Textbook Chapter No.

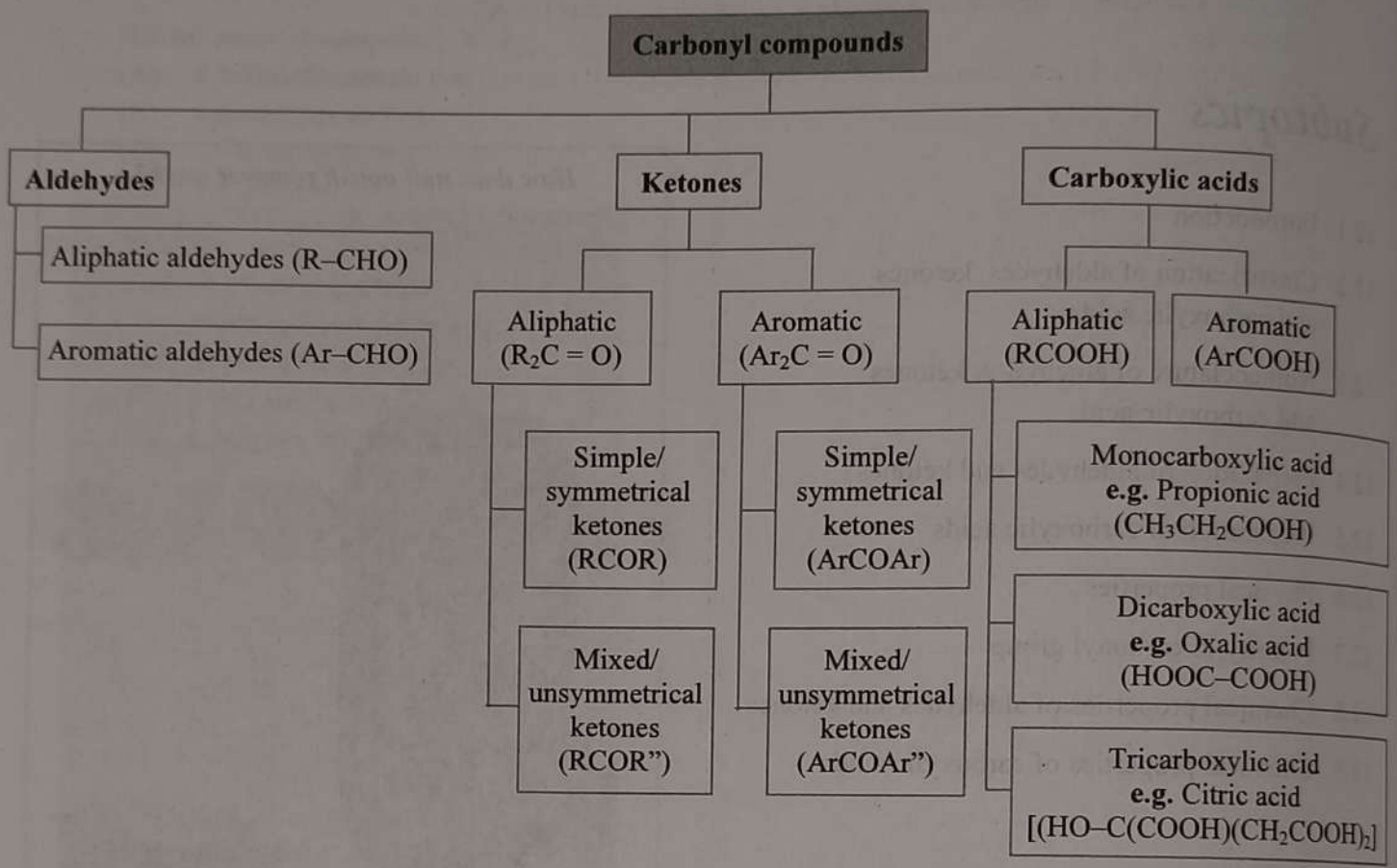
12 Aldehydes, Ketones and Carboxylic Acids

Subtopics

How does nail polish remover work?

Actually, there is no chemical reaction in the working of a nail polish remover. The process works on the principle of like dissolves like. The nail polish remover is just the organic solvent that is used as an ingredient in the nail polish. The hardened organic nail polish is dissolved by the nail polish remover (which is also organic). Generally, the remover contains acetone.

➢ **Classification of aldehydes, ketones and carboxylic acids:**



➢ **IUPAC nomenclature:**

Functional group	Types	IUPAC system (Basic rules)	Examples
Aldehydes	Aliphatic compounds	Parent name: Alkane → Alkanal Prefix – Formyl	Hexanal, 3-Formylhexanoic acid
	Alicyclic compounds	Parent name: Cycloalkanecarbaldehyde	Cyclohexanecarbaldehyde
	Aromatic compounds	Suffix – Benzaldehyde (one –CHO group) Prefix – Formyl	3-Methylbenzaldehyde, 4-Formylbenzoic acid
Ketones	Aliphatic compounds	Parent name: Alkane → Alkanone Prefix – Oxo	Hexan-2-one, 3-Oxobutanal
	Alicyclic compounds	Parent name: Cycloalkanone	4-Methylcyclohexanone
	Aromatic compounds	Suffix – phenone	Benzophenone
Carboxylic acids	Aliphatic compounds	Parent name: Alkane → Alkanoic acid	Hexanoic acid
	Alicyclic compounds	Parent name: Cycloalkanecarboxylic acid	Cyclohexanecarboxylic acid
	Aromatic compounds	Suffix – Benzoic acid (one –COOH group)	2-Hydroxybenzoic acid

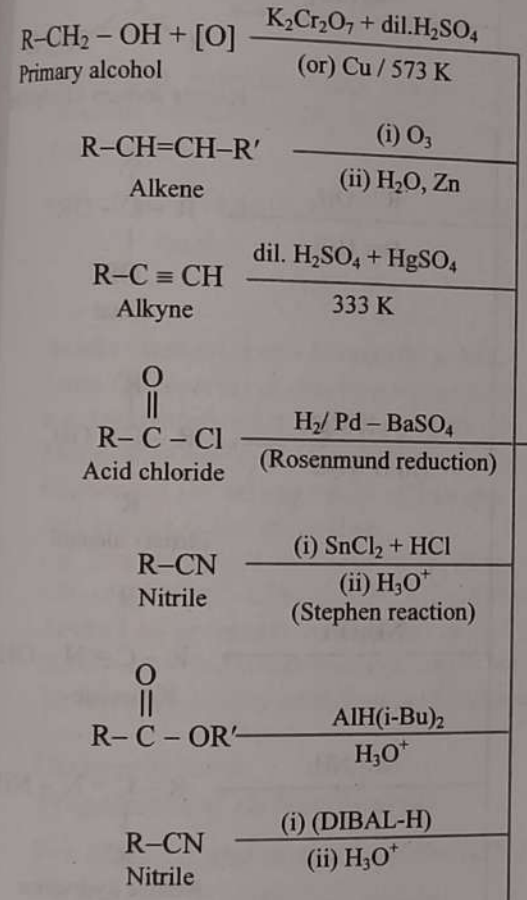
Physical properties of aldehydes, ketones and carboxylic acids:

- Boiling point in homologous series of aldehydes, ketones and carboxylic acids:
- Boiling point increases as the number of carbon atom increases.
- Order of boiling points of aldehydes, ketones and carboxylic acids with other functional groups:
- **Carboxylic acids > Alcohols > Ketones > Aldehydes > Ethers > Alkanes**
- **Solubility:**
- Solubility of aldehydes, ketones and carboxylic acids in water decreases with increase in molecular mass.

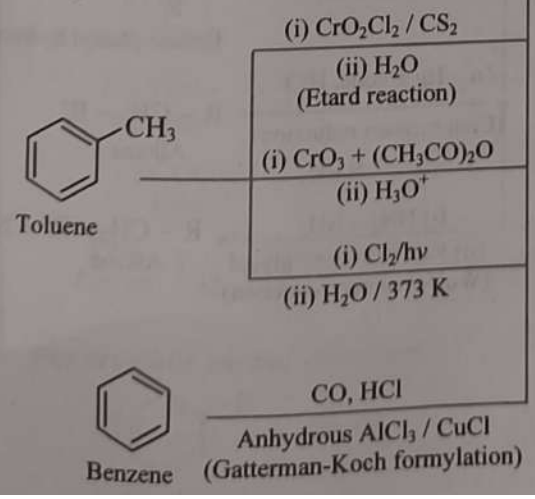
Aldehydes:

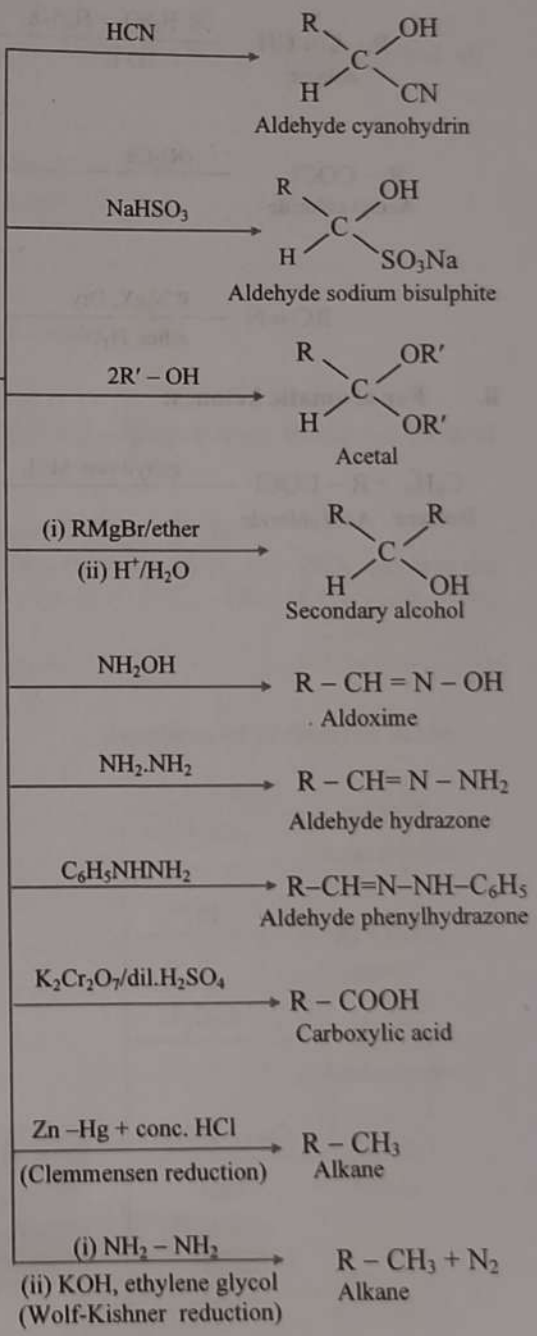
Preparation of Aldehydes:

i. **For aliphatic and aromatic aldehydes:**



ii. **For aromatic aldehydes:**

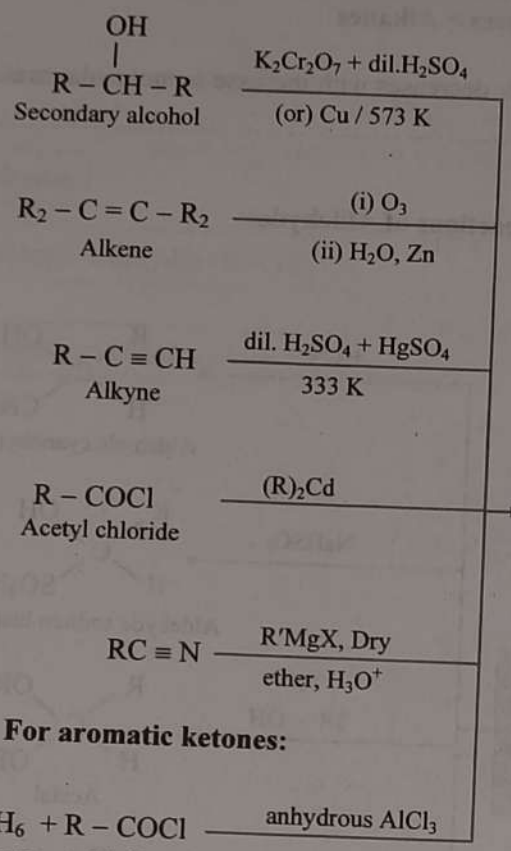




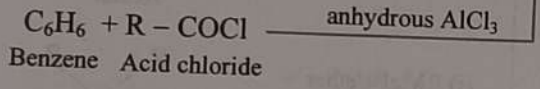
Ketones:

Preparation of ketones:

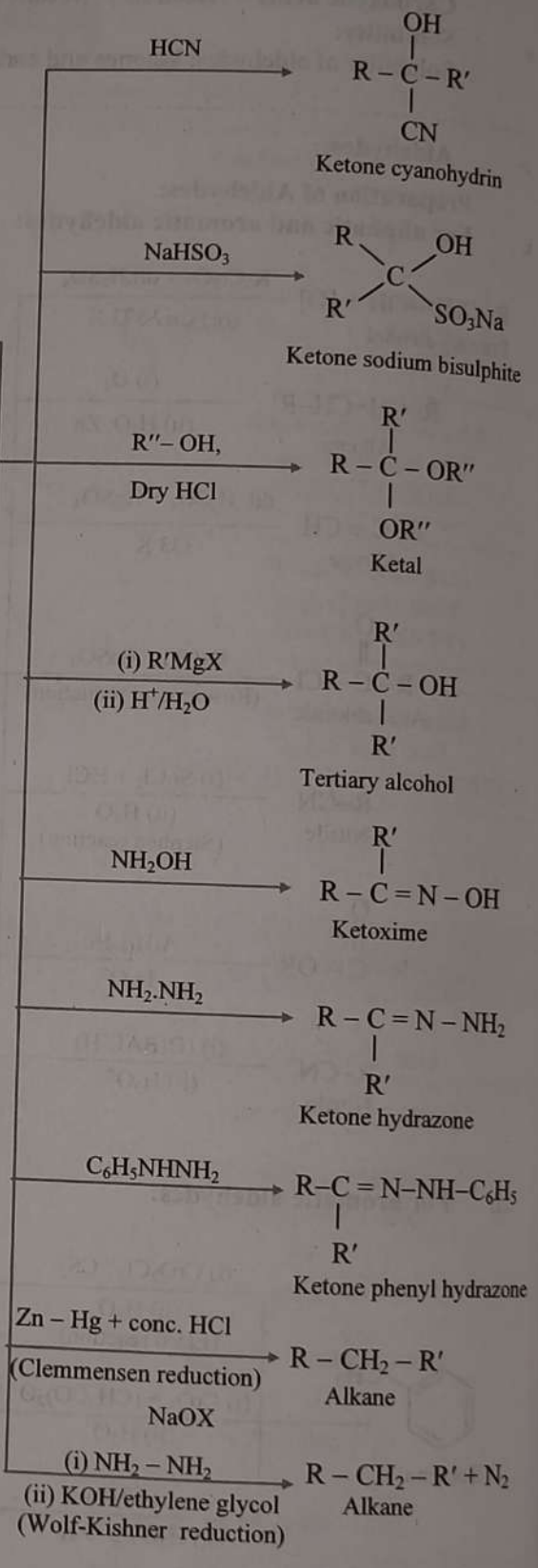
i. For aliphatic and aromatic ketones:



ii. For aromatic ketones:



Reactions of ketones:



Other reactions of aldehydes and ketones:

Aldol condensation: Aldehydes containing at least one α–hydrogen atom undergo aldol condensation.

$$2R-CH_2-CHO \xrightarrow{\text{aq. NaOH}} \underset{\text{Aldol}}{R-CH_2-\underset{OH}{\underset{|}{CH}}-CHR-CHO} \xrightarrow[\text{warm}]{-H_2O} \underset{\alpha,\beta\text{-Unsaturated aldehyde}}{R-CH=CR-CHO}$$

Aldehyde

Ketones containing at least two α-hydrogen also undergo aldol condensation reaction and give an α,β-unsaturated ketone.

Cannizzaro reaction: This reaction is given only by aldehydes having **no α-hydrogen atom**.

e.g.

$$\underset{\text{Formaldehyde}}{2H-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{Sodium hydroxide (50\%)}}{NaOH} \xrightarrow{\Delta} \underset{\text{Sodium formate}}{H-\overset{O}{\overset{\|}{C}}-O^-Na^+} + \underset{\text{Methanol}}{H-\underset{H}{\underset{|}{C}}-OH}$$

Haloform reaction: This reaction is given by acetaldehyde, all methyl ketones (CH_3–CO–R) and all alcohols containing $CH_3(CHOH)$– group.

e.g.

$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + \underset{\text{Sodium hypoiodite}}{3NaOI} \xrightarrow[\Delta]{NaOH/I_2} \underset{\text{Sodium acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+} + \underset{\text{Iodoform}}{CHI_3\downarrow} + 2NaOH$$

Acidic character of carboxylic acids:

- More the number of electron withdrawing substituents, higher is the acid strength.
  e.g. Increasing order of acid strength is:
  Monochloroacetic acid < Dichloroacetic acid < Trichloroacetic acid.
- Higher the electronegativity of halogen, greater is the stabilization of the conjugate base, stronger is the acid and smaller is the pK_a value.
  e.g. Increasing order of acid strength for haloacetic acids is:
  CH_3–COOH < I–CH_2–COOH < Br–CH_2–COOH < Cl–CH_2–COOH < F–CH_2–COOH
- **Acidity of aromatic carboxylic acids:** Electron withdrawing groups like –Cl, –CN, and $-NO_2$ increase the acidity of substituted benzoic acids while electron donating groups like $-CH_3$, –OH, $-OCH_3$ and $-NH_2$ decrease the acidity of substituted benzoic acids.

Carboxylic acids:

Preparation of carboxylic acids:

i. For aliphatic and aromatic carboxylic acids:

- $R-C\equiv N$ (Alkyl cyanide) $\xrightarrow[H_2O/\Delta]{H^+ \text{ or } OH^-}$ $R-CONH_2$ (Amide) $\xrightarrow{H^+}$ (Heat)
- $RCOCl$ (Acid chloride) $\xrightarrow{H_2O}$
- $R(CO)_2O$ (Anydride) $\xrightarrow{H_2O}$
- $RCOOR'$ (Ester) $\xrightarrow{H^+ \text{ or } OH^-, H_2O}$
- CO_2 (Dry ice) + $RMgX$ (Alkyl magnesium halide) $\xrightarrow[(ii)\ H_3O^+]{(i)\text{ dry ether}}$

ii. For aromatic carboxylic acids:

Alkylbenzene $\xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4 - KOH/\Delta}$

All of the above → **RCOOH**
Carboxylic acid
where, R is Alkyl or aryl group

Reactions of carboxylic acids:

- $\xrightarrow{PCl_3 \text{ (or) } PCl_5 \text{ (or) } SOCl_2}$ RCOCl (Acid chloride)
- $\xrightarrow{NH_3}$ $RCONH_2$ (Amide)
- $\xrightarrow{P_2O_5/\Delta}$ $(RCO)_2O$ (Acid anhydride)
- $\xrightarrow[\text{Heat}]{NaOH + CaO}$ R – R (Alkane)
- $\xrightarrow{(i)\ LiAlH_4/\text{ether}}$ $R-CH_2-OH$ (Alcohol)
- $\xrightarrow[\text{Conc. } H_2SO_4/413K]{ROH,}$ $R-COOR'$ (Ester)

➢ **Laboratory test for carbonyl group:**

Functional group	Test	Observation + Conclusion
Aldehydic group (– C(=O) – H)	Schiff's test	Pink/red/magenta colour: presence of –CHO group
	Tollens' test/Silver mirror test	Silver mirror (Ag): presence of –CHO group
	Fehling test	Red ppt of Cu_2O: presence of –CHO group Used to distinguish aliphatic aldehydes from aromatic aldehydes and ketones
Ketonic group (>C = O)	Sodium nitroprusside test	Red colouration: Presence of > C = O group
Carboxyl group (–COOH)	Litmus test	Turns blue litmus red: Presence of –COOH or phenolic –OH group
	Sodium bicarbonate	Brisk effervescence of $CO_{2(g)}$: Presence of –COOH group (used to distinguish phenolic –OH group from –COOH group)
	Ester test	Fruity smell of ester: Confirmatory test for –COOH group.