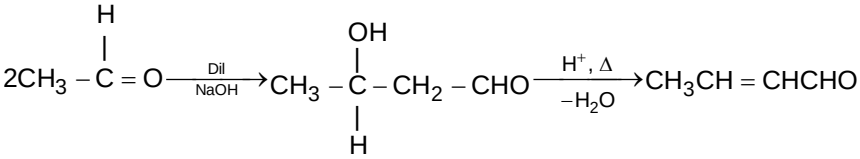
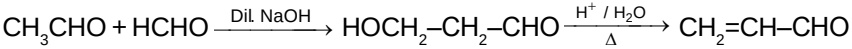
• Points to remember in Aldehyde & ketone

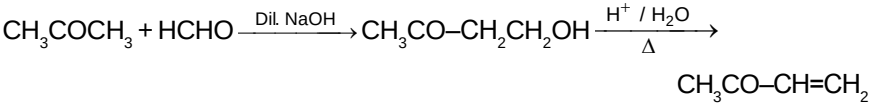
Aldol condensation :

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



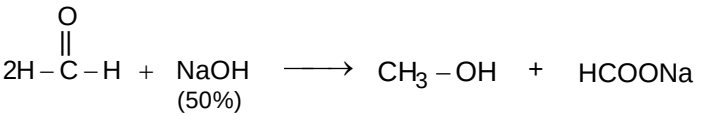
Crossed aldol condensation

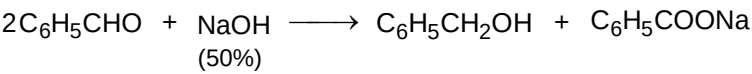
(i) 

(ii) 

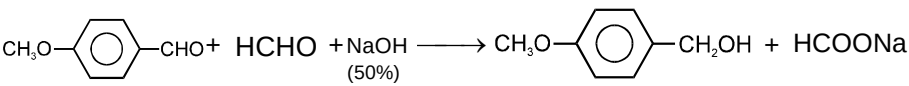
Cannizzaro reaction :

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

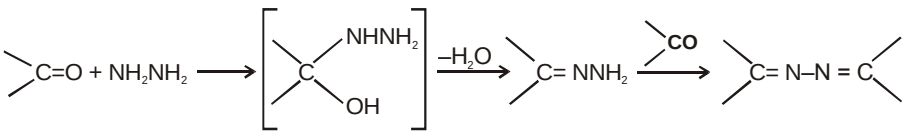




Crossed Cannizzaro reaction :



Formation of hydrzones and azines



Perkin reaction :

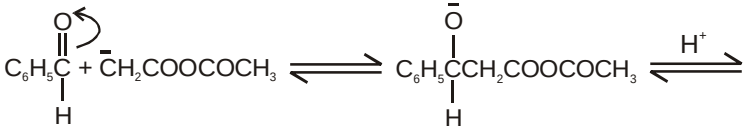
When benzaldehyde (or any other aromatic aldehyde) is heated with the

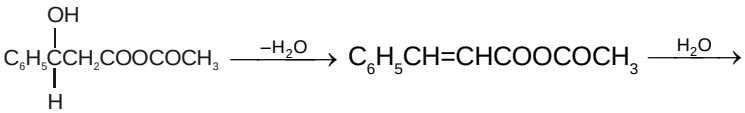
anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH = CHCO_2H$$

Mechanism :

$$CH_3COOCOCH_3 + CH_3CO_2^- \rightleftharpoons \bar{C}H_2COOCOCH_3 + CH_3CO_2H$$

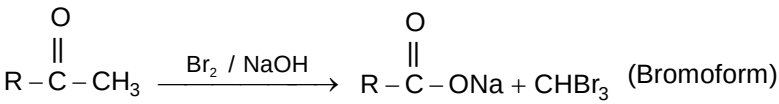




$$C_6H_5CH=CHCOOCOCH_3 \xrightarrow{H_2O} C_6H_5CH = CHCO_2H + CH_3CO_2H$$

Haloform reaction :

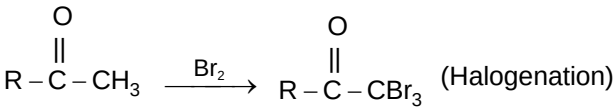
Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2, Br_2 or I_2) in the presence of alkali to give haloform and acid salt.



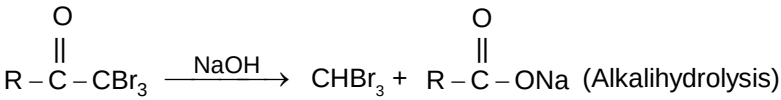
In this reaction – CH_3 of $CH_3-\overset{O}{\overset{\|}{C}}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

Preparation of haloform from methylketone involves two steps.

(a) Halogenation



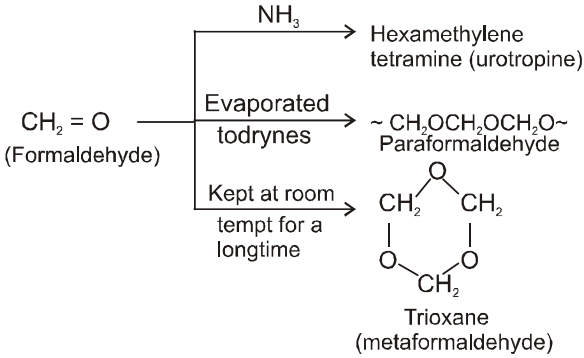
(b) Alkalihydrolysis



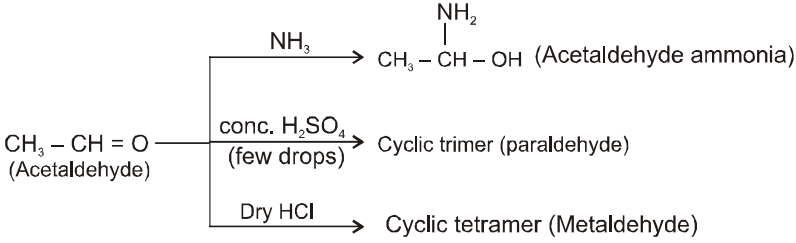
Note : This reaction is used to distinguish the presence of $CH_3 - \overset{O}{\overset{\|}{C}} -$ group.

Other reactions :

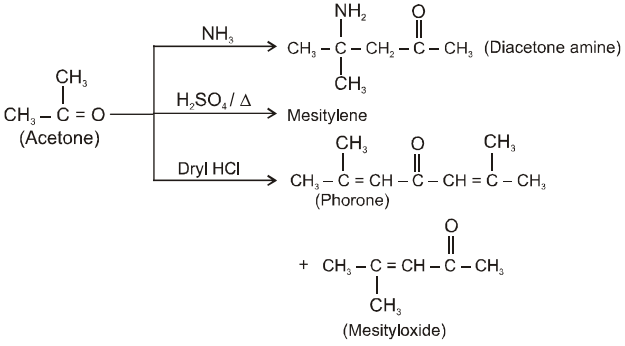
(1)

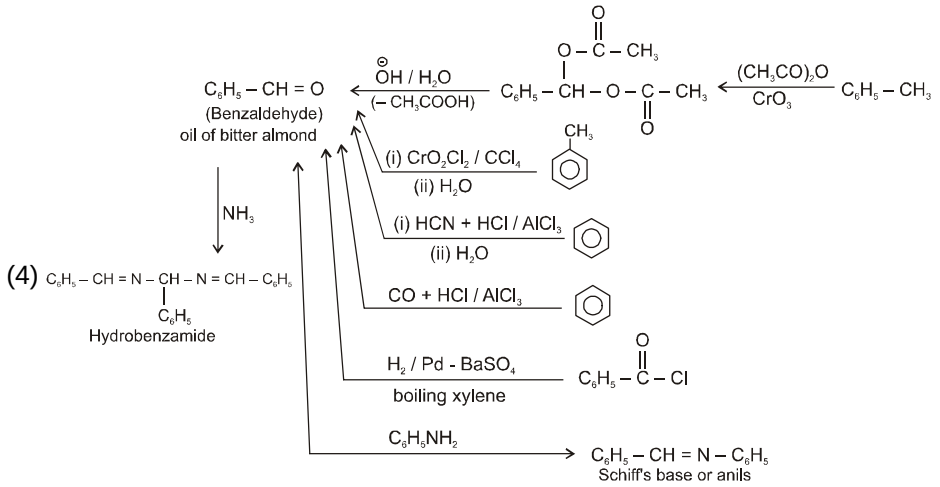


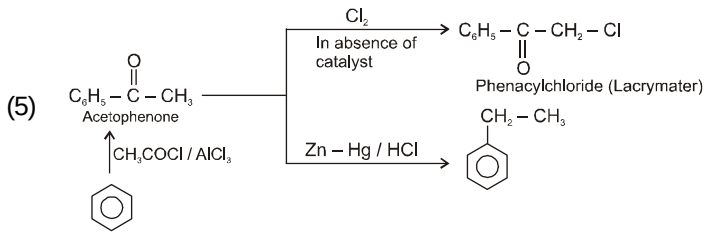
(2)

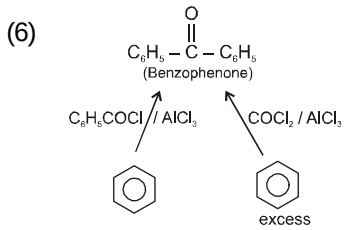


(3)




(4)
$C_6H_5 - CH = O$
(Benzaldehyde)
oil of bitter almond
$\overset{\ominus}{O}H / H_2O$
$(- CH_3COOH)$
$C_6H_5 - CH(O - C(=O) - CH_3) - CH_3$
$(CH_3CO)_2O$
CrO_3
$C_6H_5 - CH_3$
NH_3
$C_6H_5 - CH = N - CH(C_6H_5) - N = CH - C_6H_5$
Hydrobenzamide
(i) CrO_2Cl_2 / CCl_4
(ii) H_2O
(i) HCN + HCl / $AlCl_3$
(ii) H_2O
CO + HCl / $AlCl_3$
H_2 / Pd - $BaSO_4$
boiling xylene
$C_6H_5 - C(=O) - Cl$
$C_6H_5NH_2$
$C_6H_5 - CH = N - C_6H_5$
Schiff's base or anils


(5)
$C_6H_5 - C(=O) - CH_3$
Acetophenone
$CH_3COCl / AlCl_3$
Cl_2
In absence of catalyst
$C_6H_5 - C(=O) - CH_2 - Cl$
Phenacylchloride (Lacrymater)
Zn – Hg / HCl
$CH_2 - CH_3$


(6)
$C_6H_5 - C(=O) - C_6H_5$
(Benzophenone)
$C_6H_5COCl / AlCl_3$
$COCl_2 / AlCl_3$
excess