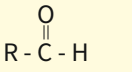
9. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

ALDEHYDES AND KETONES

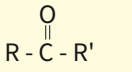
GENERAL FORMULA

Aldehyde



where R is alkyl group

Ketones



where R and R' can be same or different.

CLASSIFICATION

- **Aliphatic**
- **Aromatic**

PREPARATIONS

✦Oxidation of alcohol

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

$R{-}CH_2OH \xrightarrow{K_2Cr_2O_7 + H_2SO_4} R{-}CHO + H_2O$

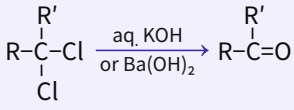
$2° \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Ketone}$

$R{-}CH(OH)R' \xrightarrow{K_2Cr_2O_7 + H_2SO_4} R{-}CO{-}R' + H_2O$

✦Ozonolysis of alkenes

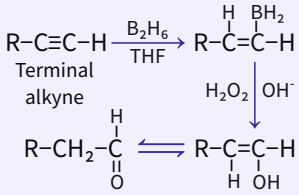
$CH_3{-}CH{=}CH{-}CH_3 + O_3 \xrightarrow{H_2O,\ Zn} 2CH_3CHO$

✦From Gem-Dihalides

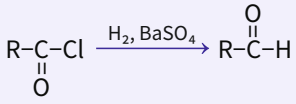


(Aldehyde when R' = H
Ketone when R' = alkyl group)

✦Hydroboration Oxidation of Alkynes



✦Rosenmund Reduction



PHYSICAL PROPERTIES

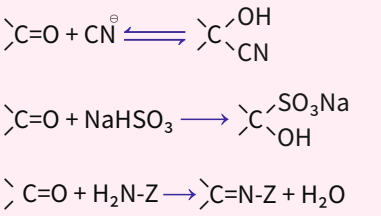
- **Odour:** Lower Aldehyde have an unpleasant odour.
- **Physical State:** HCHO is a gas. All other aldehyde and ketone upto C_{11} are volatile liquids.
- **Solubility:** Larger Carbonyl compounds are soluble in water due to the formation of H-bond.
- **Boiling Point and Melting Point:** Boiling/Melting point ∝ Molecular weight
- 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.

CHEMICAL PROPERTIES

Aldehyde > Ketones

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

✦Nucleophilic Addition-reaction



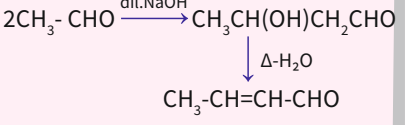
✦Clemmensen Reduction

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

✦Wolf-kishner reduction

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

✦Aldol Condensation



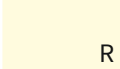
✦Cannizaro reaction

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

DISTINCTION TEST

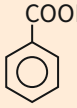
TEST	ALDEHYDES	KETONES
Schiff's reagent	Pink Colour	No colour
Fehling's solution	Red ppt.	No ppt.
Tollen's reagent	Silver Mirror	No ppt.

CARBOXYLIC ACIDS



CLASSIFICATION

Aliphatic CH_3COOH **Aromatic** COOH



PREPARATIONS

✦ **Oxidation of primary alcohols**

$$RCH_2OH \xrightarrow[2)\ H_3O+]{1)\ alk.\ KMnO_4} R{-}COOH$$

✦ **Hydrolysis of Esters**

$$RCOOR' + H_2O \xrightarrow{H+} R{-}COOH + R'OH$$

✦ **Hydrolysis of Nitriles and Amides**

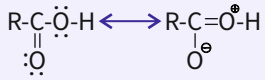
$$R{-}C{\equiv}N + H_2O \xrightarrow[or\ OH^-]{H+} R{-}COOH + NH_3$$

✦ **From Grignard Reagent**

$$CO_2 + RMgBr \xrightarrow[H+,\ H_2O]{Dry\ ether} R{-}COOH + Mg(OH)Br$$

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

ACIDIC ORDER

Caboxylic Acid > Phenol > Alcohol

DISTINCTION TEST FOR CARBOXYLIC ACID

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

USES

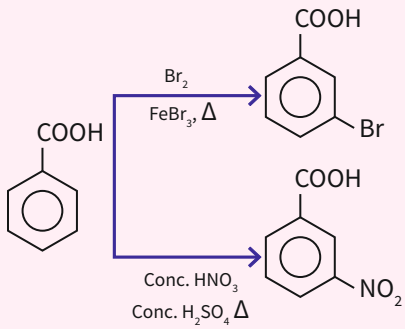
- ✦ Rubber, textiles.
- ✦ Food industry.
- ✦ Manufacture of soap and detergent.

CHEMICAL PROPERTIES

✦ **Esterification**

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

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



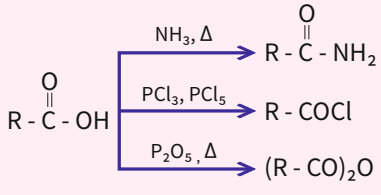
✦ **Reduction of Carboxylic Acid**

$$R{-}COOH \xrightarrow[2)\ H_3O+]{1)\ LiAlH_4/\ ether} R{-}CH_2OH$$

✦ **Decarboxylation of Carboxylic Acid**

$$R{-}COOH \xrightarrow[CaO]{NaOH} R{-}H + Na_2CO_3$$

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



✦ **Hell-volhard Zelinsky Reaction**

$$RCH_2COOH \xrightarrow[2)\ H_2O]{1)\ X_2,\ Red\ P} R{-}CH(X)COOH$$