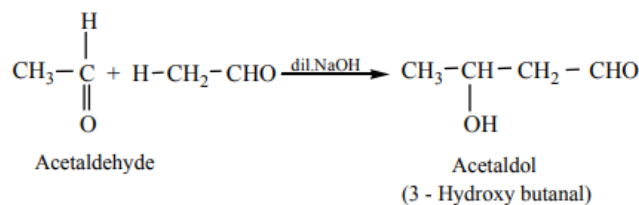


19. Aldol condensation The carbon attached to carbonyl carbon is called  $\alpha$  - carbon and the hydrogen atom attached to  $\alpha$  - carbon is called  $\alpha$  - hydrogen. In presence of dilute base NaOH, or KOH, two molecules of an aldehyde or ketone having  $\alpha$  - hydrogen add together to give  $\beta$  - hydroxyl aldehyde (aldol) or  $\beta$  - hydroxyl ketone (ketol). The reaction is called aldol condensation reaction. The aldol or ketol readily loses water to give  $\alpha, \beta$  - unsaturated compounds which are aldol condensation products.

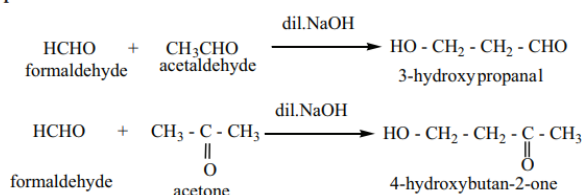
a) Acetaldehyde when warmed with dil NaOH gives  $\beta$  - hydroxyl butraldehyde (acetaldol).



20. Crossed aldol condensation:

Aldol condensation can also take place between two different aldehydes or ketones or between one aldehyde and one ketone such an aldol condensation is called crossed or mixed aldol condensation. This reaction is not very useful as the product is usually a mixture of all possible condensation products and cannot be separated easily

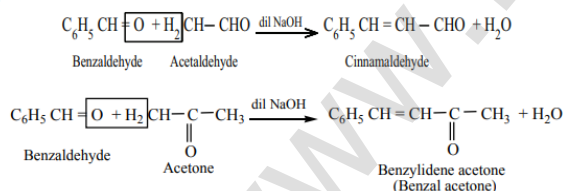
Example :



21. Claisen – Schmidt Condensation

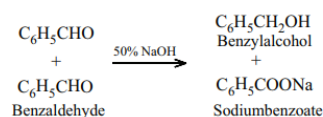
Benzaldehyde condenses with aliphatic aldehyde or methyl ketone in the presence of dil. alkali at room temperature to form unsaturated aldehyde or ketone. This type of reaction is called Claisen – Schmidt condensation.

Example



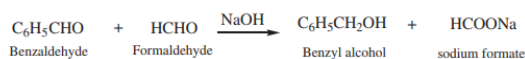
22. Cannizaro reaction

In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have  $\alpha$  - hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid. This reaction is called Cannizaro reaction. Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.



This reaction is an example disproportionation reaction

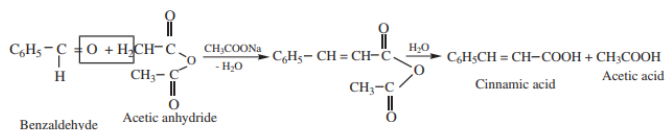
23. Crossed Cannizaro reaction When Cannizaro reaction takes place between two different aldehydes (neither containing an  $\alpha$  hydrogen atom), the reaction is called as crossed cannizaro reaction.



In crossed cannizaro reaction more reactive aldehyde is oxidized and less reactive aldehyde is reduced.

24. Perkins' reaction When an aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the acid corresponding to the anhydride, condensation takes place and an  $\alpha, \beta$  unsaturated acid is obtained. This reaction is known as Perkin's reaction.

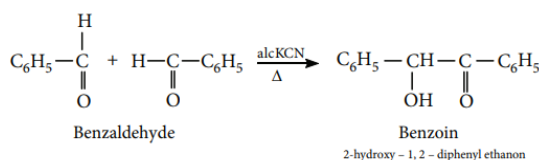
Example:



25. Benzoin condensation The Benzoin condensation involves the treatment of an aromatic aldehyde with aqueous alcoholic KCN. The products are a hydroxy ketone.

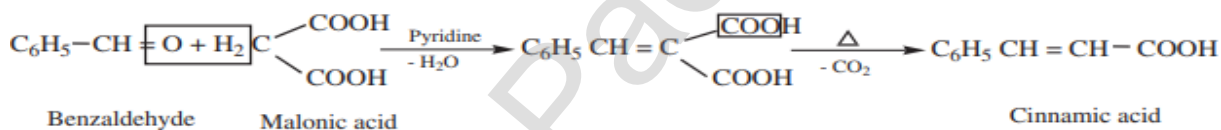
Example

Benzaldehyde reacts with alcoholic KCN to form benzoin



26.

### 1) Knoevenagel reaction

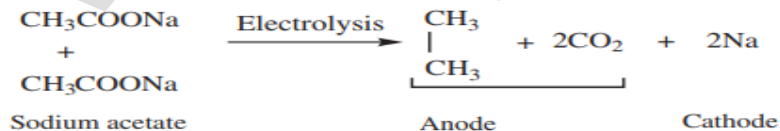


Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, Pyridine act as the basic catalyst.

27.

### 3) Kolbe's electrolytic decarboxylation

The aqueous solutions of sodium or potassium salts of carboxylic acid on electrolysis gives alkanes at anode. This reaction is called kolbes electrolysis.

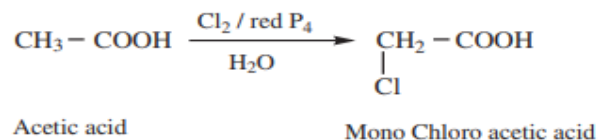


Sodium formate solution on electrolysis gives hydrogen

28.

**1)  $\alpha$  - Halogenation**

Carboxylic acids having an  $\alpha$  - hydrogen are halogenated at the  $\alpha$  - position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to form  $\alpha$  halo carboxylic acids. This reaction is known as **Hell - Volhard - Zelinsky reaction** (HVZ reaction) The  $\alpha$  - Halogenated acids are convenient starting materials for preparing  $\alpha$  - substituted acids.



29.

**4. Claisen Condensation**

Esters containing at least one  $\alpha$ -hydrogen atom undergo self condensation in the presence of a strong base such as sodium ethoxide to form  **$\beta$ - keto ester**.

