{\Delta} \text{RCOOH}$
- From Grignard reagents  $\text{R-Mg-X} + \text{CO}_2 \rightarrow \text{R-C(=O)-OMgX} \xrightarrow{\text{H}_3\text{O}^+} \text{RCOOH}$
- From acyl halides and anhydrides
 
$$\text{ROCl} \xrightarrow[\text{OH}^-/\text{H}_2\text{O}]{\text{OH}^-} \text{RCOO}^- + \text{Cl}^- \xrightarrow{\text{H}_3\text{O}^+} \text{RCOOH}$$
- From esters
 
$$\text{C}_6\text{H}_5\text{COOCOC}_6\text{H}_5 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{COOH}$$

$$\text{C}_6\text{H}_5\text{COOCOC}_6\text{H}_5 \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{COONa} + \text{C}_6\text{H}_5\text{COOH}$$

$$\text{C}_6\text{H}_5\text{COOCOC}_6\text{H}_5 \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{COOH}$$

**Aldehydes, Ketones and Carboxylic Acids**

**Preparations**

**Nomenclature and uses**

**Properties**

**1. Aldehydes and Ketones**

**Common names:**

- Replace corresponding carboxylic acids with aldehyde.
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.

**IUPAC names:**

- Replacing -e with -al and -one as required.
- Structure of Carbonyl group

$\text{sp}^2$   $\text{C}=\text{O}$   $\text{sp}^2$

**2. Carboxylic Acids**

**Common names:** end with -oic acid

**IUPAC names:** replace -e in the corresponding alkane with -oic acid.

**Structure of Carboxyl Group**

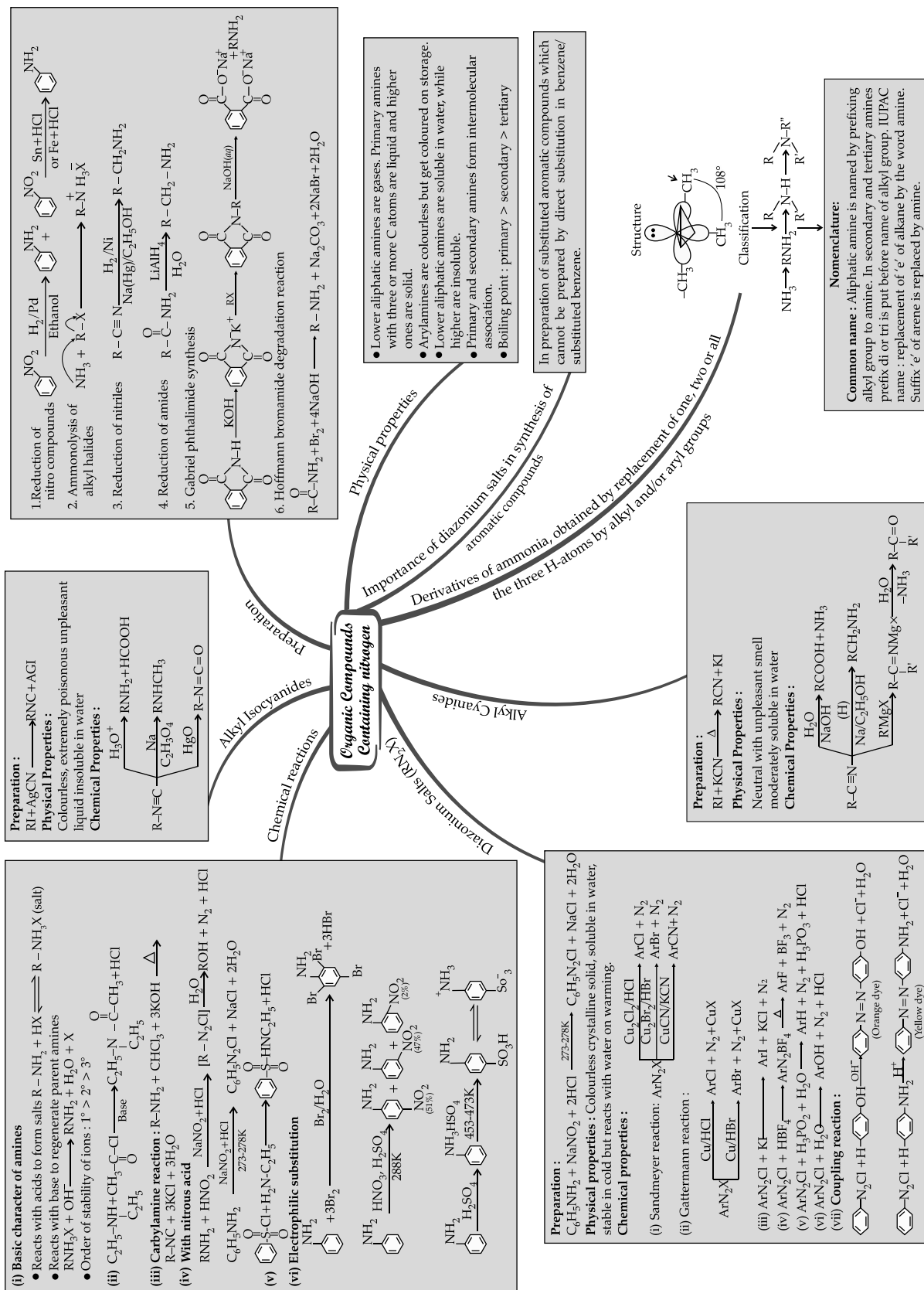
**USES**

(a) **Carboxylic acids**

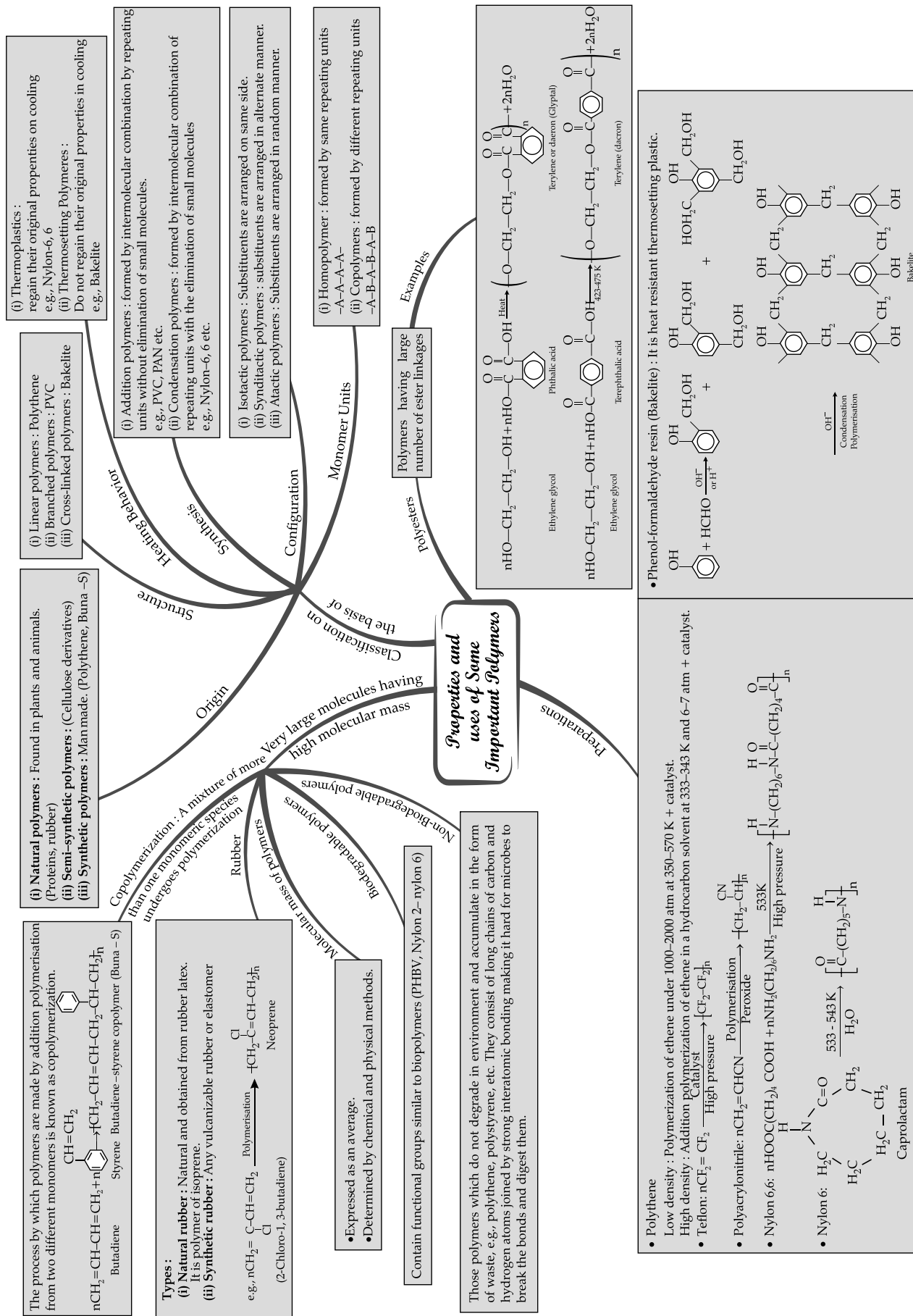
- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent
- Higher fatty acids in manufacture of soaps and detergents.

(b) **Aldehydes of ketones**

- As solvents.
- Starting materials and reagents for synthesis of products.

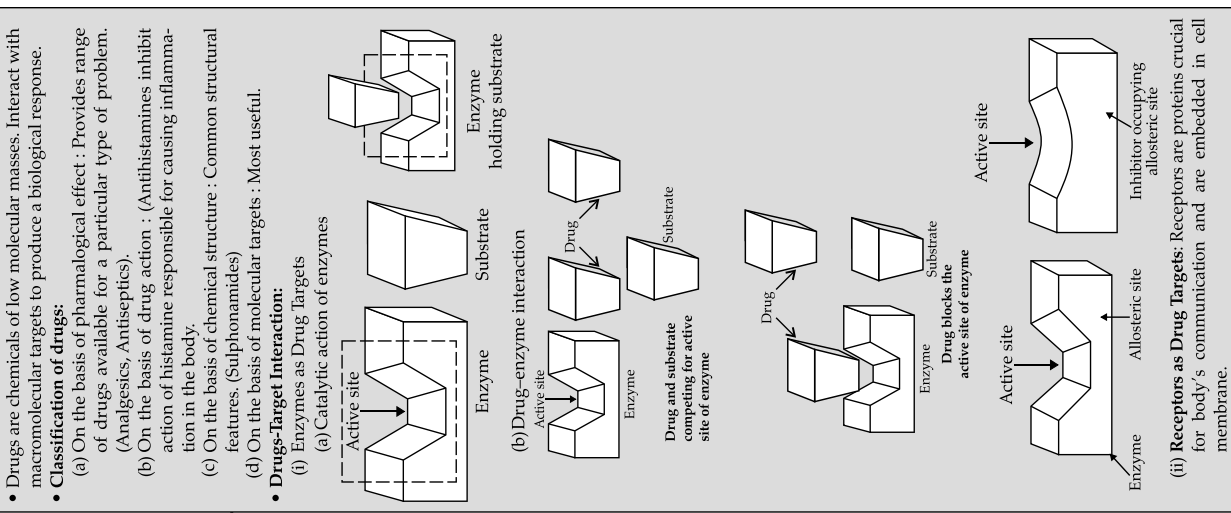












• **Antacids** : Substances that neutralize the excess HCl and raise pH in stomach (Ranitidine, Cimetidine).

• **Antihistamines** : Interfere with natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

• **Neurologically Active Drugs**

(a) **Tranquilizers** : Class of chemical compounds used for the treatment of stress and mild or even severe mental diseases. (Iproniazid, Phenelzine)

(b) **Analgesics** : Reduce/abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or other disturbances of nervous system. These are classified as:

(i) Non-narcotic (non-addictive) : (Aspirin, Paracetamol)

(ii) Narcotic : (Morphine)

• **Antimicrobials**

(a) **Antibiotics** : Drugs to treat infections because of their low toxicity for humans and animals. (Prontosil)

(b) **Antiseptics and Disinfectants** : Chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to living tissues whereas disinfectants are applied to inanimate objects.

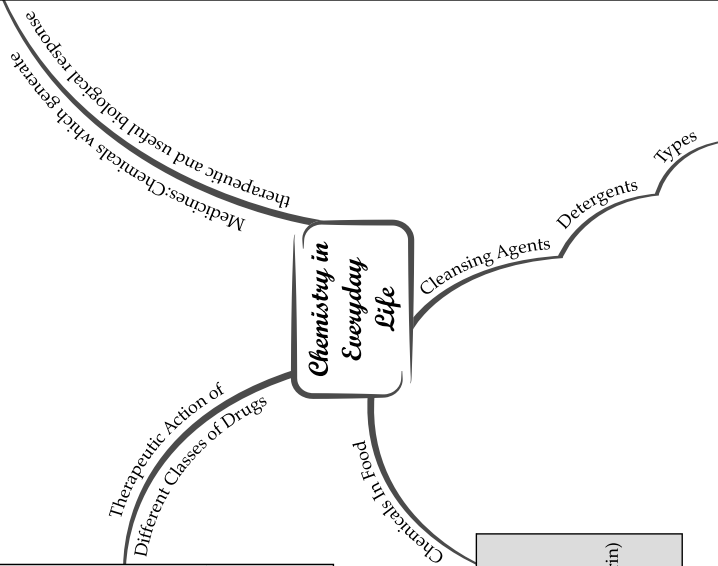
• **Antifertility Drugs** : Birth control pills. (Norethindrone, ethinyl/estradiol)

**Purpose:**

- For their preservation.
- Enhancing their appeal.
- Adding nutritive value.

(a) Artificial Sweetening Agents : Natural sweeteners (sucrose), artificial sweeteners (Aspartame, Saccharin)

(b) Food Preservatives : Prevent spoilage of food due to microbial growth. (Table salt, sugar)



(i) **Soap (Saponification)**  
Glyceryl ester + Sodium hydroxide  $\longrightarrow$  Sodium stearate + Glycerol

(ii) **Synthetic Detergents :**

- Anionic detergents : Sodium salts of sulphonated long chain alcohols or hydrocarbons. (Sodium salts of alkyl benzene sulphonates)
- Cationic detergents : Quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. (Cetyltrimethylammonium bromide)
- Non-ionic Detergents : Non-ionic type.