Points to remember in Aldehyde & ketone

Aldol condensation:

Carbonyl compounds having acidic sp 3 α -H shows this reaction in presence of dil. NaOH or dil. acid.

$$2CH_3-C=O \xrightarrow[NaOH]{Dil} CH_3-C-CH_2-CHO \xrightarrow[-H_2O]{H^+,\,\Delta} CH_3CH=CHCHO$$

Crossed aldol condensation

(i)
$$CH_3CHO + HCHO \xrightarrow{Dil. NaOH} HOCH_2 - CH_2 - CHO \xrightarrow{H^+ / H_2O} CH_2 = CH - CHO$$

(ii)
$$CH_3COCH_3 + HCHO \xrightarrow{Dil. NaOH} CH_3CO-CH_2CH_2OH \xrightarrow{H^+ / H_2O} \Delta$$

 $CH_3CO-CH=CH_2$

Cannizzaro reaction:

Carbonyl compounds not having $sp^3\alpha$ -H shows following disproportion reaction

O | |
$$2H-C-H + NaOH \longrightarrow CH_3-OH + HCOONa$$
 | (50%) | $2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$ | (50%)

Crossed Cannizzaro reaction:

$$CH_3O - \bigcirc CHO + HCHO + NaOH \longrightarrow CH_3O - \bigcirc CH_2OH + HCOONa$$

Formation of hydrzones and azines

$$C = O + NH_2NH_2 \longrightarrow OH \longrightarrow C = NNH_2 \longrightarrow C = N-N = C$$

Perkin reaction:

When benzaldehyde (or any other aromatic aldehyde) is heated with the

anhydride of an aliphatic acid (containing two α -hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β -arylacrylic acid; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$$\begin{array}{c} C_{6}H_{5}CHO+(CH_{3}CO)_{2}O \xrightarrow{CH_{3}CO_{2}Na} C_{6}H_{5}CH=CHCO_{2}H \\ \textbf{Mechanism}: \\ \\ CH_{3}COOCOCH_{3}+CH_{3}CO_{2}^{-} & \stackrel{-}{\longrightarrow} \overset{-}{C}H_{2}COOCOCH_{3}+CH_{3}CO_{2}H \\ \\ C_{6}H_{5}\overset{-}{C}+\overset{-}{C}H_{2}COOCOCH_{3} & \stackrel{-}{\longleftarrow} C_{6}H_{5}\overset{-}{C}CH_{2}COOCOCH_{3} & \stackrel{+}{\longleftarrow} \\ H & OH \\ \\ C_{6}H_{5}\overset{-}{C}CH_{2}COOCOCH_{3} & \stackrel{-}{\longleftarrow} C_{6}H_{5}CH=CHCOOCOCH_{3} & \stackrel{+}{\longleftarrow} \\ \\ C_{6}H_{5}\overset{-}{C}CH_{2}COOCOCH_{3} & \stackrel{-}{\longleftarrow} C_{6}H_{5}CH=CHCOOCOCH_{3} & \stackrel{+}{\longleftarrow} \\ \\ C_{6}H_{5}CCH_{2}COOCOCH_{3} & \stackrel{-}{\longleftarrow} C_{6}H_{5}CH=CHCOOCOCH_{3} & \stackrel{+}{\longleftarrow} C_{6}H_{5}CH=CHCOOCOCH_{3} & \stackrel{+}{\longleftarrow} C_{6}H_{5}CH=CHCO_{2}H+CH_{3}CO_{2}H \\ \end{array}$$

Haloform reaction:

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of alkali to give haloform and acid salt.

$$\begin{array}{ccc}
O & O \\
\parallel & \parallel & \parallel \\
R - C - CH_3 & \xrightarrow{Br_2 / NaOH} & R - C - ONa + CHBr_3
\end{array}$$
(Bromoform)

O \parallel In this reaction – CH_3 of CH_3 – C – group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

Preparation of haloform from methylketone involves two steps.

(a) Halogenation

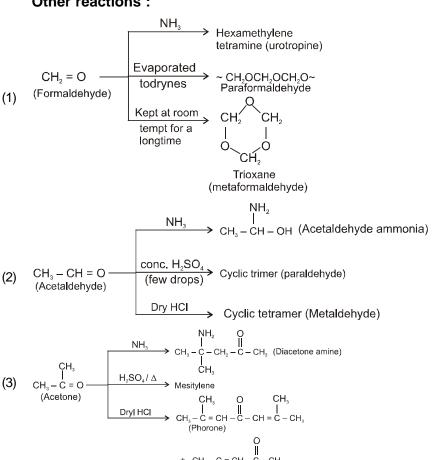
$$\begin{array}{cccc}
O & O \\
\parallel & \parallel \\
R-C-CH_3 & \xrightarrow{Br_2} & R-C-CBr_3
\end{array}$$
(Halogenation)

(b) Alkalihydrolysis

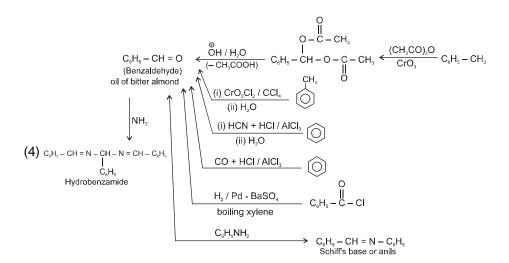
O
$$\parallel$$
 $R-C-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-C-ONa (Alkalihydrolysis)$

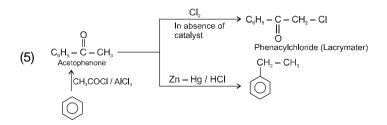
Note : This reaction is used to distinguish the presence of $CH_3 - C - group$.

Other reactions:



(Mesityloxide)





(6)
$$C_{e}H_{s} - C - C_{e}H_{s}$$
(Benzophenone)
$$C_{e}H_{s}COCI / AICI_{s}$$

$$CocI_{z} / AICI_{s}$$
excess