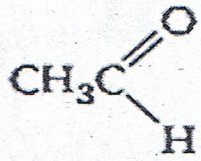
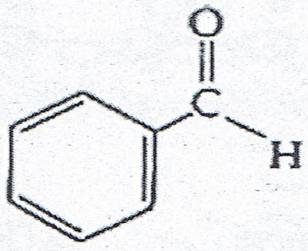
lec. 14 Chemistry

Aldehydes and ketones

An aldehyde contains a carbonyl group whose carbon is bonded to one hydrogen and either an alkyl or an aryl group.For example:

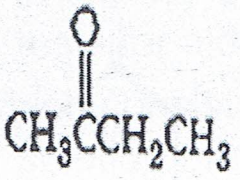


Acetaldehyde
(an aliphatic aldehyde)

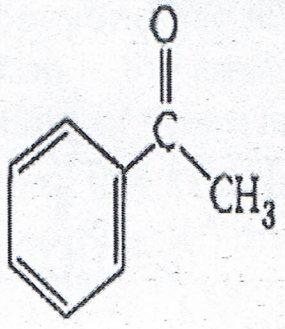


Benzaldehyde
(an aromatic aldehyde)

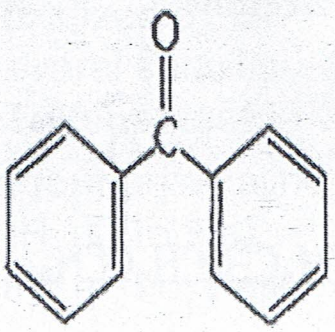
A ketone contains a carbonyl group whose carbon is bonded to two alkyl groups, two aryl groups, or one alkyl and one aryl group.For example:



2-Buranone
(an aliphatic ketone)



Acetophenone
(an aryl alkyl ketone)



Benzophenone
(an aromatic ketone)

Naming Aldehydes and Ketones

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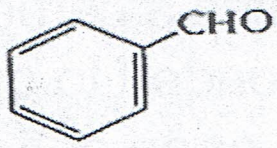
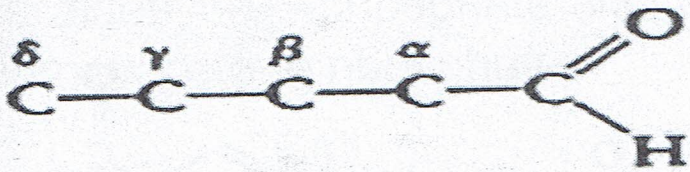
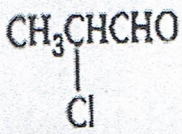


CH_3CH_2CHO
Propionaldehyde

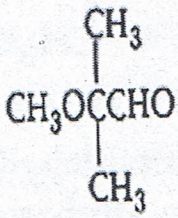
Benzaldehyde

$CH_3CH_2CH_2CHO$
Butyraldehyde





$BrCH_2CH_2CH_2CHO$



α-Chloropropionaldehyde

γ-Bromobutyraldehyde

α-Methoxyisobutyraldehyde

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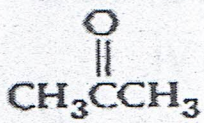
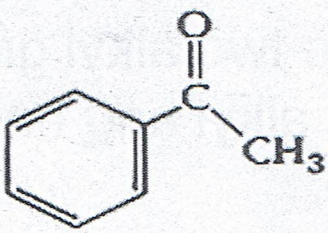
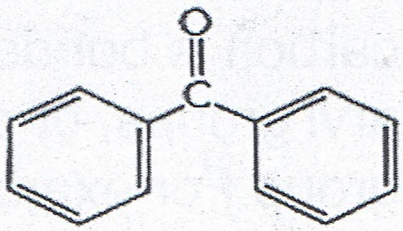


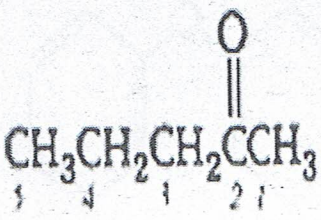


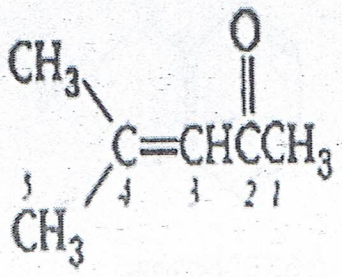


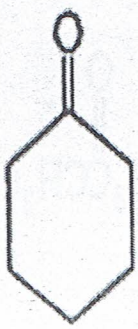
Acetone

Acetophenone

Benzophenone







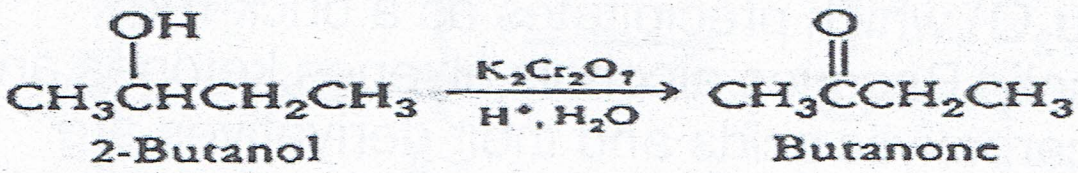
2-Pentanone

4-Methyl-3-penten-2-one

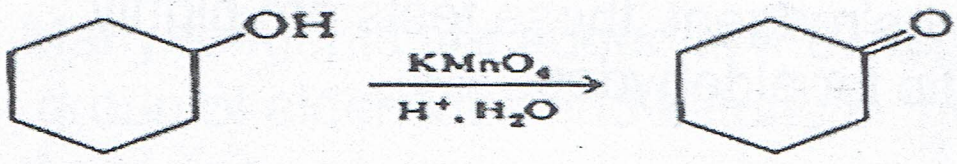
Cyclohexanone

Preparing Aldehydes and Ketones

Primary alcohols are oxidized first to aldehydes, which are then further oxidized to carboxylic acids. Secondary alcohols are oxidized to ketones.



2-Butanol Butanone



Cyclohexanol Cyclohexanone

Tests For Aldehydes

Most of the reactions of aldehydes and ketones are very similar, but their ability to be oxidized differs greatly.Ketones are oxidized only under the most vigorous conditions, whereas aldehydes are easily oxidized. In fact,aldehyded are slowly oxidized by air. This ease of oxidation is the basis of several specific tests for aldehyde.One of these is the **Tollens' test,**

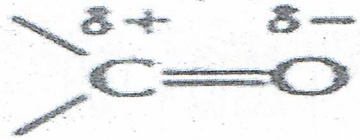
Which consists of adding the **Tollens'reagent**,an alkaline solution of di(ammine)Silver(I)ion,$Ag(NH_3)^+_2$,to the aldehyde.The aldehyde is oxidized to the carboxylate ion, and the silver ion is reduced to silver metal:

$$2\,Ag(NH_3)_2^+ + RCHO + 3\,OH^- \longrightarrow RCO_2^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O$$

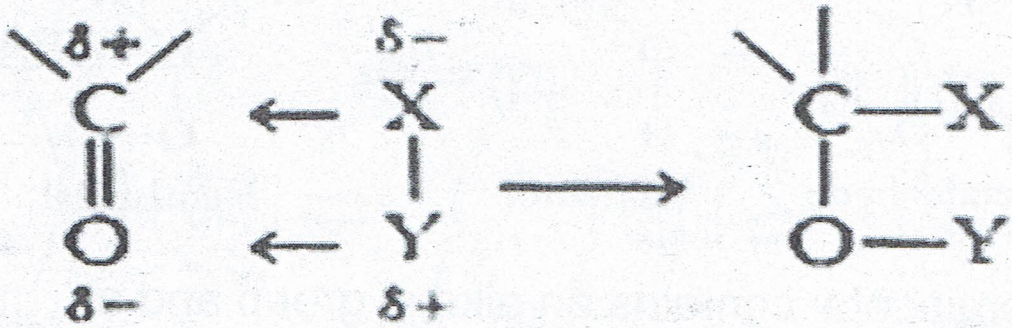
Another reagent often used to test for aldehydes is the Fehling's Solution. This is an alkaline solution of cupric ion (Cu^{+2}) complexed with tartrate ion. The aldehyde is oxidized to the carboxylate ion and the cupric ion is reduced to cupric oxide (Cu_2O),which precipitates as a brick-red solid.Becaues alcohols,alkenes,ketones,and carboxylic acids and their derivatives are not oxidized by either the Tollens' or the Fehlings'reagent ,these tests are highly specific for aldehydes.

Addition Reactions of Aldehydes and Ketones

The carbon – oxygen double bound is made up of two atoms of different electronegativities.The bonding electrons are not shared equally and the carbonyl group is polarized so that the carbon is slightly positive and the oxygen is slightly negative:



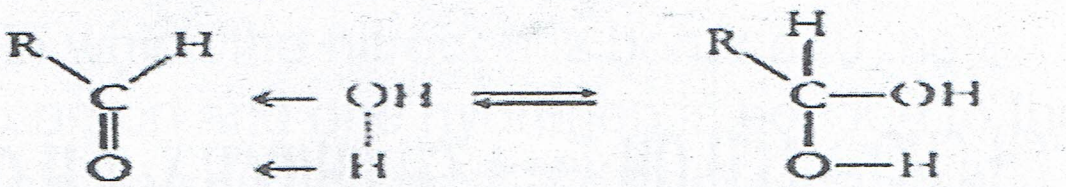
As a result, the carbon of the carbonyl group forms bonds with the more nucleophilic part of the reagent X –Y .Thus,



Many reagents are added to the carbonyl group of aldehydes and ketons in this way.

Addition Of Water

Most aldehydes react with water to form an equilibrium mixture of the aldehyde and an aldehyde hydrate:

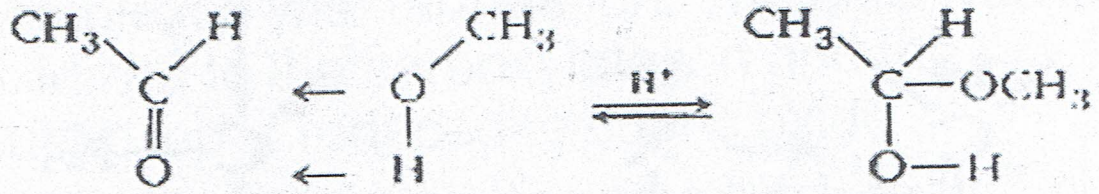


Aldehyde Aldehyde hydrate

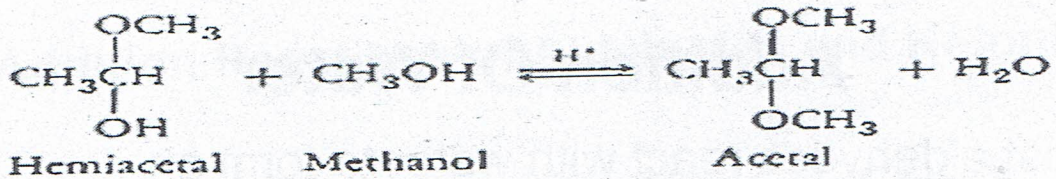
These aldehyde hydrates are 1,1-diols .They are usually too unstable to isolate and purify because they easily lose water to reform the aldehyde.Most ketones are less readily hydrated.

Addition Of Alcohols

Aldehydes react with alcohols in the presence of an acid catalyst to form a hemiacetal as product:



A hemiacetal contains an alkoxy group and an alcohol group,both bonded to the original carbon of the carbonyl group. In the presence of excess alcohol, a hemiacetal can react to form an acetal and water.

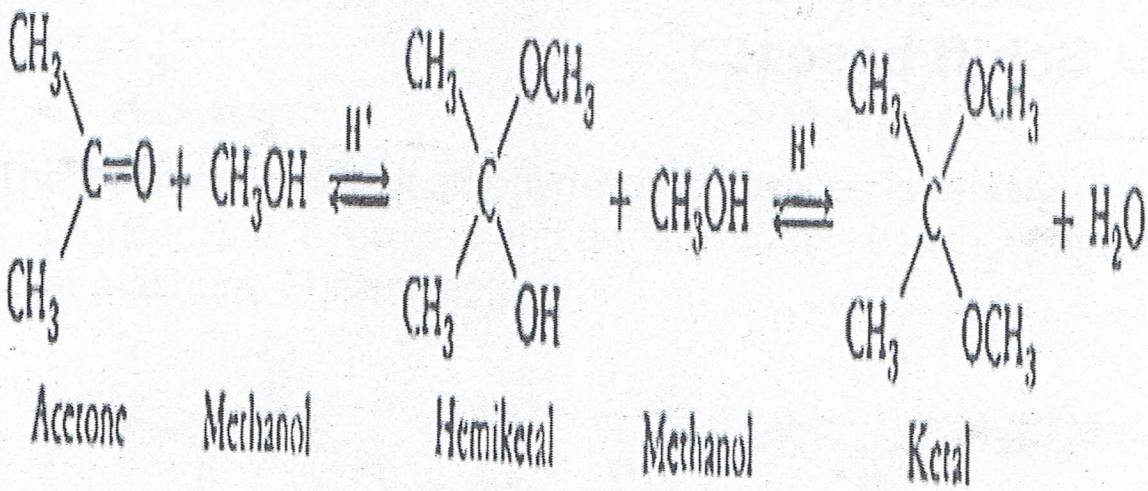


These two steps can be summarized by the following equations:

$$CH_3CHO + 2\,CH_3OH \overset{H^+}{\rightleftharpoons} CH_3CH(OCH_3)_2 + H_2O$$

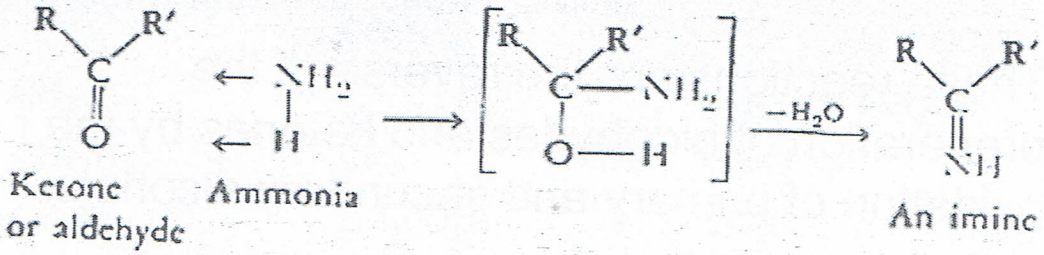
An acetal contains two alkoxy groups bonded to the same carbon.thus,an acetal resembles an ether, and its reactions are similar to those of ethers.

Ketones react with alcohols in a similar manner to form **hemiketals** and **ketals**.For example:



Addition Of Ammonia and Its Derivatives: Schiff Bases

Ammonia adds to the carbonyl group of aldehydes and ketones.The initial product, in which the nitrogen is bonded to the carbon and one hydrogen is bonded to the oxygen, is unstable and spontaneously loses water to form an **imine**:

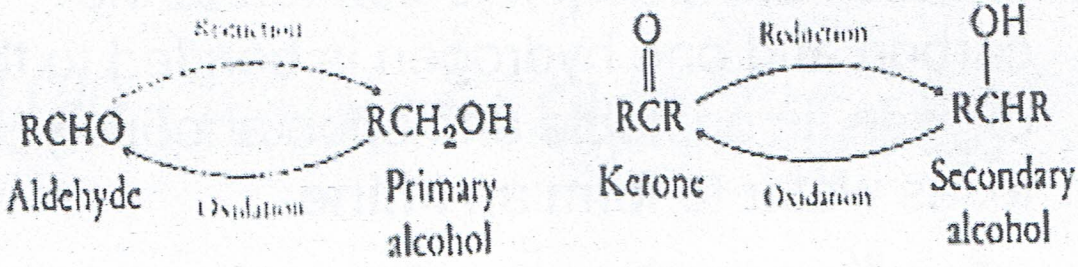


Compounds having the general structures RHC=NR̈ and R_2C=NR̈ are called aldimines and ketimines,respectively.

These compounds are also generally called **Schiff bases**.

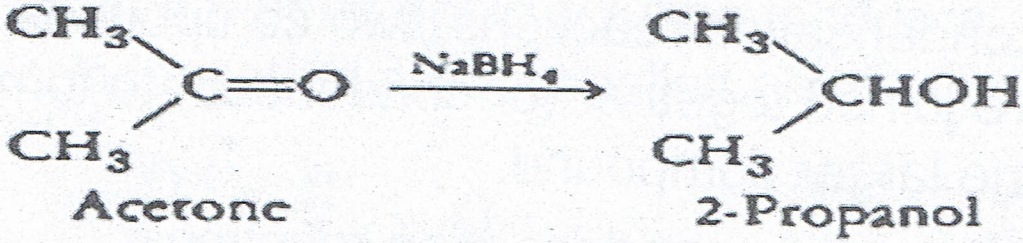
Reduction Of Aldehydes and Ketones

The **reduction** of aldehydes and ketones form alcohols. Primary alcohols are formed from aldehydes,whereas secondary alcohols are formed from ketones:



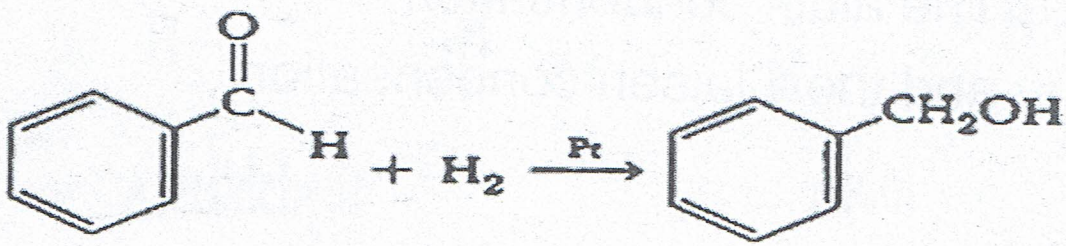
These reactions are the reverse of the preparation of aldehydes and ketones by the oxidation of primary and secondary alcohols.

Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) are metallic hydrides that reduce aldehydes and ketones to alcohols. For example:



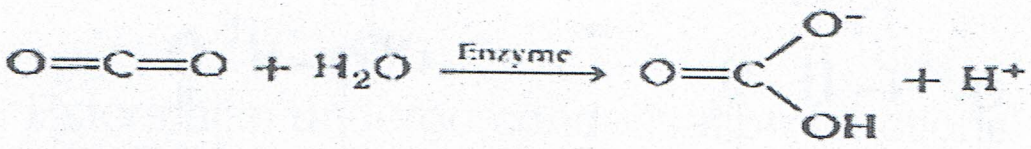
Acetone 2-Propanol

The carbonyl group of aldehydes and ketones is readily reduced with hydrogen and a metal catalyst such as nickel or platinum. For example:

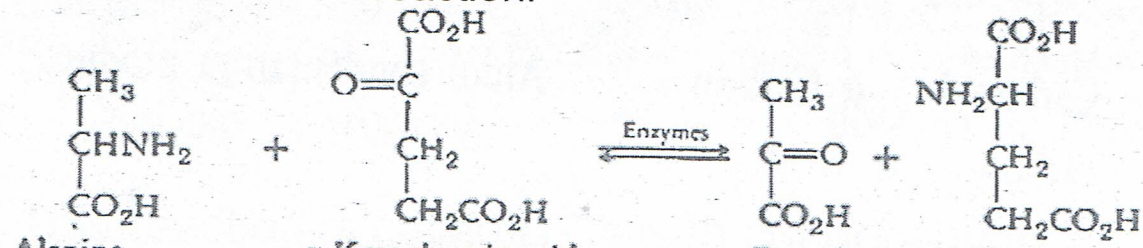


Addition Reactions of Aldehydes and ketones in Living Systems

The enzyme-catalyzed hydration of carbon dioxide to bicarbonate ion according to the following equation:



The formation of Schiff bases is an important in the formation of many compounds in living systems. One example is the **transamination** reaction.



Alanine (an amino acid) α-Ketoglutaric acid (an α-keto acid) Pyruvic acid Glutamic acid

Condensation Reactions

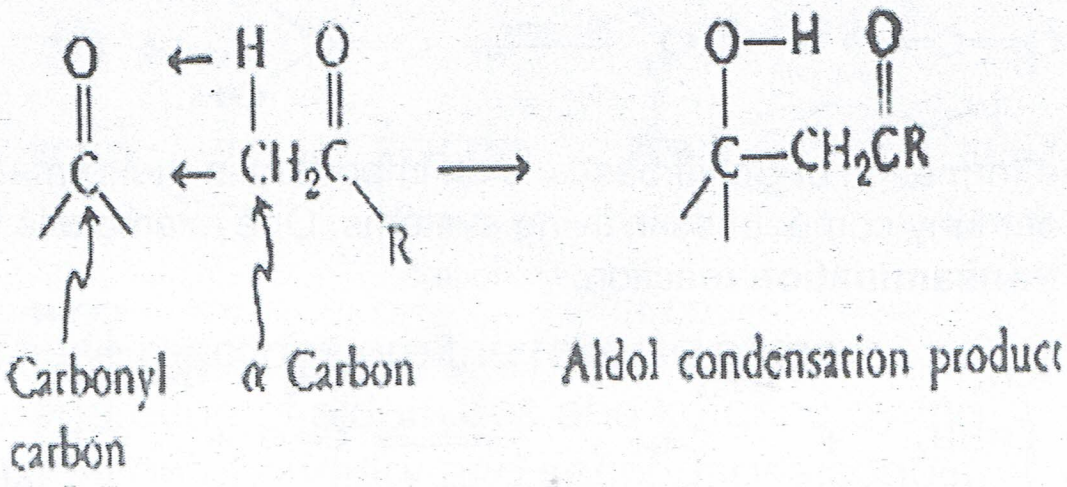
In condensation reactions, two compounds are joined together (or condensed) to form one larger compound.

There are two condensation reactions:

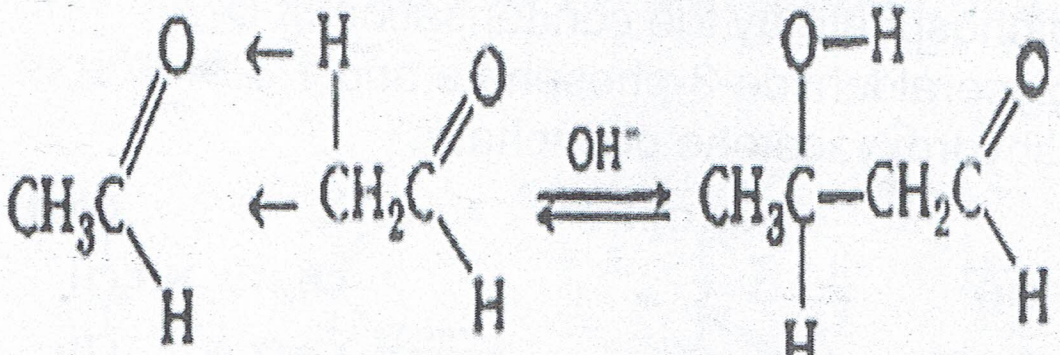
The aldol condensation

and the Claisen condensation

- **An aldol condensation reaction** is a reaction in which the carbonyl carbon of one molecule forms a bond with α carbon of another carbonyl containing molecule.

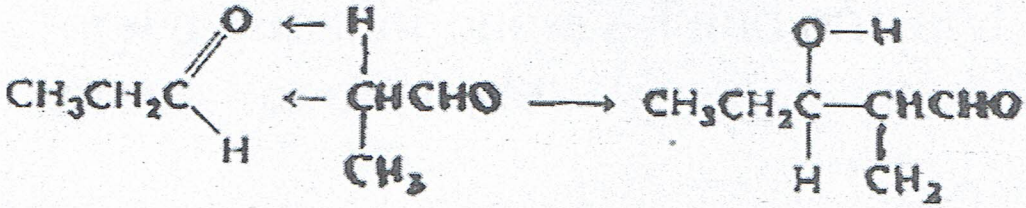


Aldehydes and ketones undergo this type of reaction. For example, acetaldehyde react in an aqueous basic solution to form a condensation product called aldol:

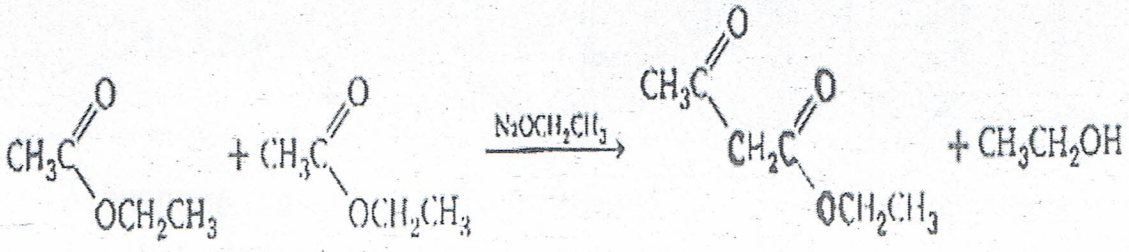


Acetaldehyde Aldol

- Most aldehydes and many ketones that have α hydrogens undergo the aldol condensation.



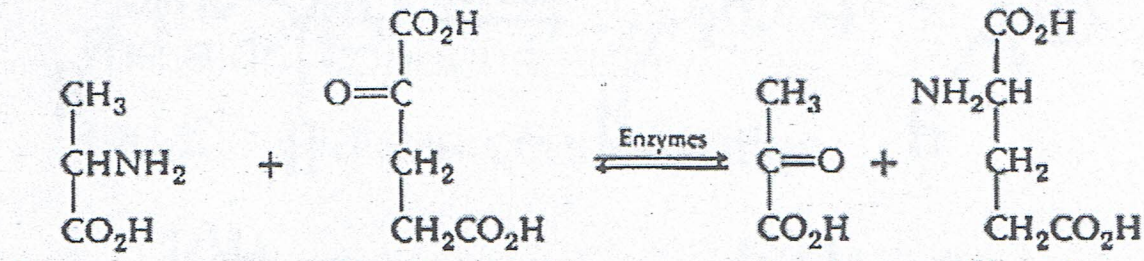
- Esters also undergo condensation reactions when treated with base. for example:



This reaction is called a Claisen condensation.

Condensation Reactions in living Systems

Carbohydrates are prepared in living systems by an enzyme-catalyzed aldol condensation. A specific example is the preparation of D-fructose-1,6-diphosphate by the condensation of D-glyceraldehyde-3-phosphate and 1,3-dihydroxyacetone phosphate:



Alanine (an amino acid) | α-Ketoglutaric acid (an α-keto acid) | Pyruvic acid | Glutamic acid