Reactions given by Aldehydes only

Tollens's test: Aldehydes are oxidised to corresponding acids with Tollens's reagent (ammoniacal solution of silver nitrate):

$$RCHO + 2[Ag(NH_3)_2]^* + 3 \overline{O}H \longrightarrow RCOO + 2Ag + 2H_2O + 4NH_3$$

The reaction occurs in alkaline medium.

Fehling's test: Aliphatic aldehydes are oxidised to corresponding acid with Fehling solution (ammoniacal solution of Cu(II)-tartarate):

$$R\text{-}CHO + 2Cu^{2+} + 5\overline{O}H \longrightarrow RCO\overline{O} + Cu_2O + 3H_2O$$

Red-brown ppt

Reactions given by Ketones only

Halo-form test: Methyl ketone gives haloform test:

$$R \xrightarrow{C} CH_3 \xrightarrow{NaOX} R \xrightarrow{C} ONa + CHX_3 \quad (X=Cl, Br, l)$$

$$H \xrightarrow{C} CH_3 \xrightarrow{NaOCl} H_3C \xrightarrow{C} ONa + CHCl_3$$

lodoform reaction with sodium hypoiodite is also used for detection of CH₃CO group or CH₃CH(OH) group which produces CH₃CO group on oxidation.

Ketones do not give Tollens's test or Fehling's test.

Aldol condensation: Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively.

Intramolecular Aldol Condensation:

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

Intramolecular aldol is preferred when five or six membered ring is formed.

Cross aldol condensation:

$$H-C \stackrel{O}{=} + \stackrel{x}{H} - \stackrel{x}{C}H_2 - C \stackrel{O}{=} \stackrel{NaOH}{=}$$

Formaldehyde

Acetaldehyde

OH
$$H - C \xrightarrow{\beta} CH_2 - C \xrightarrow{O} H$$

3-Hydroxypropanal

Cannizzaro reaction: Aldehydes which do not have an α -hydrogen atom, undergo self-oxidation and reduction (disproportionation) reaction on heating with concentrated alkali.

$$H$$
 $C=O$ + $C=O$ + Conc. KOH $\xrightarrow{\Delta}$ H $C=OH$ + H C OK

Formaldehyde

Methanol Potassium formate

2 CHO + Conc. NaOH
$$\xrightarrow{\Delta}$$
 CH₂OH + COONa Benzaldehyde Benzyl alcohol Sodium benzoate