ALDEHYDE, KETONES AND CARBOXYLIC ACID

CARBOXYLIC ACIDS

STRUCTURE

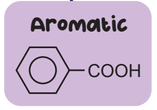
R - C(=O) - OH

USES

- Rubber, Textiles.
- Food Industry.
- Manufacture of Soap and Detergent.

CLASSIFICATION

Aliphatic CH_3COOH

Aromatic 

PREPARATIONS

- **Oxidation of 1° alcohols**

$$RCH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\text{alk. } KMnO_4} R-COOH$$

- **Hydrolysis of Nitriles and Amides**

$$R-C\equiv N + 2H_2O \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH + N_3H$$

- **Hydrolysis of Esters**

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

- **From Grignard Reagent**

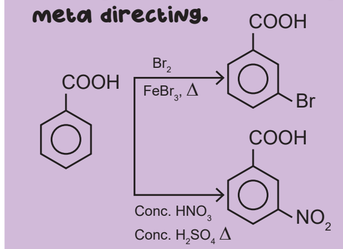
$$CO_2 + RMgBr \xrightarrow[H^+,\ H_2O]{\text{Dry ether}} RCOOH + Mg(OH)Br$$

CHEMICAL PROPERTIES

- **Esterification**

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

- **Ring Substitution in Aromatic Acids:** COOH group is deactivating and meta directing.



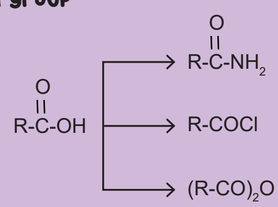
- **Reduction of Carboxylic Acid**

$$R-C(=O)-OH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/\text{ether}} R-CH_2OH$$

- **Decarboxylation of Carboxylic Acid**

$$R-C(=O)-OH \xrightarrow[CaO]{NaOH \text{ or}} R-H + Na_2CO_3$$

- **Reaction involving cleavage of -OH group**

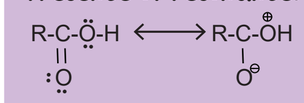


- **Hell-Volhard Zelinsky Reaction**

$$R-CH_2-OH \xrightarrow[(ii)H_2O]{(i)\ X_2,\ Red\ P} R-CH(x)COOH$$

PHYSICAL PROPERTIES

- **Physical State:** Polar substances soluble in organic solvents.
- **Acidity:** The acidic character is due to the presence of resonance.



- **Boiling Points:** High boiling point due to intermolecular hydrogen bonding.

COMPARISON OF METLING AND BOILING POINT OF AROMATIC AND ALIPHATIC ACID

- Melting Point and Boiling Point of aromatic acid greater than aliphatic acid.

ACIDIC ORDER

Caboxylic Acid > Phenol > Alcohol

ALDEHYDES AND KETONES

GENERAL FORMULA

Aldehyde: R - C(=O) - H

Where R is alkyl and H is Hydrogen.

Ketones R - C(=O) - R'

Where R and R' can be same or different.

CLASSIFICATION

Aliphatic | Aromatic

PREPARATIONS

- **Oxidation of alcohol**

$$1^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Aldehyde}$$

$$2^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Ketone}$$

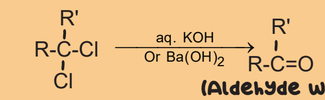
$$R\ CH_2OH \xrightarrow{K_2Cr_2O_7 + H_2SO_4} RCHO\ H_2O$$

$$R-\underset{2^\circ \text{ alcohol}}{CH(OH)R'} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} R-CO-R' + H_2O$$

- **Ozonolysis of alkenes**

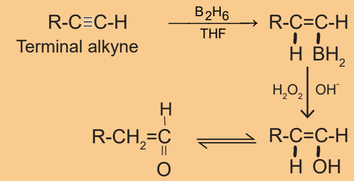
$$CH_3-CH=CH-CH_3 + O_3 \xrightarrow{H_2O,\ Zn} 2CH_3CHO$$

- **From Gem-Dihalides:**



(Aldehyde when R' = H
Ketone when R' = alkyl group)

- **Hydroboration Oxidation of Alkynes**



- **Rosenmund Reduction**

$$R-C(=O)-Cl \xrightarrow{H_2,\ Pd\text{-}BaSO_4} R-C(=O)-H$$

DISTINCTION TEST FOR CARBOXYLIC ACID

- Brisk effervescence of CO_2 gas with $NaHCO_3$
- Gives buff coloured ppt. with $FeCl_3$

PHYSICAL PROPERTIES

Odour: Lower Aldehyde have an impleasant odour.

Physical State: HCHO is a gas. All other aldehyde and ketone upto C_{11} are volatile liquids.

Solubility: Larger Carbonyl compounds are soluble in water due to the formation of H-bond.

Boiling Point and Melting Point: Boiling Point or Melting Point $\propto$ Molecular weight $\propto \frac{1}{\text{Branching}}$

Due to electron donating alkyl group ketones have higher boiling point than aldehye.

Reactivity: It depends on the nature of alkyl group. Smaller the group, more reactive will be compound.

DISTINCTION TEST FOR ALDEHYDE

TEST	ALDEHYDE	KETONES
Schiff's reagent	Pink Colour	No colour
Fehling's Solution	Red ppt.	No ppt.
Tollen's reagent	Silver Mirror	No ppt.

CHEMICAL PROPERTIES

Aldehyde > Ketones

Reactivity $\propto \frac{1}{\text{Steario factor and electronic factror}}$

Nucleophilic Addition-reaction

$$>C=O + CN^- \rightleftharpoons >C(OH)(CN)$$

$$>C=O + NaHSO_3 \longrightarrow >C(OH)(SO_2Na)$$

$$>C=O + H_2N-Z \longrightarrow >C=N-z + H_2O$$

Clemmensen Reduction:

$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

Wolff-kishner reduction

$$>C=O \xrightarrow[KOH/\text{ethyl glycol}]{(i)\ NH_2-NH_2} >CH_2 + N_2$$

Aldol Condensation

$$2CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO \xrightarrow{\Delta - H_2O} CH_3-CH=CH-CHO$$

Cannizaro reaction

$$2HCHO \xrightarrow{\text{Conc. KOH}} CH_3OH + HCOOK$$