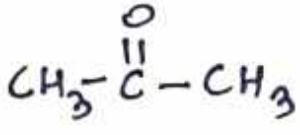
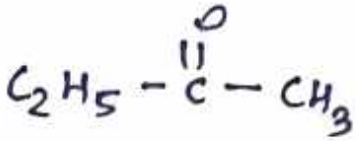
Nomenclature of Ketone

✱ Common Name :

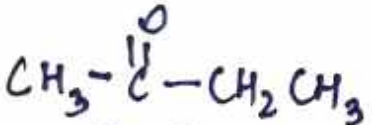


Dimethyl Ketone
(acetone)

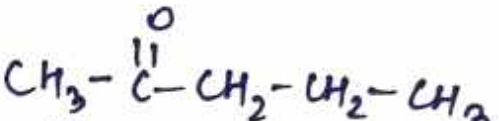


Ethyl methyl Ketone

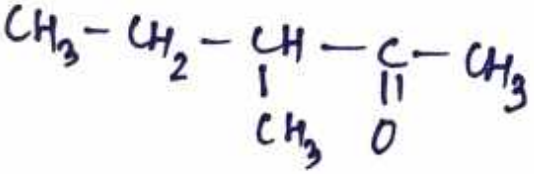
✱ IUPAC Name :



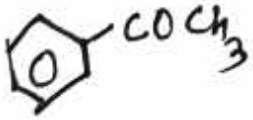
Butanone



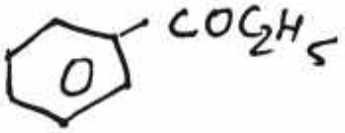
Pent-2-one



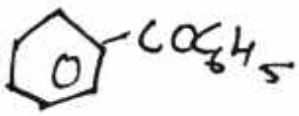
✱ Aromatic Ketones :-



Acetophenone
(Methylphenyl Ketone)



Ethylphenyl
Ketone



Diphenyl
Ketone.

Preparation of Aldehydes & Ketones

① From acid Chloride :-

ⓐ Preparation of aldehydes – (Rosenmund's Reaction) –

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd\text{-}BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd\text{-}BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl.$$

Ethanoyl chloride. — Ethanal.

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd\text{-}BaSO_4} (?)$$

Mechanism :-

It involves hydrogenation of carbonyl group followed by the elimination of HCl.

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{catalyst}]{Pd\text{-}BaSO_4} R-\underset{H}{\overset{\overset{\ddot{O}-H}{|}}{C}}-Cl \xrightarrow{-Cl^{\ominus}} R-\overset{\overset{\oplus}{O}-H}{\overset{\|}{C}}-H \xrightarrow{-H^{\oplus}} R-\overset{O}{\overset{\|}{C}}-H$$

Aldehyde.

Imp. Point → Formaldehyde ($H-\overset{O}{\overset{\|}{C}}-H$) can not be prepared.

⇒ Ketones also can not be prepared by this method.

$$+ H_2 \xrightarrow[\text{'S'}]{Pd\text{-}BaSO_4}$$

Benzoyl Chloride. — Benzaldehyde + HCl

⊛ Preparation of Ketones from acid chloride :-

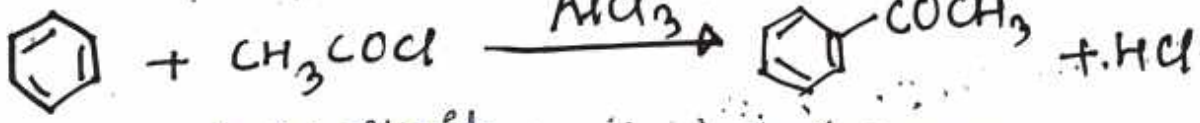
$$2\ R-\overset{O}{\overset{\|}{C}}-Cl + R_2Cd \xrightarrow{\text{Dry ether}} 2\ R-\overset{O}{\overset{\|}{C}}-R + CdCl_2$$

R_2Cd : Organometallic compound

Ketone

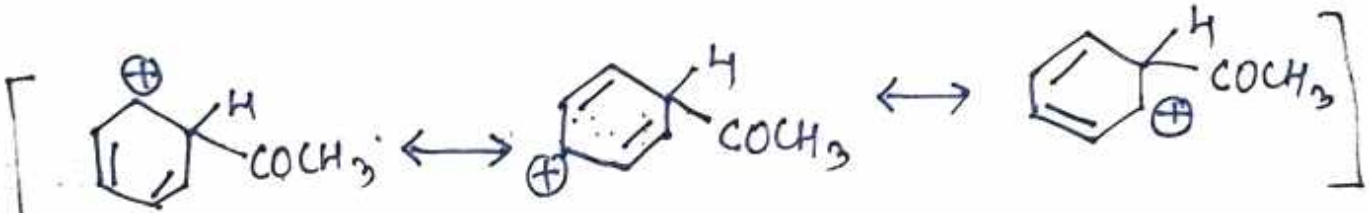
$$2\ CH_3COCl + (C_2H_5)_2Cd \xrightarrow[\text{Ether}]{\text{Dry}} ?$$

Preparation of acetophenone → Friedel – Craft Reaction

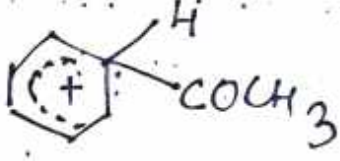


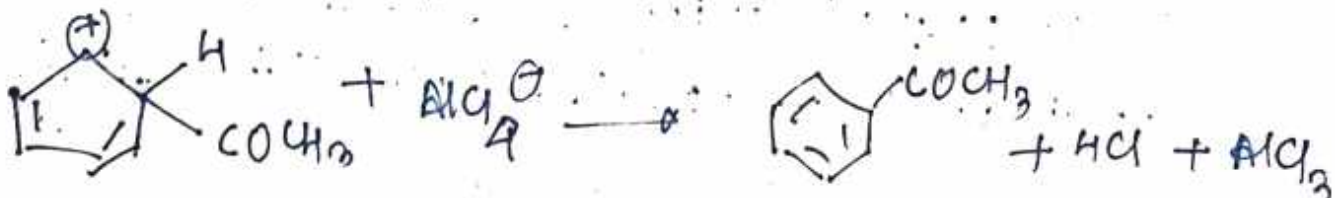
Benzene Acetyl chloride Acetophenone

Mechanism :-



Contributing structures III





(#) From Nitriles (Using Organometallics)–

⇒ (a) Aldehydes can be prepared by the reduction of alkyl/acyl cyanides with stannous chloride and HCl in ethyl/ethyl formate/ethyl acetate solution. This is called Stephen's method.

$$CH_3C\equiv N + 2H \xrightarrow{Sn/HCl} CH_3CH=NH$$

$$CH_3-C(=NH)-H + H_2O \longrightarrow CH_3-C(=O)-H + NH_3 .$$

⇒ (b) Kerones can be prepared by treating alkyl cyanide with Grignard's reagent followed by hydrolysis.

$$R'MgX + R-C\equiv N \longrightarrow R-C(R')=NMgX \xrightarrow{H_3O^{\oplus}} R-C(R')=O$$

Kerone.

$CH_3MgBr + CH_3C\equiv N \longrightarrow$ complete.

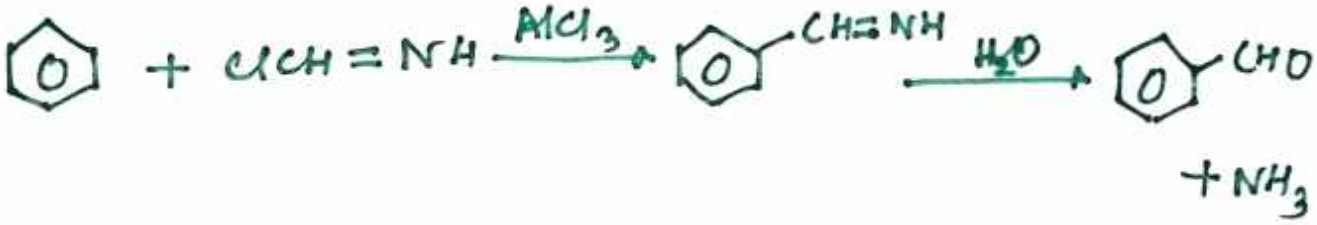
(c) Aldehydes can also be prepared from nitriles. The reaction involves reduction of nitriles by di-isobutyl aluminium hydride (DIBAL-H) to form imines followed by hydrolysis to produce aldehydes.

$$R-C\equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} R-CH=O$$

⊛ Preparation of Aldehyde by Gattermann Reaction :-

When benzene is heated with ClCH=NH in the presence of $AlCl_3$, an intermediate is formed ($C_6H_5CH=NH$) which on hydrolysis gives benzaldehyde.

$$HC\equiv N + HCl \xrightarrow{AlCl_3} ClCH=NH$$



Properties of Aldehydes & Ketones

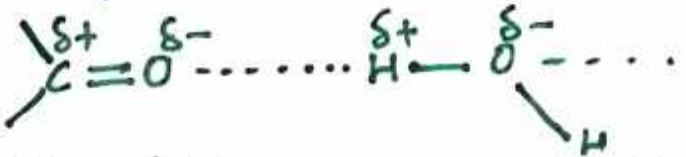
⊛ Physical Properties :

⇒ Formaldehyde → gaseous, Others to C_9 → liquid

$> C_9$ → solids.

⇒ Ketones upto C_{11} → colourless liquid, higher → solids.

⇒ Solubility :- Lower members in the aldehydes and ketones series are soluble in water. This is because of H-bonding with H_2O molecule as shown below -



But, solubility falls rapidly with increase in the size of alkyl group.

⇒ Boiling points :- Aldehydes & Ketones have higher b.pt. than non-polar compounds of comparable mol. mass. But, b.pt. of aldehydes & ketones are lower than those of alcohols and carboxylic acids.