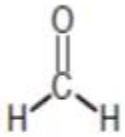
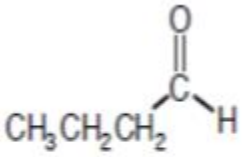
Lec.5

Aldehydes and Ketones

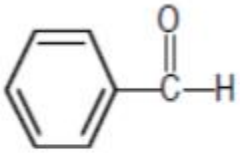
An aldehyde contains a carbonyl group whose carbon is bonded to one hydrogen and either an alkyl or an aryl group. For example:



formaldehyde

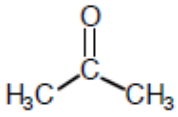


butylaldehyde

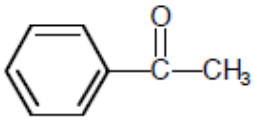


benzaldehyde

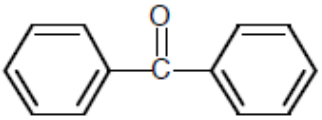
A ketone contains a carbonyl group whose carbon is bonded to two alkyl groups, two aryl groups, or one alkyl and one aryl group. For example:



acetone

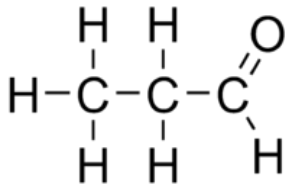


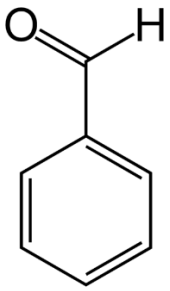
acetophenone

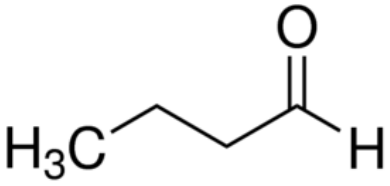


benzophenone

Naming aldehydes and Ketones







Propionaldehyde Benzaldehyde Butyl Aldehyde

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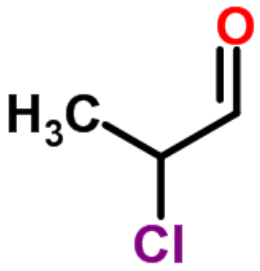
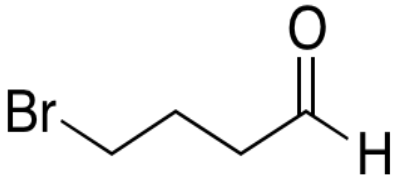
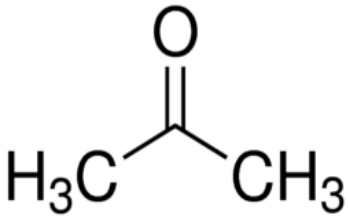
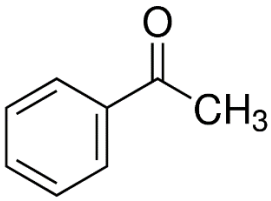
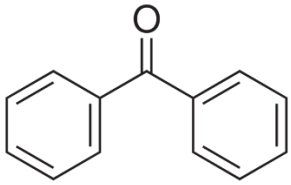




α-Chloropropionalaldehyde γ-Bromobutylaldehyde

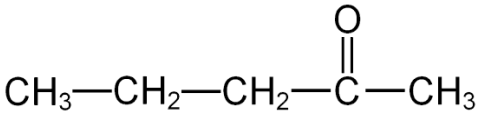


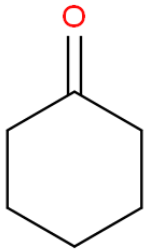




Dimethyl Ketone Acetophenone Benzophenone

Acetone





Methyl propyl ketone 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.

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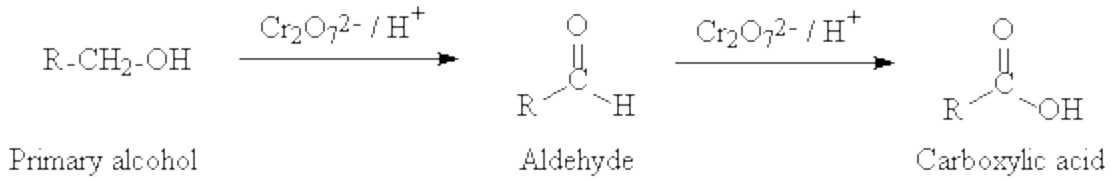

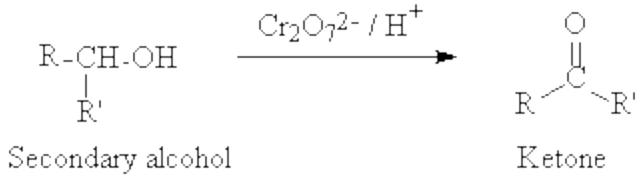

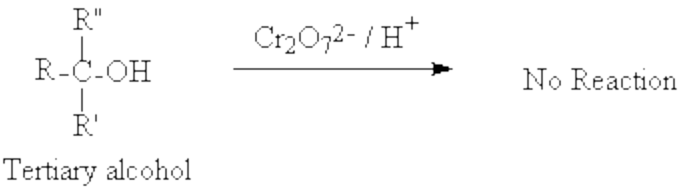

Tests for Aldehydes

Most of the reaction of aldehydes and ketones are very similar, but their ability to be oxidized differs greatly. Ketone are oxidized only under the most vigorous conditions, whereas aldehydes are easily oxidized. In fact, aldehyde 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:

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

Another reagent often used to test for aldehydes is the Fehling's solution. This is an alkaline solution of 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 Tollen's or the fehling's reagent these tests are highly specific for aldeydes.

$$RCHO + Cu^{+2} + OH^{-} \longrightarrow RCOO^{-} + Cu_2O\downarrow$$

$$Cu^{+2} \xrightarrow{+e} Cu^{+1}$$

Addition reaction 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 froms bonds with the more nucleophilic (X^-) part of the reagent X-Y. thus many reagent are added to the carbonyl group of aldehydes and ketons in this way.

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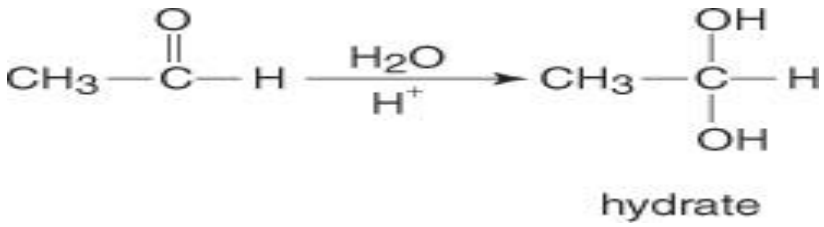
Addition of water

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



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:

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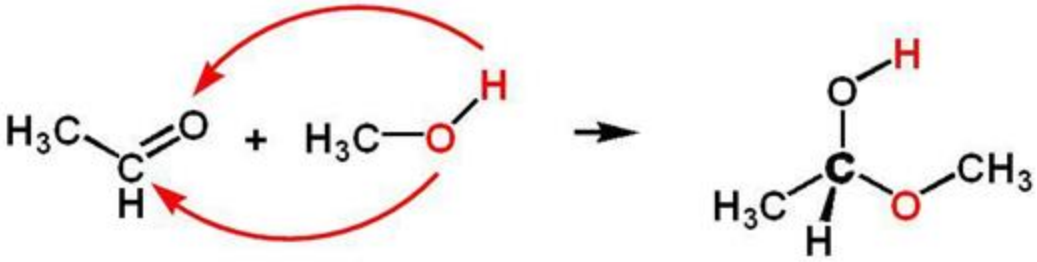
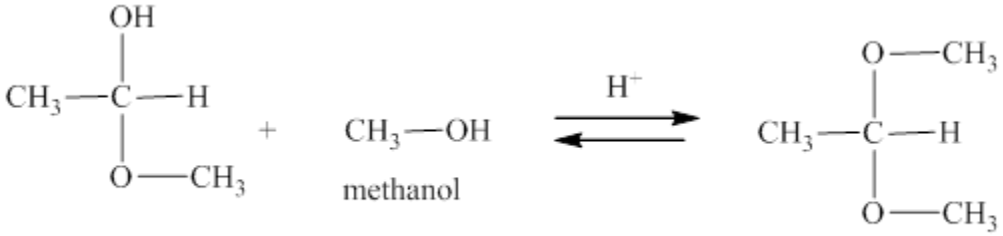
Hemiacetal Synthesis: aldehyde + hydrogen

- Alcohol + aldehyde --> hemiacetal
- Ethanal + methanol
- Alcohol oxygen becomes an ether
- Carbon double bond oxygen becomes an alcohol



Acetaldehyde Methanol Hemiacetal

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.



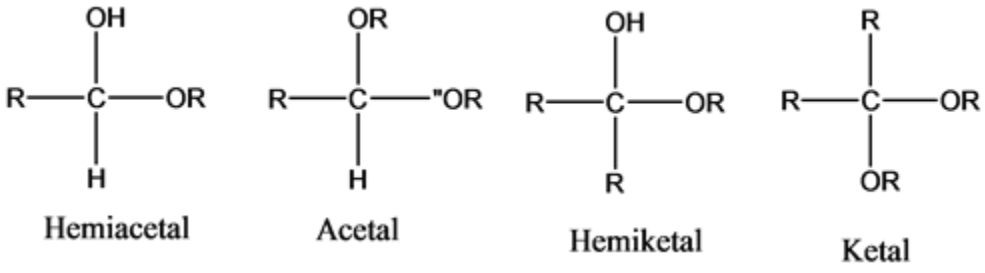
Hemiacetal methanol Acetal

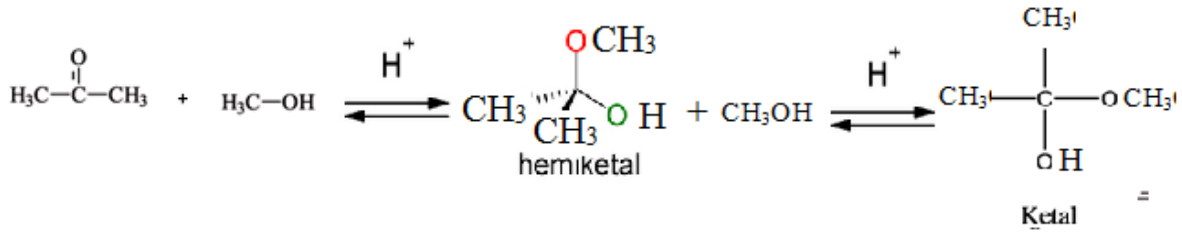
These two steps can be summarized by the following equations:

$$CH_3CHO + 2CH_3OH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3CH(OCH3)_2 + H_2O$$

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 carbon and one hydrogen is bonded to the oxygen, is unstable and spontaneously loses water to form an imine:

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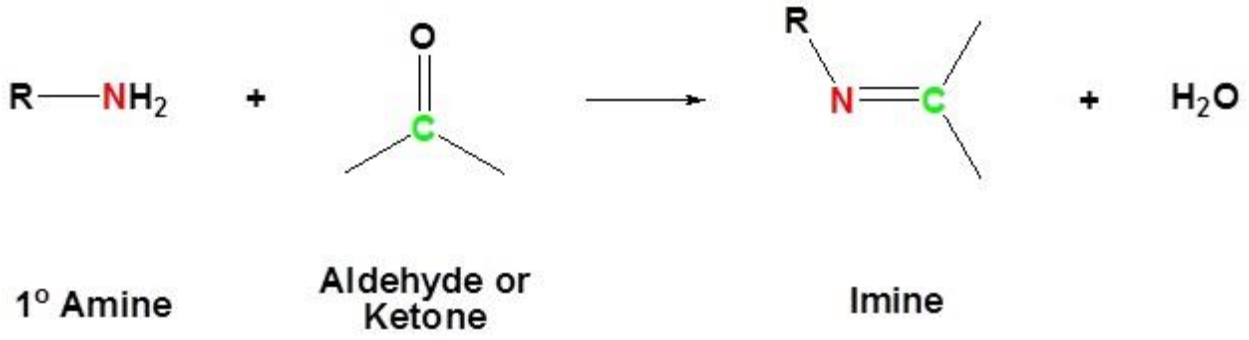
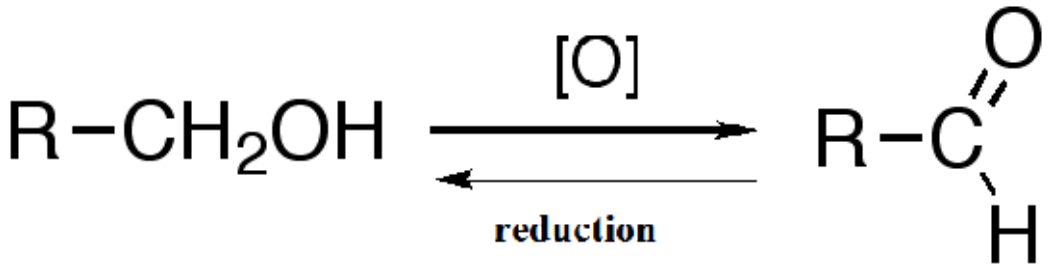
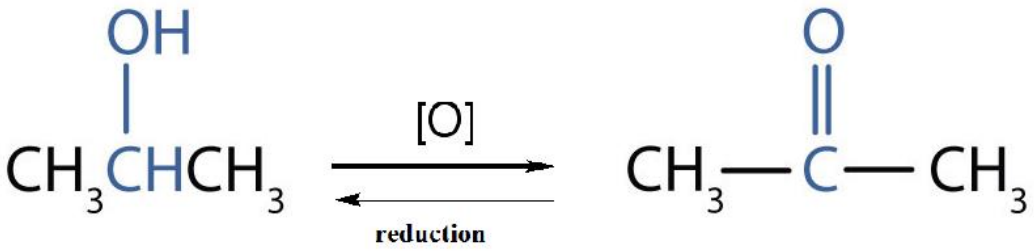


Reduction of aldehydes and Ketones

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



primary alcohol aldehyde



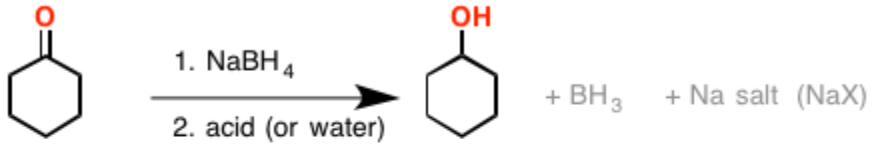
Isopropyl alcohol (a secondary alcohol)

Acetone (a ketone)

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

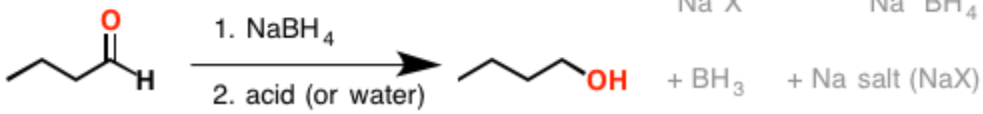
Lithium aluminium hydride ($LiAlH_4$), nickel, platinum and sodium brohydride ($NaBH_4$) are metallic hydrides that reduce aldehydes and ketones to alcohols. The carbonyl group of aldehydes and ketones is readily reduced with hydrogen and a metal catalyst such as. For example:

Example 1: Reduction of ketones



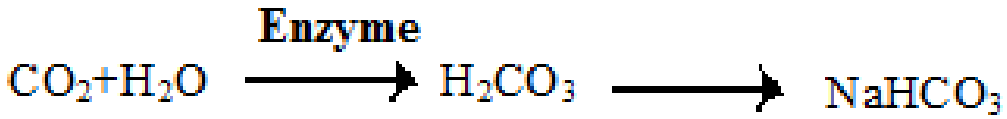
Form	Break
C–H	C–O
O–H	B–H
Na X	Na BH4

Example 2: Reduction of aldehydes

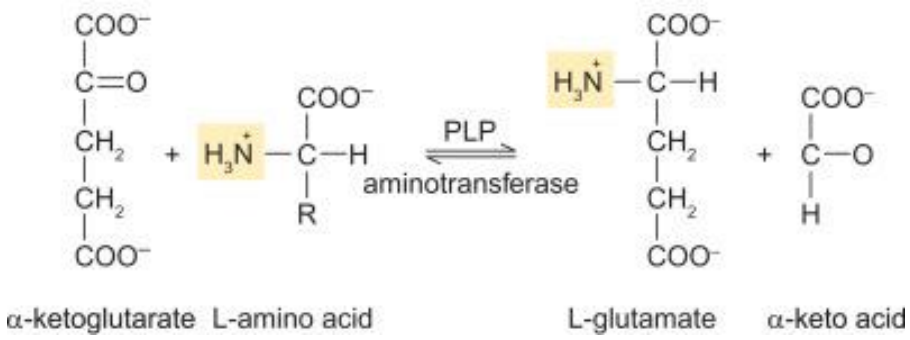


Addition reduction of aldehydes and ketones in Living systems

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



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



Condensation reactions

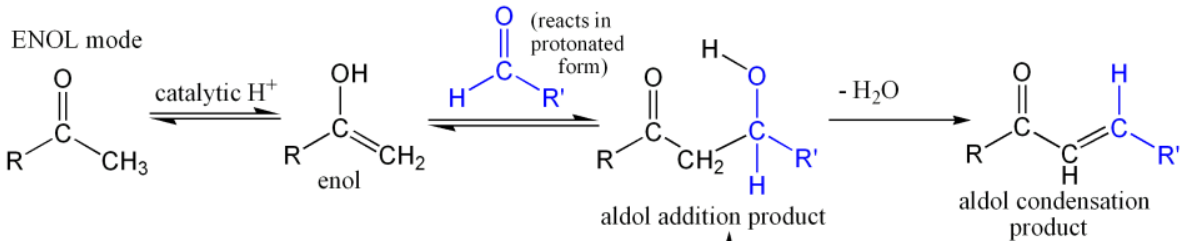
In condensation reactions, two compounds are joined together (or condensed) to form one large compound.

There are two condensation reaction:

1-The aldol condensation.

2- 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:

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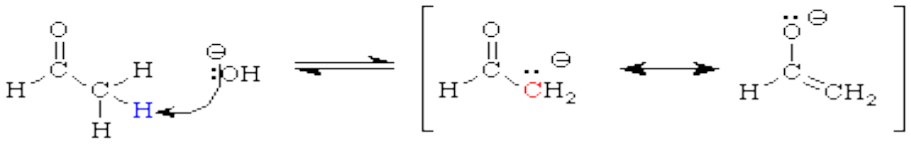
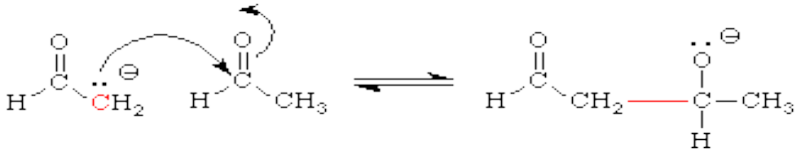
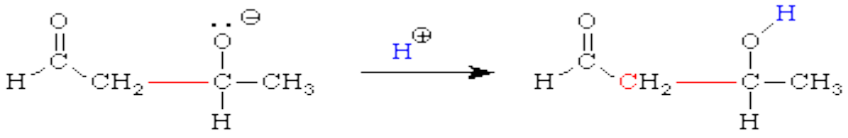
Step 1-Deprotonation of the α-carbon; generation of an enolate ion.



Step 2-Nucleophilic addition of the enolate ion to the carbonyl group.

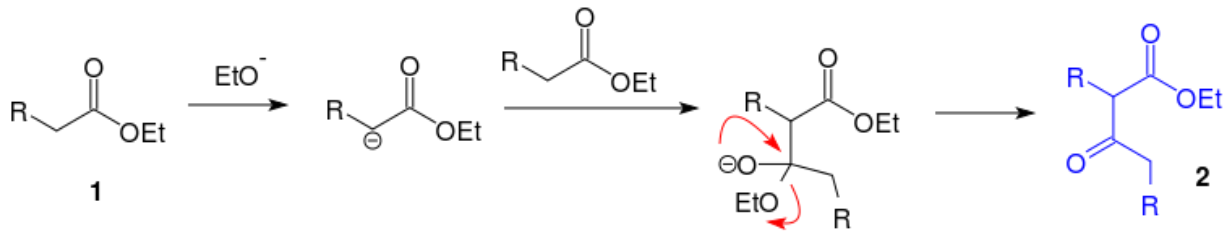


Step 3-Protonation of the tetrahedral intermediate; formation of aldol.



aldol

- Most aldehydes and many ketones that have α-hydrogens undergo the aldol condensation.
- Ester also undergo condensation reactions when treated with base, these reaction is called a Claisen condensation.



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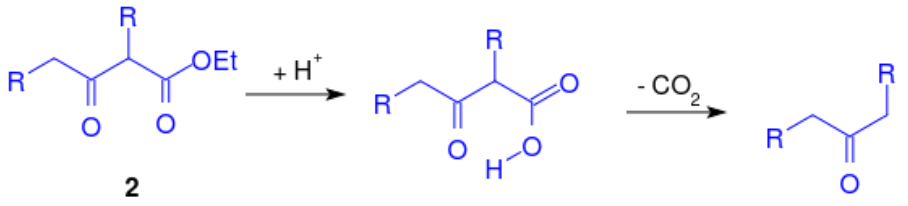

2

Et: CH_2CH_3