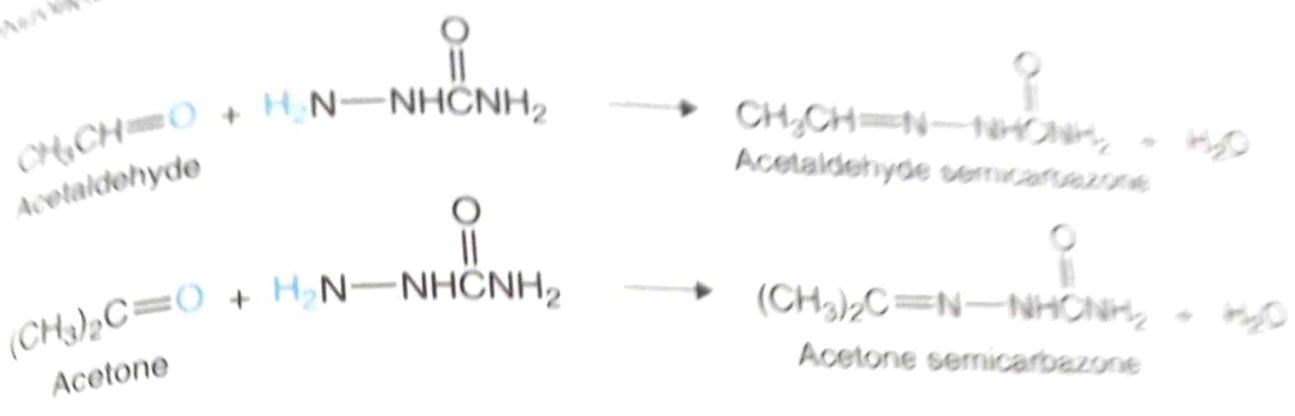
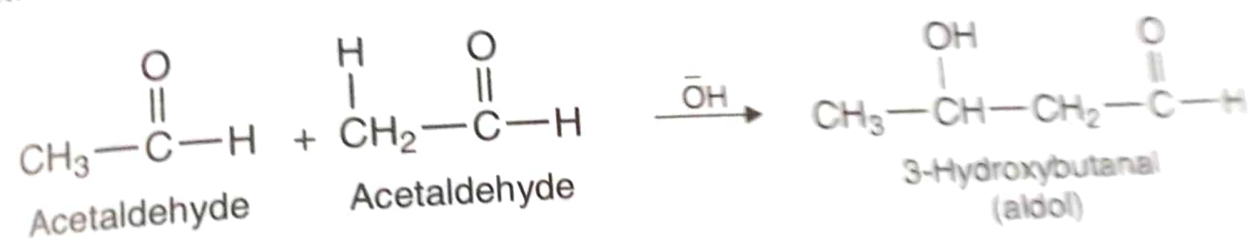


**Reaction with Semicarbazide.** Aldehydes and ketones react with semicarbazides to form



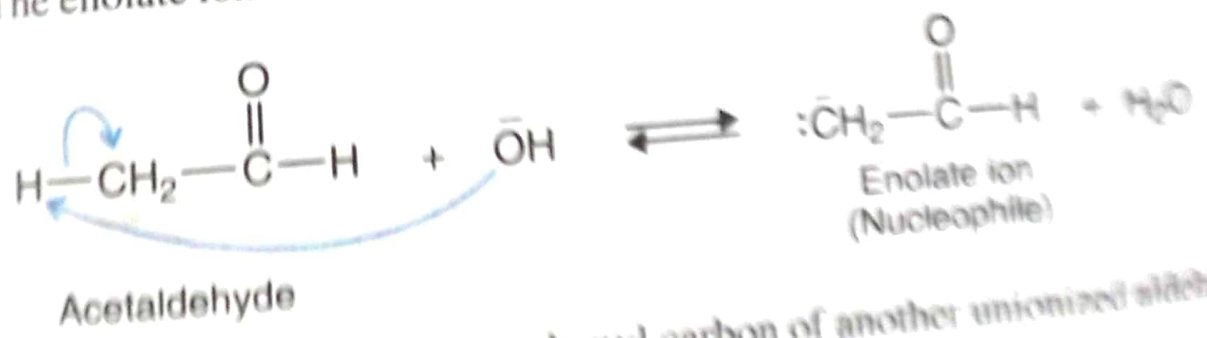
### REACTIONS INVOLVING ALKYL GROUPS

(7) **Aldol Condensation.** Aldehydes containing  $\alpha$ -hydrogens undergo self-addition in the presence of a base to form products called **Aldols**. The reaction is called **Aldol Condensation**. The term aldol is derived from the combination of the words Aldehyde and Alcohol, the two functional groups present in the product. For example, two molecules of acetaldehyde combine with each other in the presence of dilute NaOH to form 3-hydroxybutanal.

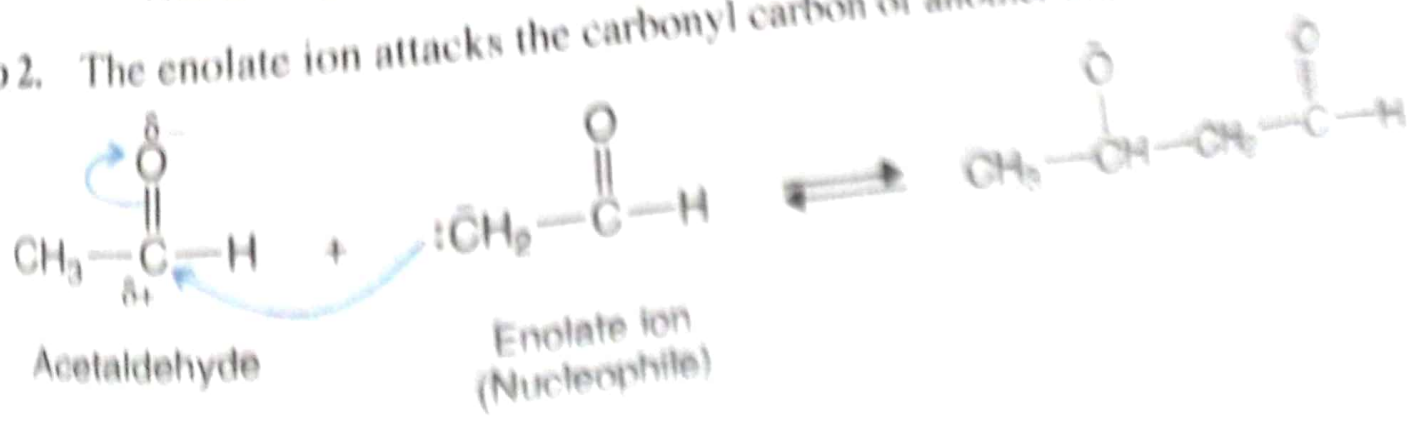


**MECHANISM.** The reaction is reversible and involves the following steps :

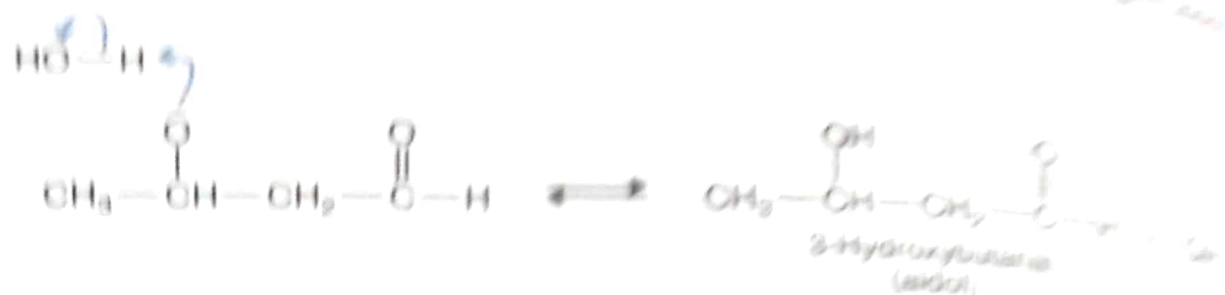
Step 1. The enolate ion is formed



Step 2. The enolate ion attacks the carbonyl carbon of another unionized aldehyde molecule



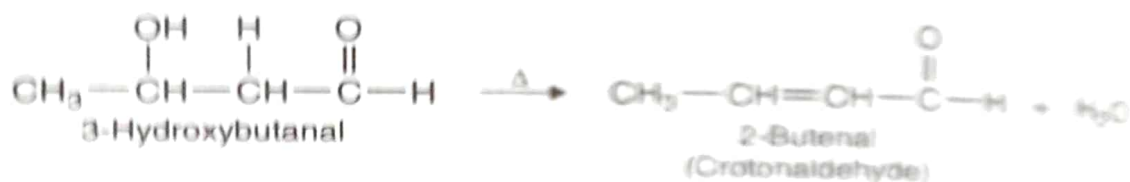
Step 3. The negative oxygen in the product accepts a proton from water to give



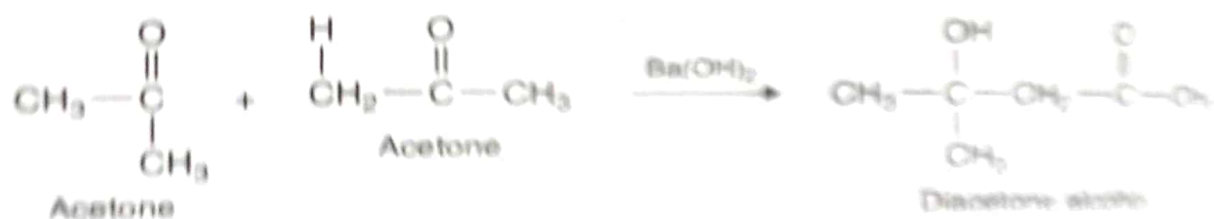
The product in all aldol condensations has several common structural characteristics:

1. The product is a larger molecule that contains a newly formed carbon-carbon bond.
2. The newly formed C-C bond occurs between the  $\alpha$  carbon of one aldehyde and what was originally the carbonyl carbon of the second aldehyde molecule.
3. The product contains two functional groups: one carbonyl group and one hydroxyl group.
4. The hydroxyl group is always attached to the beta carbon ( $\beta$  carbon), which is two carbons away from the carbonyl group.

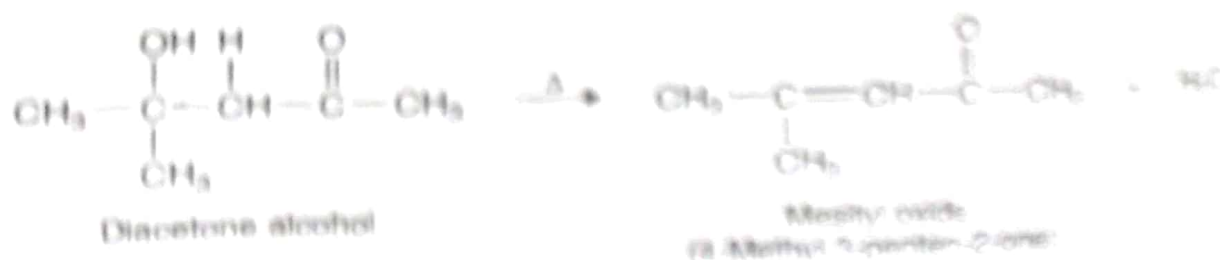
Aldols are easily dehydrated either by heating or by treatment with dilute acid to form  $\alpha,\beta$ -unsaturated aldehydes. For example,



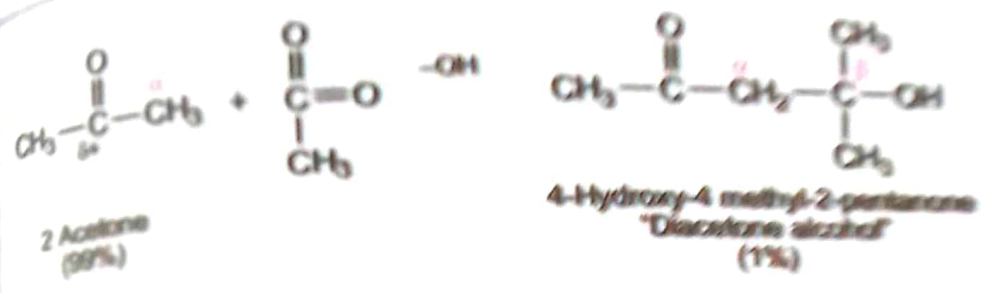
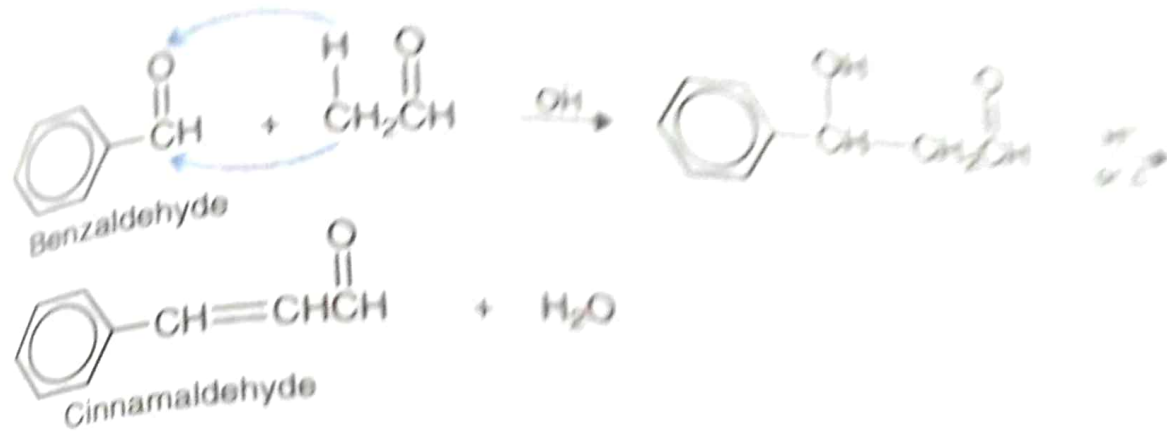
Ketones containing  $\alpha$ -hydrogens also undergo aldol condensation to form **ketols**. For example, two molecules of acetone combine with each other in the presence of barium hydroxide to form 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol).



Ketols are also easily dehydrated by heating or by treatment with dilute acid to form  $\alpha,\beta$ -unsaturated ketones. For example,

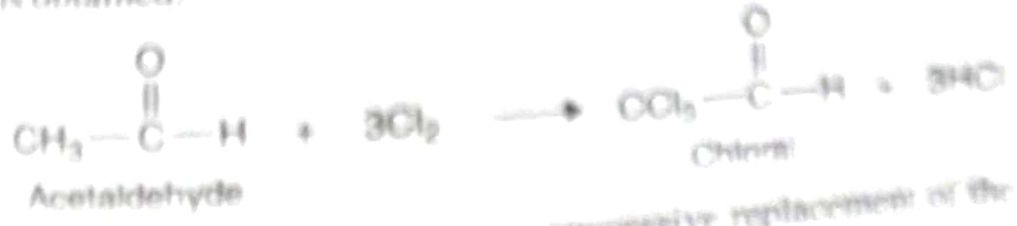


**Mixed Aldol Condensation** The reaction of two different carbonyl compounds that must have an  $\alpha$  H in the presence of a base is known as mixed aldol condensation. For example, acetaldehyde reacts with benzaldehyde (which has no  $\alpha$ -H) in the presence of a base to form

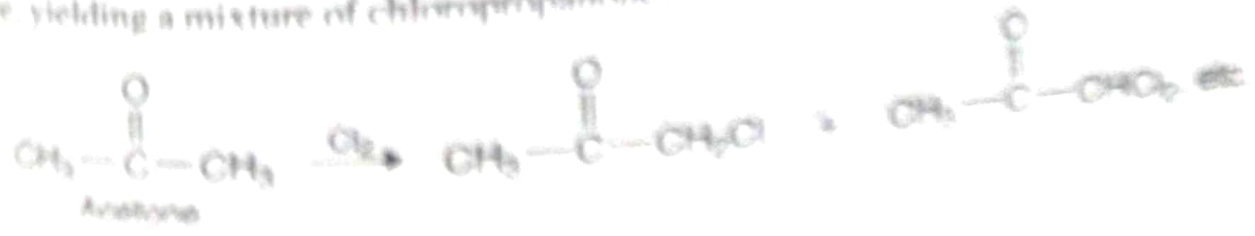


The Aldol condensation of acetone gives only 1% product at equilibrium, yet a clever technique gives a good yield. Acetone refluxes onto a basic catalyst such as  $\text{Ba(OH)}_2$ . The nonvolatile diacetone alcohol does not reflux, so its equilibrium concentration gradually increases until all the acetone is converted to diacetone alcohol.

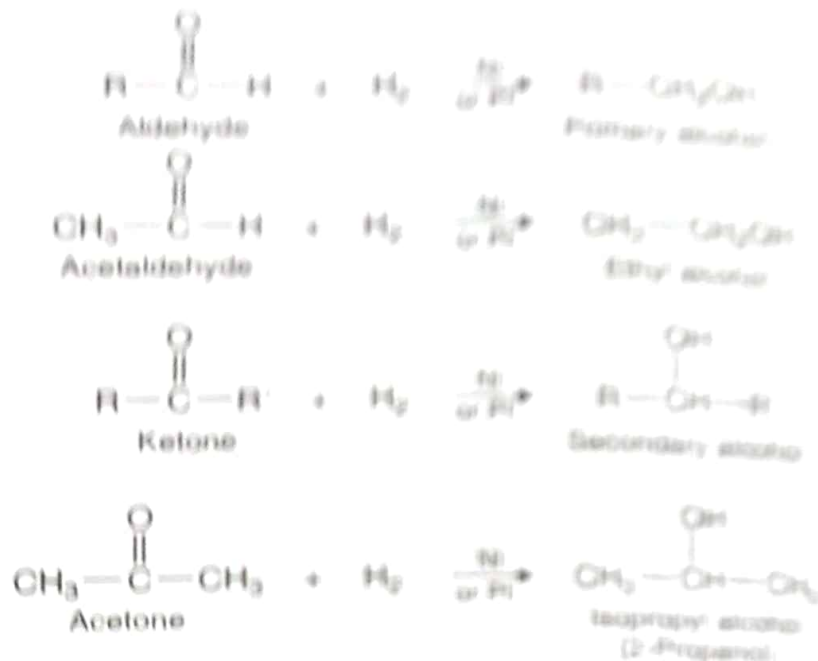
(b) **Chlorination.** Under suitable conditions, chlorine will successively replace the  $\alpha$ -hydrogen of aldehydes and ketones. For example, when chlorine is bubbled through acetaldehyde, chloroacetaldehyde (chloroethanal) is obtained.



If chlorine is bubbled through warm acetone, successive replacement of the methyl hydrogens takes place, yielding a mixture of chloroacetones.



(9) **Reduction to Alcohols** Aldehydes and ketones can be reduced to alcohols using hydrogen and Ni or Pt catalyst. Aldehydes give primary alcohols. Ketones give secondary alcohols.



The same results can be achieved with chemical reducing agents such as lithium aluminium hydride ( $\text{LiAlH}_4$ ) or sodium borohydride ( $\text{NaBH}_4$ ). For example,



(10) **Reduction to Alkanes.** Aldehydes and ketones can be reduced to alkanes by Clemmensen reduction or the Wolf-Kishner reduction.

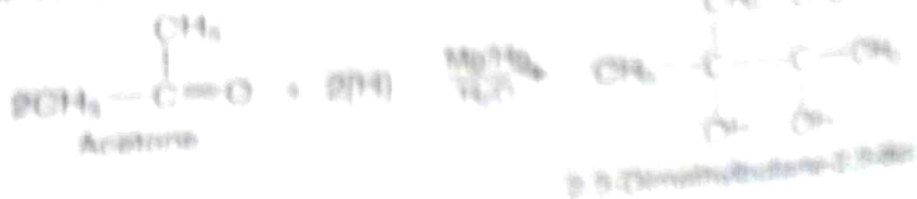
(a) **Clemmensen Reduction.** This involves the use of zinc-mercury amalgam or hydrochloric acid as the reducing agent.



(b) **Wolf-Kishner Reduction.** This involves the use of a basic solution of hydrazine as the reducing agent.



(11) **Reduction to Pinacols** Ketones when reduced in neutral or alkaline solution, form pinacols (symmetrical 1,2-diols). For example, acetone undergoes reductive coupling to form 2,3-dimethylbutane-2,3-diol.



Aldehydes do not give this reaction.