

Carbonyl Containing Compounds

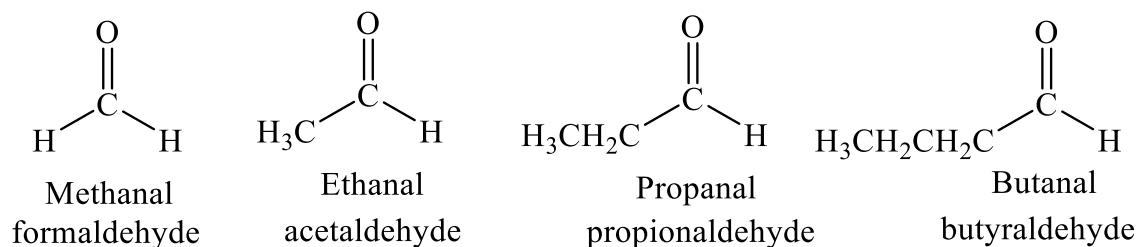
<u>Formula</u>	<u>Family</u>	<u>Formula</u>	<u>Family</u>
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Aldehyde	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	Carboxylic acid
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	Ketone	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$	Ester
		$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	Amide
		$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$	Acid halide
		$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	Acid anhydride

Properties

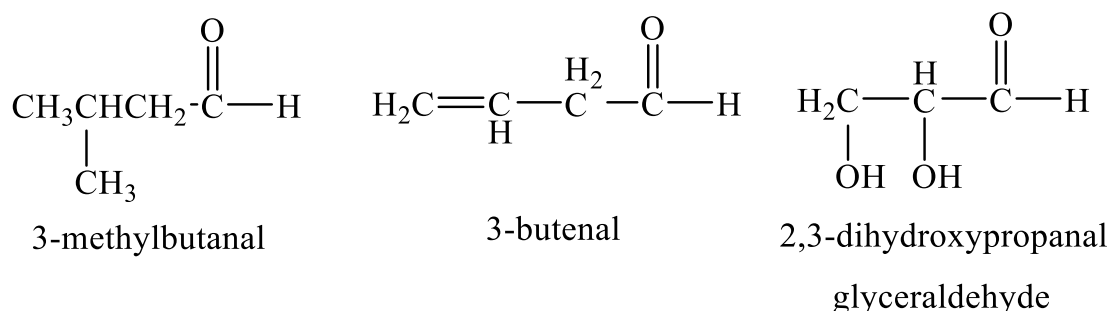
1. Moderately polar due to $\text{C}=\text{O}$ group
2. Boiling point :- Lower than alcohols and higher than alkane
3. Solubility :- Low molecular weight species are soluble in water , Decreases as the R chain gets longer.

Nomenclature of Aldehydes and Ketones

In the IUPAC system, the characteristic ending for aldehydes is *-al* (from the first syllable of *aldehyde*). The following examples illustrate the system:

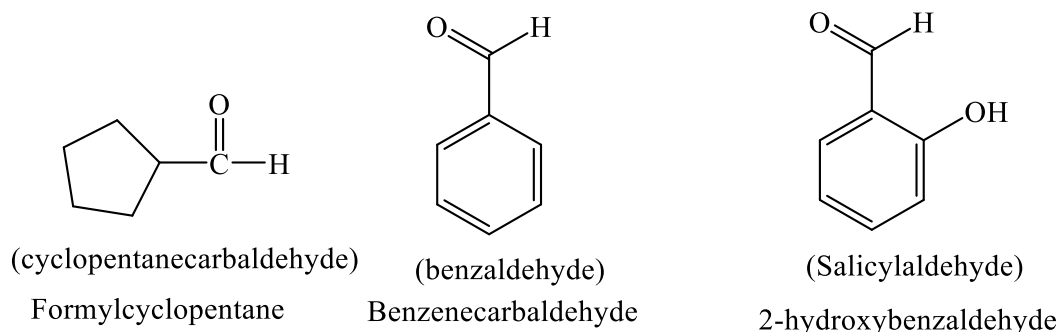


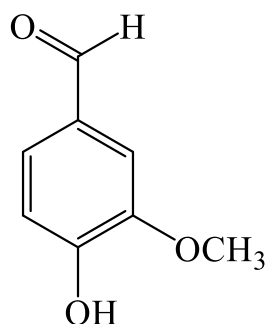
The common names shown below the IUPAC names are frequently used, so you should learn them. For substituted aldehydes, we number the chain starting with the aldehyde carbon, as the following examples illustrate:



Notice from the last two examples that an aldehyde group has priority over a double bond or a hydroxyl group, not only in numbering but also as the suffix. For cyclic aldehydes, the suffix *-carbaldehyde* is used.

Aromatic aldehydes often have common names:

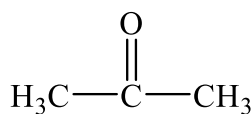




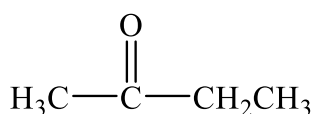
(Vaniline)

4-hydroxy-3-methoxybenzaldehyde

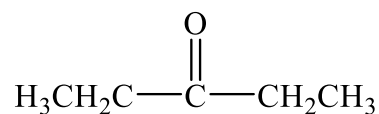
In the IUPAC system, the ending for ketones is *-one* (from the last syllable of *ketone*). The chain is numbered so that the carbonyl carbon has the lowest possible number. Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl group attached to the carbonyl carbon. In still other cases, traditional names are used. The following examples illustrate these methods:



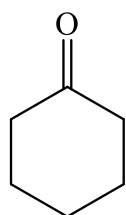
propanone
acetone



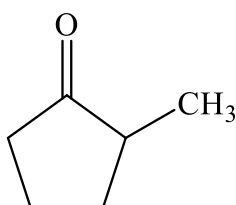
2-butanone
ethylmethylketone



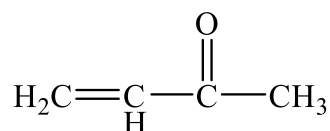
3-pentanone
diethylketone



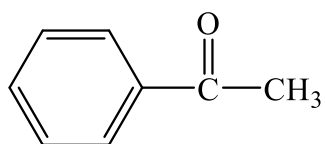
cyclohexanone



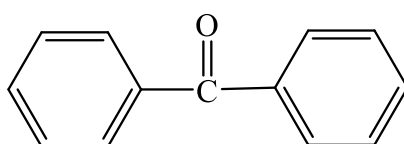
2-methylcyclopentanone



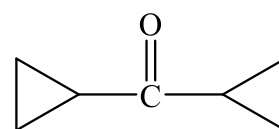
3-buten-2-one
methylvinylketone



acetophenone
(methylphenylketone)



benzophenone
(diphenylketone)



dicyclopropylketone

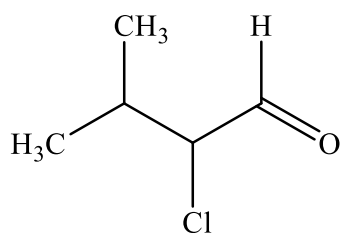
Nomenclature of aldehydes and ketones

(al) aldehyde

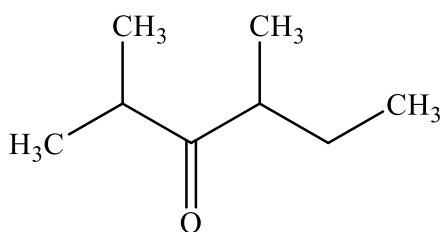
(one) ketone

alkanes < alkenes < alcohols < ketones < aldehydes < acids < esters

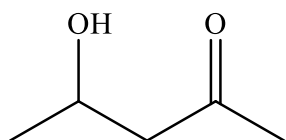
Examples :-



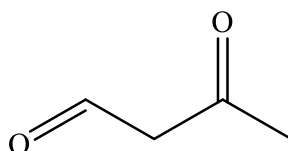
2-chloro-3-methylbutanal



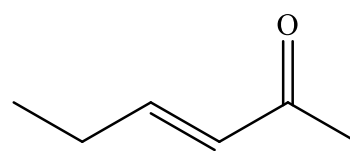
2,4-dimethyl-3-hexanone



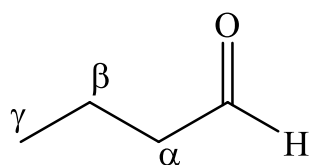
4-hydroxy-2-pentanone



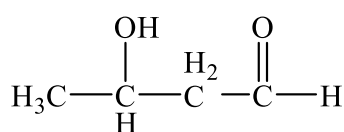
3-oxobutanal



3-hexene-2-one



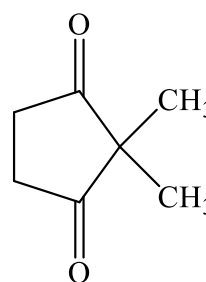
Aldehyde



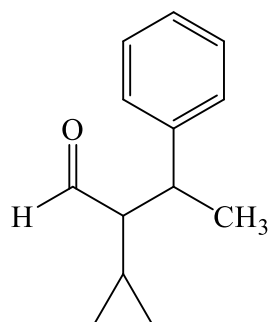
3-hydroxybutanal

β -hydroxybutyraldehyde

Ketone

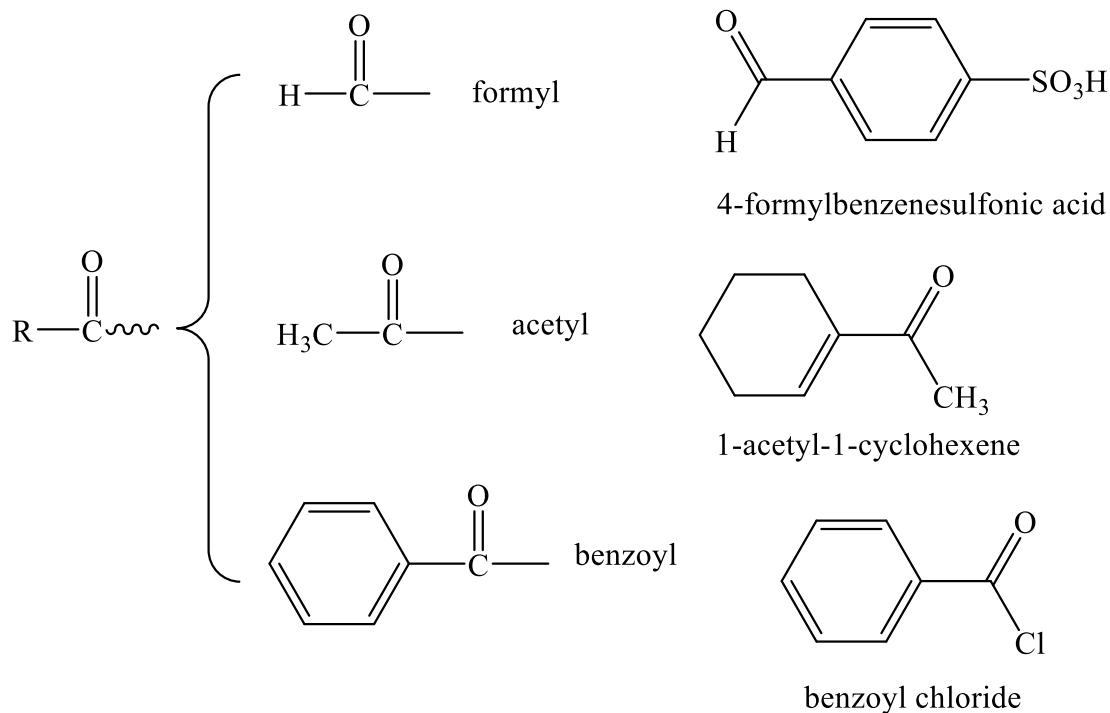


2,2-dimethylcyclopentane-1,3-dione



2-cyclopropyl-3-phenylbutanal

Acyl groups

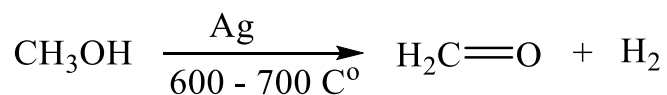


Benzyl group

Benzyl alcohol

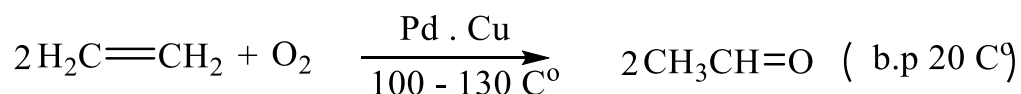
Common Aldehyde and Ketones

Formaldehyde

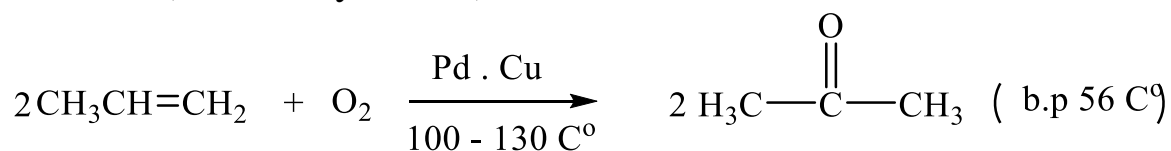


Formaldehyde is a gas (b.p -21C°) Formalin (37% aqueous solution of formaldehyde).

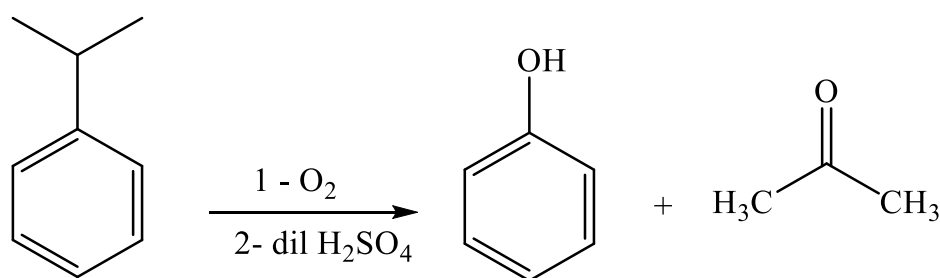
Acetaldehyde (Wacker synthesis)



Acetone (Wacker synthesis)



From isopropyl benzene

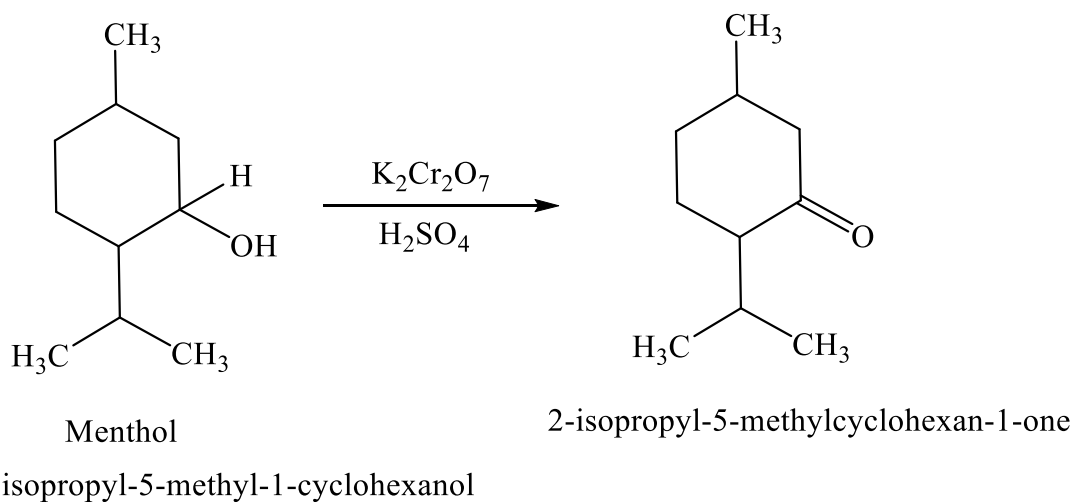
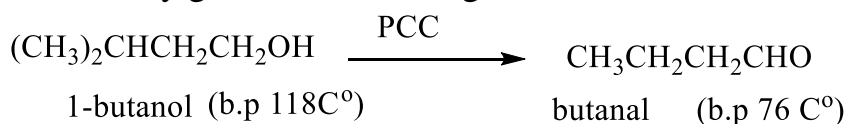


Synthesis of Aldehyde and Ketones

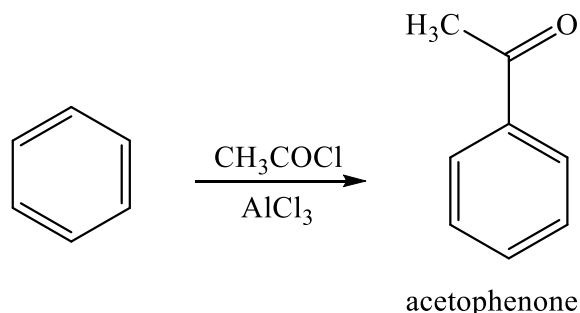
1. Oxidation of Alcohols

Primary gives aldehydes using pcc (pyridinium chloro chromate)

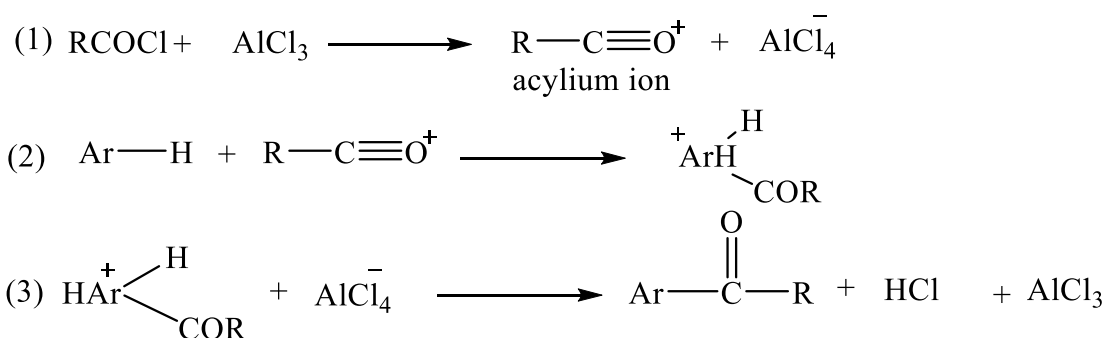
Secondary gives ketones using KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$



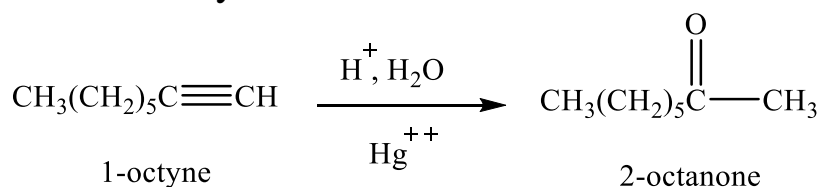
2. Friedel- Crafts



The most likely mechanism for Friedel – Crafts acylation is analogous to the carbonium ion Mechanism for Friedel – Crafts alkylation , which Involves the following steps:-

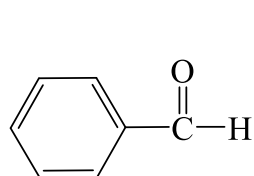


3. From Alkynes

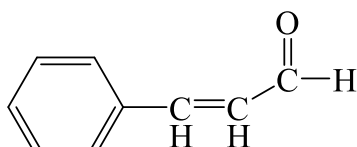


Naturally occurring Aldehyde and Ketones

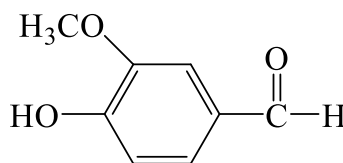
Aldehydes and ketones occur very widely in nature. give several more. Many aldehydes and ketones have pleasant odors and flavors and are used for these properties in perfumes and other consumer products (soaps, bleaches, and air fresheners, for example). However, the gathering and extraction of these fragrant substances from flowers, plants, and animal glands are extremely expensive.



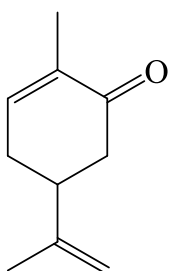
benzaldehyde
oil of almonds
b.p 178.1C°



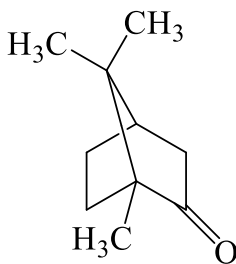
Cinnamaldehyde
Cinnamon
b.p 235 C°



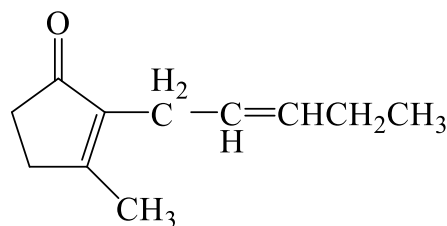
Vanillin
(Vanilla bean)
m.p 80C°, b.p 285 C°



Carvone(Spearmint oil)
b.p 231C°

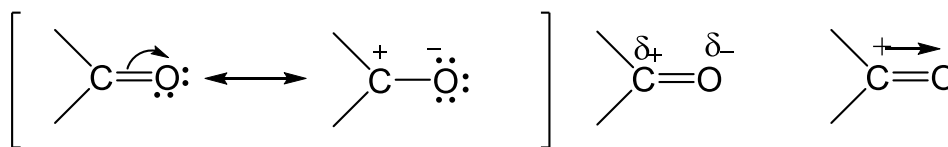


Camphor
m.p 179C°



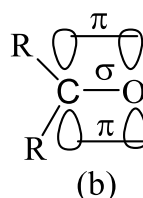
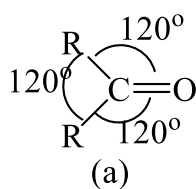
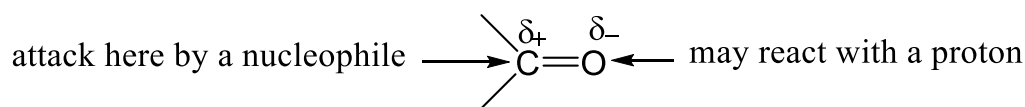
yasmone
from oil of yasmine

The Carbonyl Group



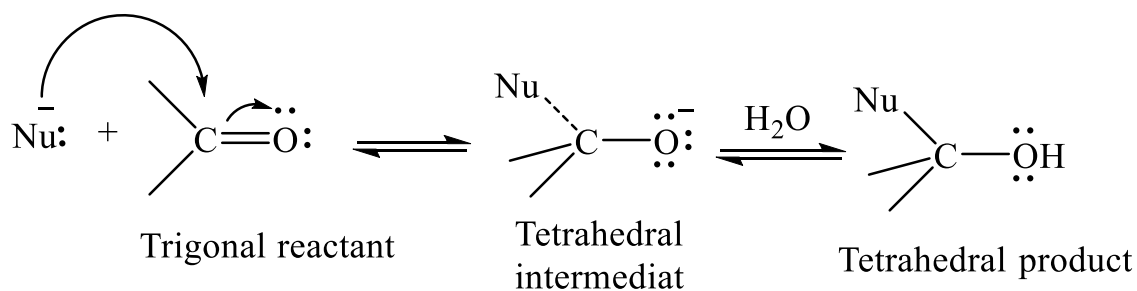
resonance contributos
to the carbonyl group

polarization of the carbonyl group

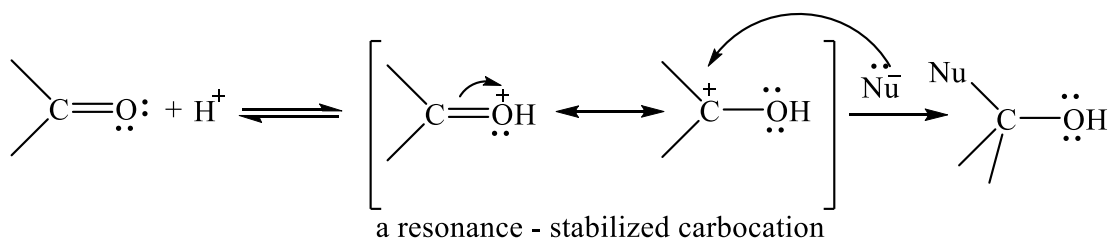


Bonding in the carbonyl group: (a) carbonyl carbon is sp²-hybridized, (b) C=O group consists of sigma and pi bonds,

Reaction of the Carbonyl group



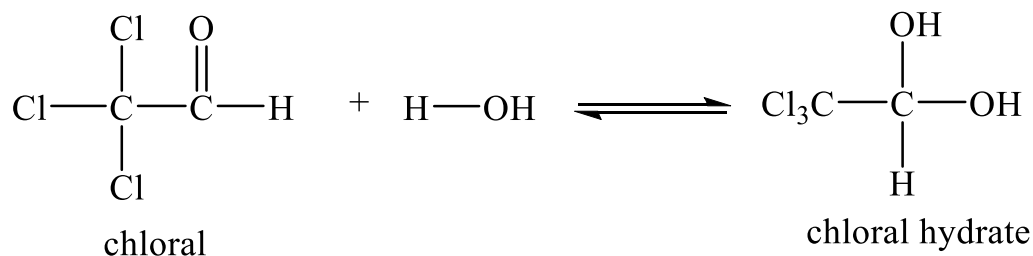
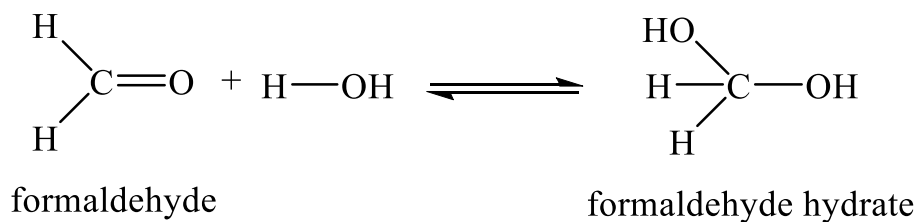
The carbonyl carbon, which is Trigonal and *sp*²-hybridized in the starting aldehyde or ketone, becomes tetrahedral and *sp*³-hybridized in the reaction product. Because of the unshared electron pairs on the oxygen atom carbonyl compounds are weak Lewis bases and can be protonated. *Acids can catalyze the addition of weak nucleophiles to carbonyl compounds* by protonating the carbonyl oxygen atom.



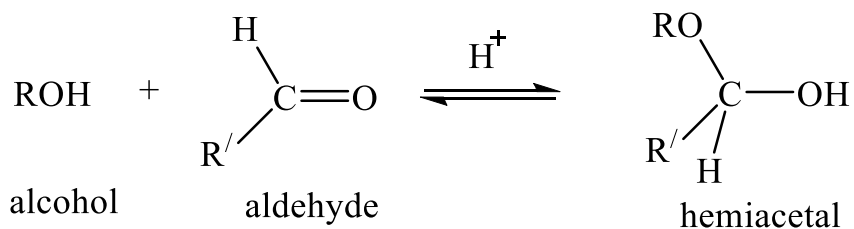
This converts the carbonyl carbon to a carbocation and enhances its susceptibility to attack by nucleophiles.

A-Hydration and Hemi acetal formation

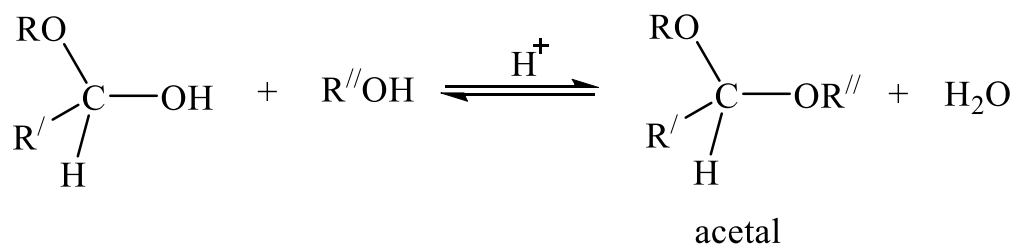
- Water adds rapidly to the carbonyl function of aldehydes and ketones . in most cases the resulting hydrate (a geminal-diol) is unstable relative to the reactants and cannot isolated .
- One being formaldehyde (a gas in its pure monomeric state) .
- Thus a solution formaldehyde in water (formalin) is almost exclusively the hydrate , or polymers of the hydrate.
- Another is chloral hydrate.



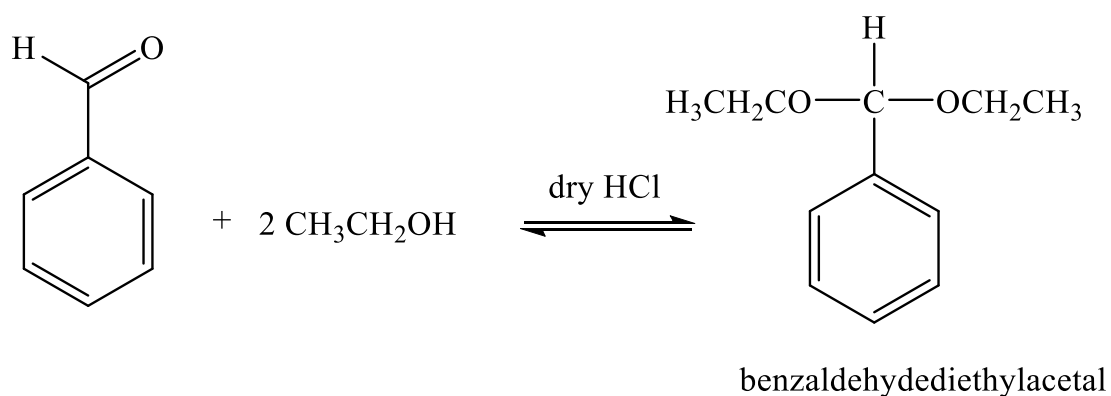
B- Addition of Alcohols

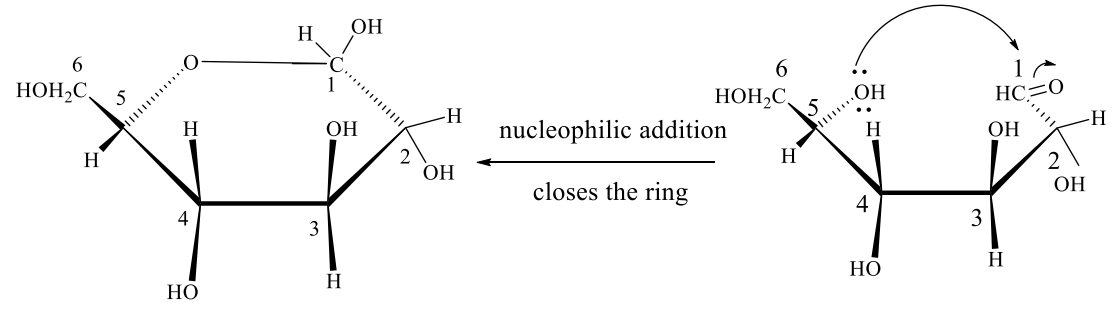
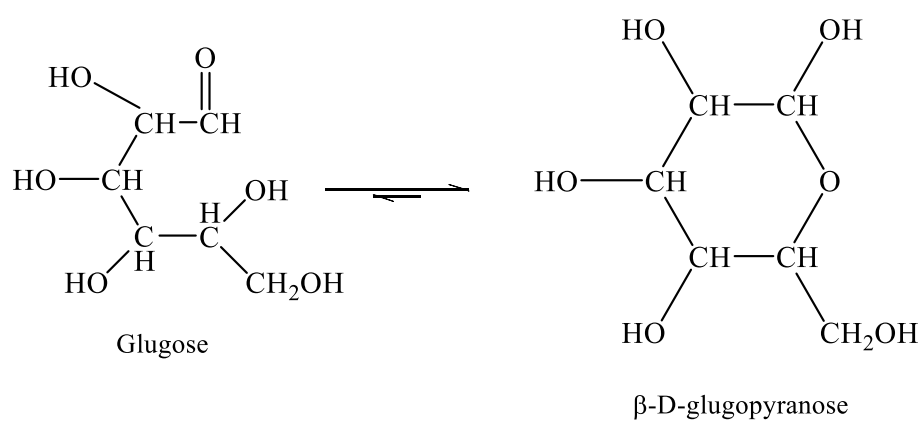
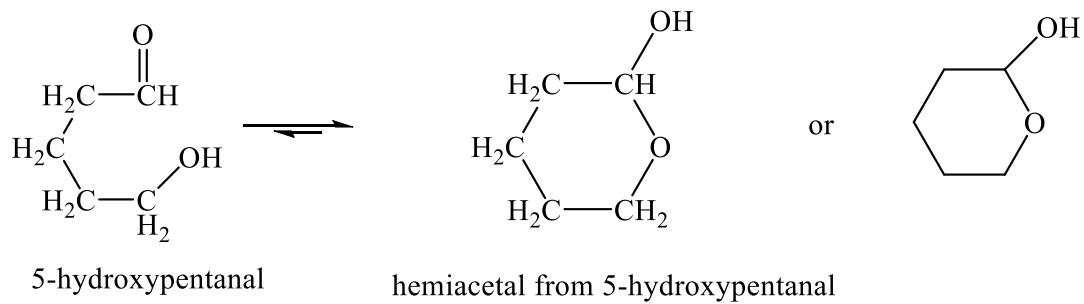


In the presence of excess alcohol hemiacetal react further from **acetal**.

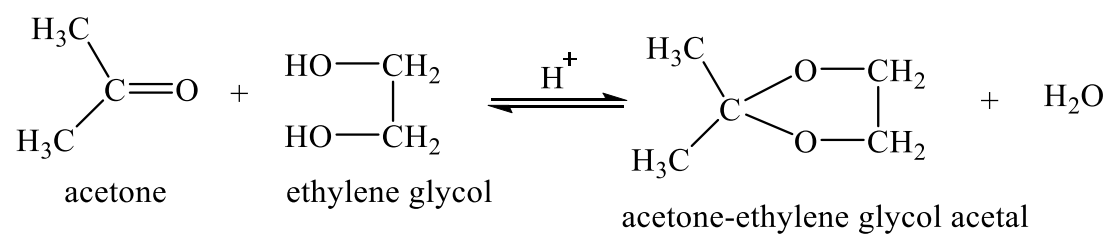


Examples



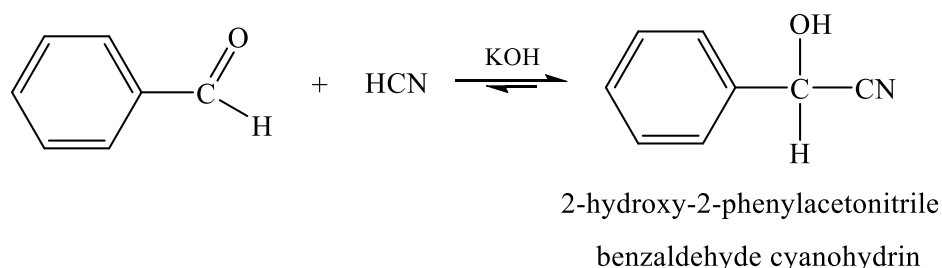
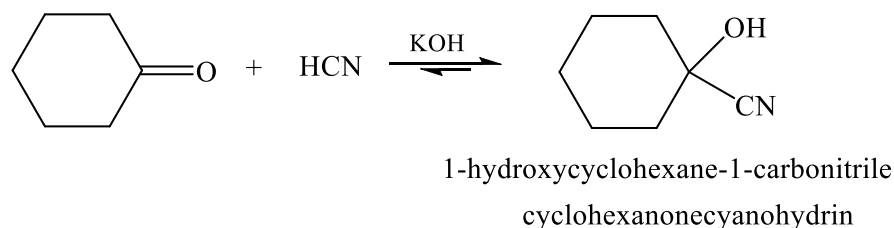
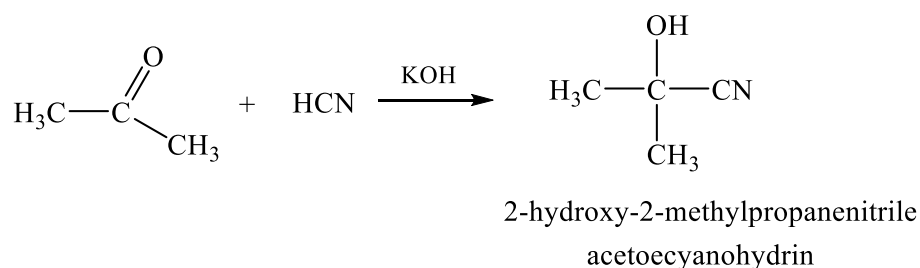
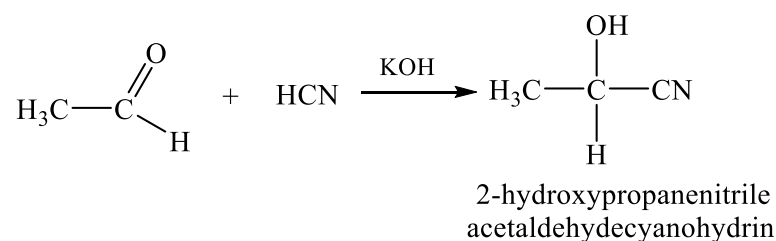


Manipulation of the Fischer projection formula of D-glucose to bring the C-5 hydroxyl group in position for cyclization to the hemiacetal form



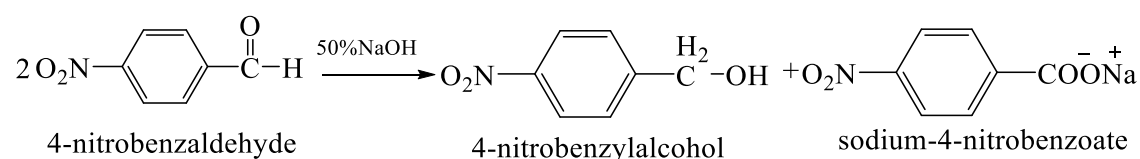
C- Addition of hydrogen cyanide to aldehydes and ketones

Hydrogen cyanide adds reversibly to the carbonyl group of aldehydes and ketones to form cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon. A basic catalyst is required



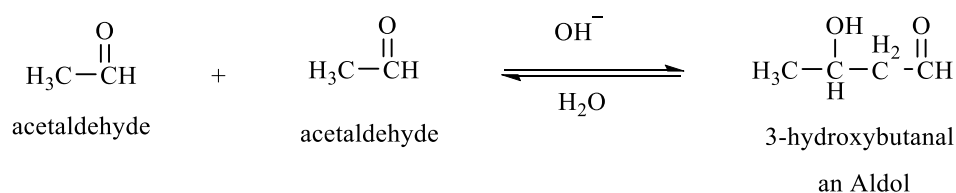
D- Cannizzaro reaction

In the presence of concentrated alkaline, aldehydes that do not contain α -hydrogen undergo **self-oxidation** and **reduction** to yield a mixture of an **alcohol** and **salt of carboxylic acid**. This reaction is called the Cannizzaro reaction.

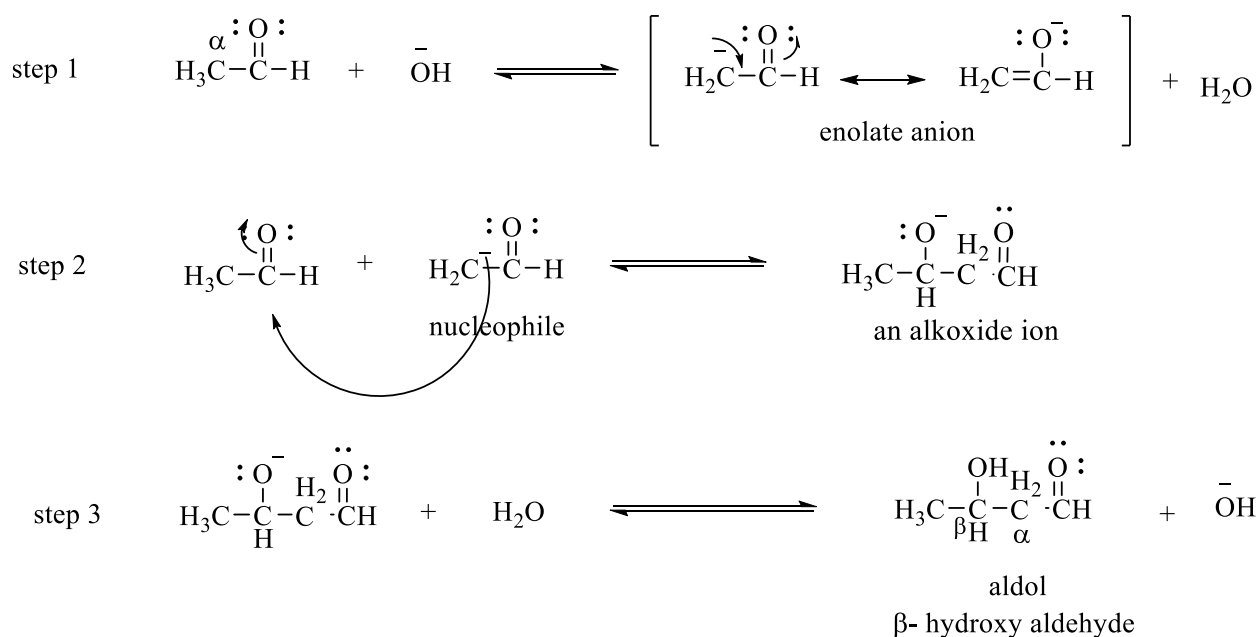


E- The Aldol Condensation

Enolate anions may act as carbon nucleophiles. They add reversibly to the carbonyl group of another aldehyde or ketone molecule in a reaction called the **Aldol condensation**, an extremely useful carbon–carbon bond-forming reaction. The simplest example of an aldol condensation is the combination of two acetaldehyde molecules, which occurs when a solution of acetaldehyde is treated with catalytic amounts of aqueous base.

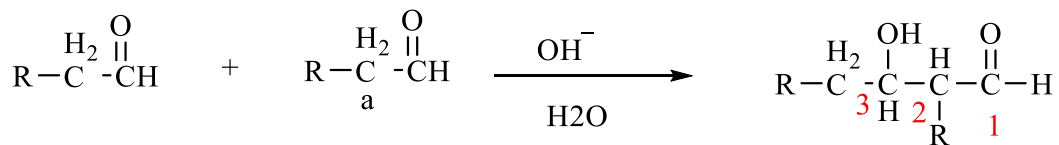


The product is called an aldol (so named because the product is both an **aldehyde and an alcohol**). The aldol condensation of acetaldehyde occurs according to the following three step mechanism:



In step 1, the base removes an α -hydrogen to form the Enolate anion. In step 2, this anion adds to the carbonyl carbon of another acetaldehyde molecule, forming a new carbon–carbon bond. Ordinary bases convert only a small fraction of the carbonyl compound to the Enolate anion so that a substantial fraction of the aldehyde is still present in the un-ionized carbonyl form needed for this step. In step 3, the alkoxide ion formed in

step 2 accepts a proton from the solvent, thus regenerating the hydroxide ion needed for the first step. In the aldol condensation, the α -carbon of one aldehyde molecule becomes connected to the carbonyl carbon of another aldehyde molecule.

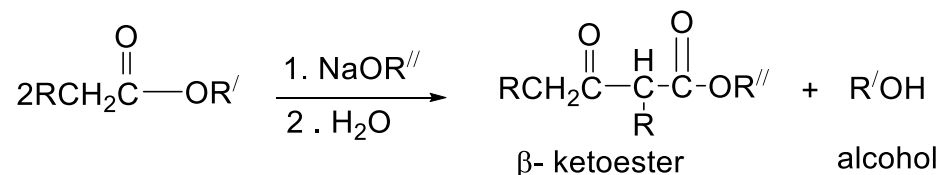


3- hydroxy aldehydes

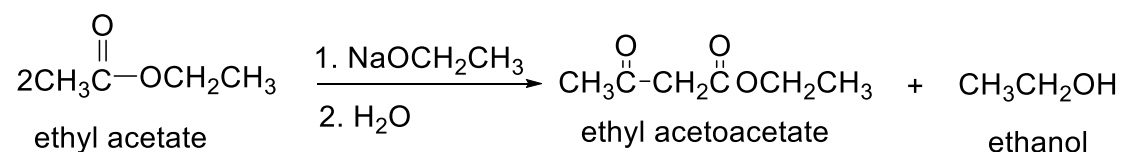
Aldols are therefore 3-hydroxyaldehydes. Since it is always the α -carbon that acts as a nucleophile, the product always has just one carbon atom between the aldehyde and alcohol carbons, regardless of how long the carbon chain is in the starting aldehyde

F- The Claisen Condensation

The main method for preparation of **β - Keto esters** is the **Claisen Condensation** . which occurs when an ester is treated with an **alkoxide base** :-

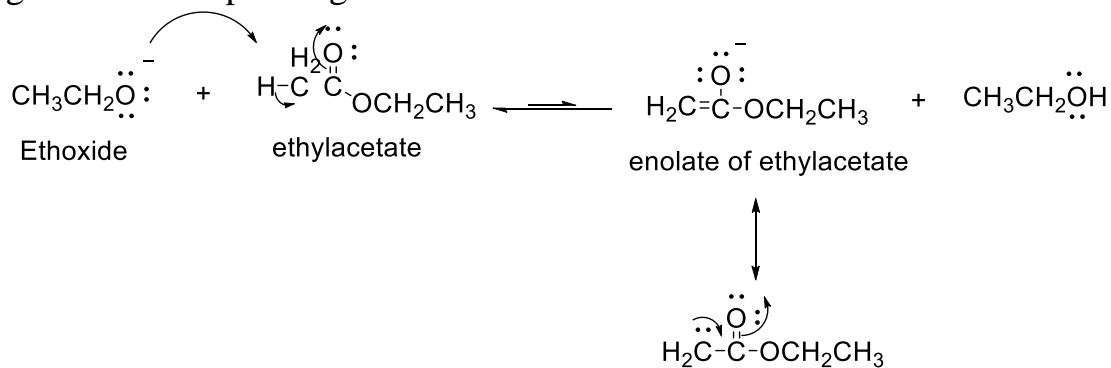


The product of the Claisen Condensation of ethyl acetate is ethyl acetoacetate.

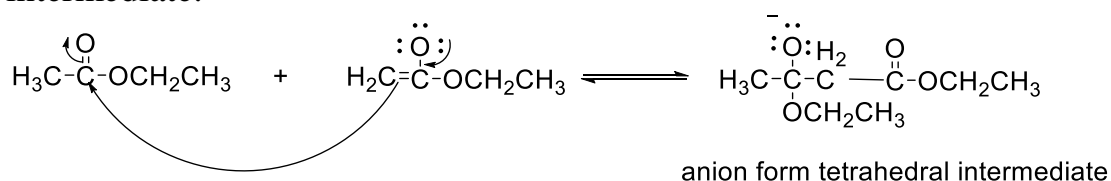


Mechanism of the Claisen Condensation

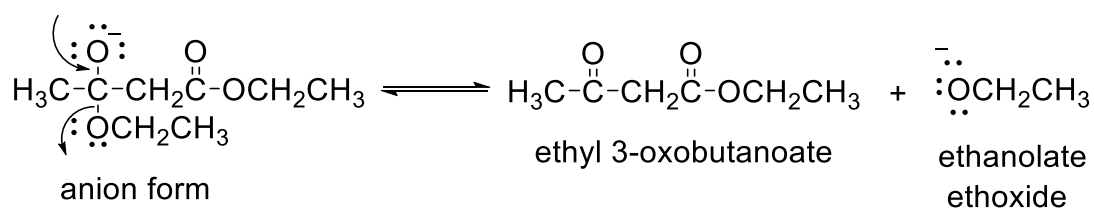
Step 1:- proton abstraction from the α – carbon atom of ethyl acetate to give the corresponding Enolate.



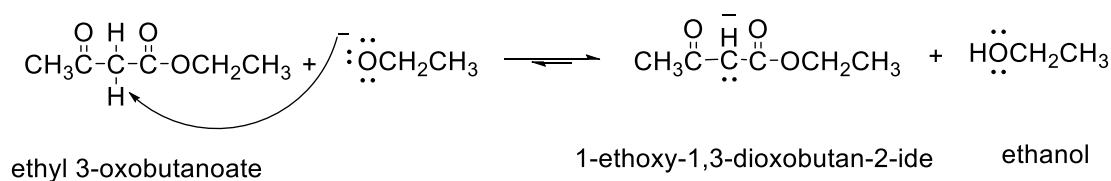
Step 2:- nucleophilic addition of the ester Enolate to the carbonyl group of neutral ester. the product is the anion form of the tetrahedral intermediate.



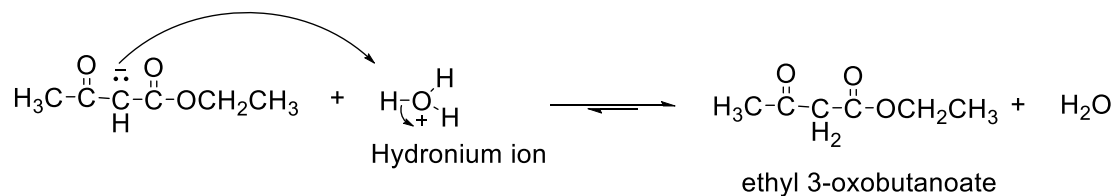
Step 3:- dissociation of the tetrahedral intermediate



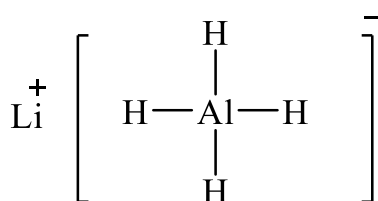
Step 4:- DE protonation of the β - Keto ester product.



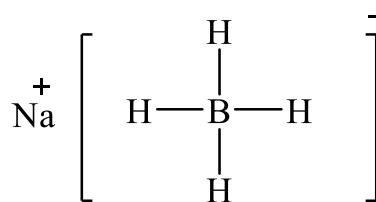
Step 5:- Acidification of the reaction mixture .



Reducing Agents



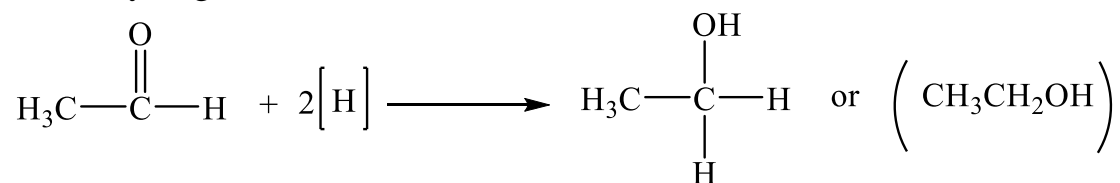
Lithiumtetrahydridoaluminate



Sodiumtetrahydridoborate

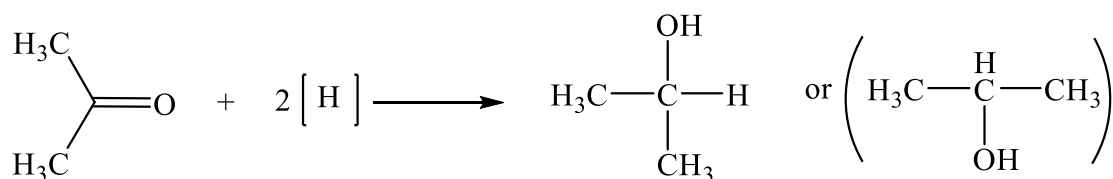
The reduction of an aldehyde

You get exactly the same organic product whether you use lithium tetra hydrido aluminate or sodium tetra hydrido borate. For example with ethanal you get ethanol.



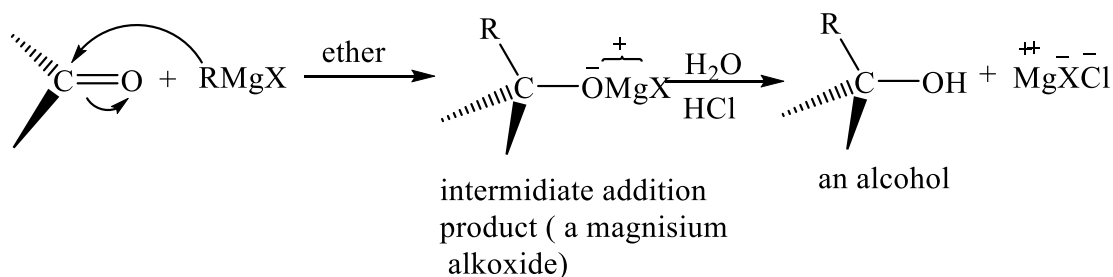
The reduction of a ketone

- Again the product is the same whichever of the two reducing agents you use.
- For example , with propanone you get 2-propanol.
- Reduction of a ketone leads to a secondary alcohol.

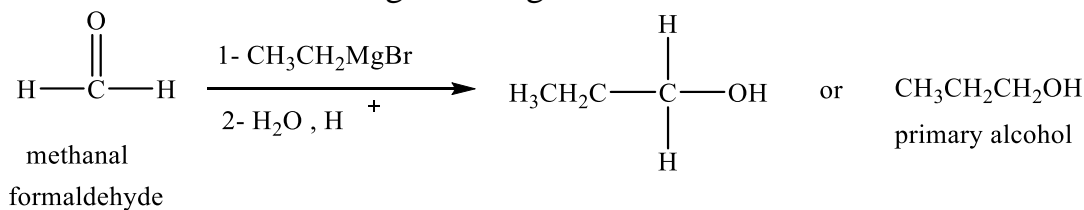


Reaction of Aldehydes and Ketones with Grignard Reagents

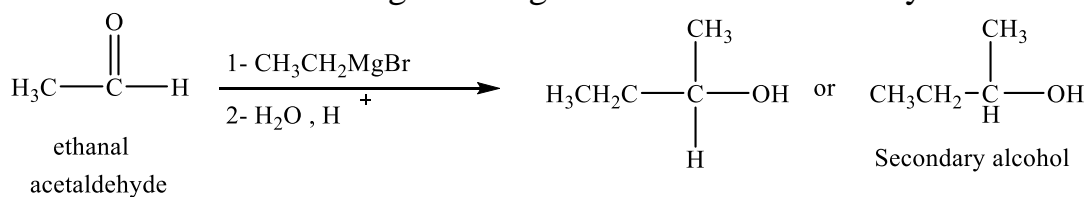
Grignard reagents act as carbon nucleophiles toward carbonyl compounds. The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon-carbon bond. In terms of acid-base reactions, the addition is favorable because the product (an alkoxide) is a much weaker base than the starting carbanions (Grignard reagent). The alkoxide can be protonated to give an alcohol.



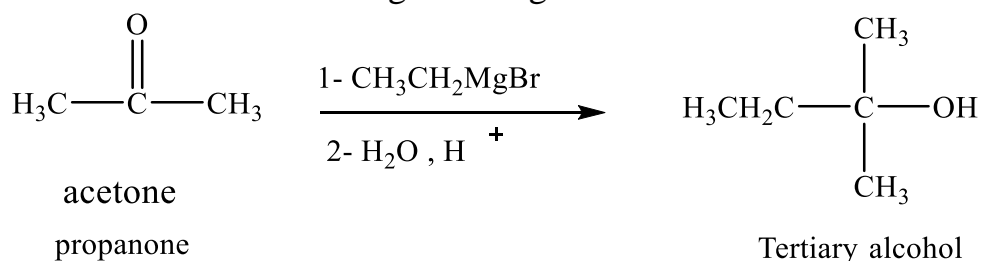
The reaction between Grignard reagents and methanal.



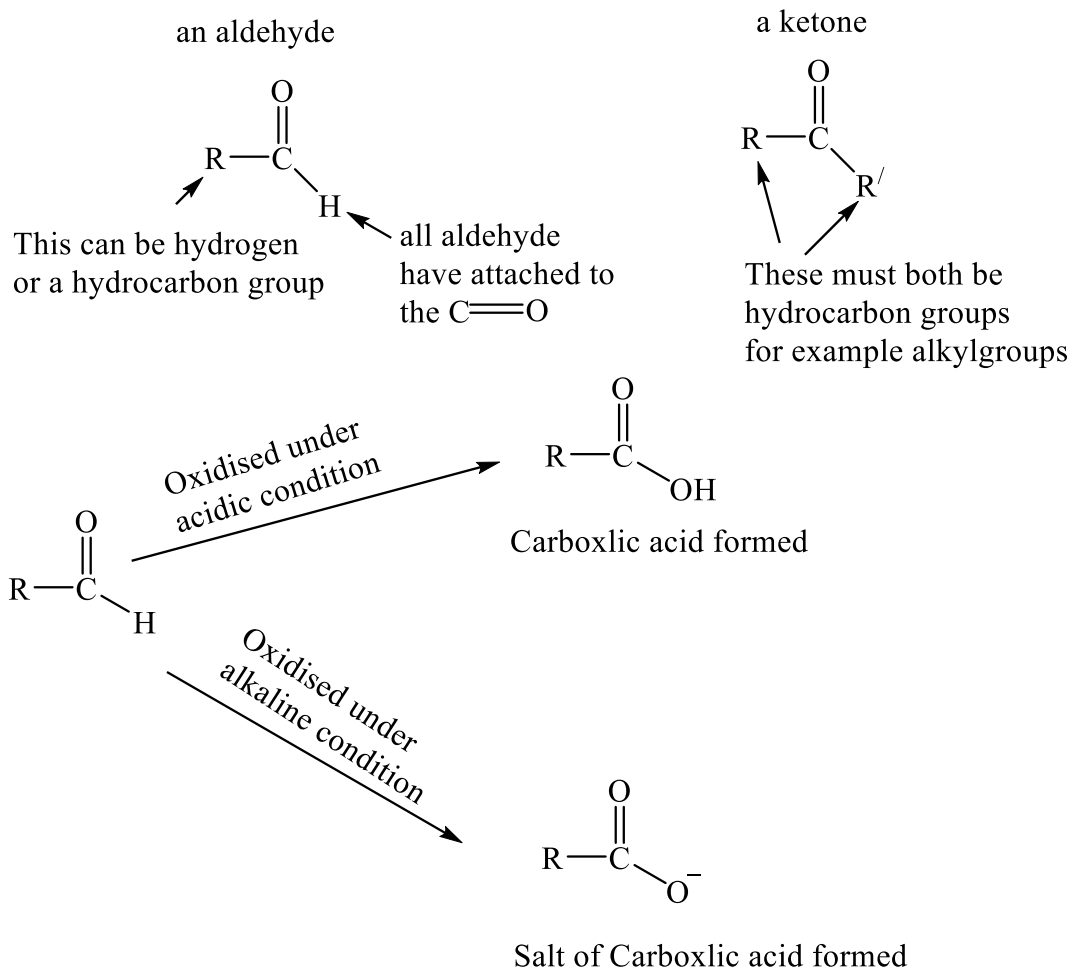
The reaction between Grignard reagents and the other aldehydes.



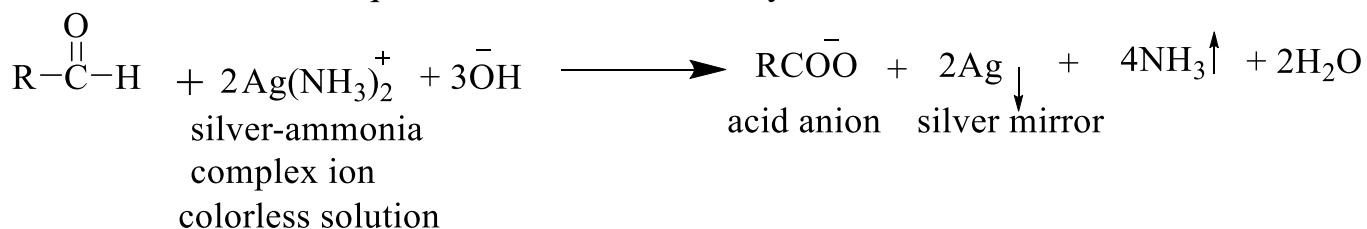
The reaction between Grignard reagents and ketones



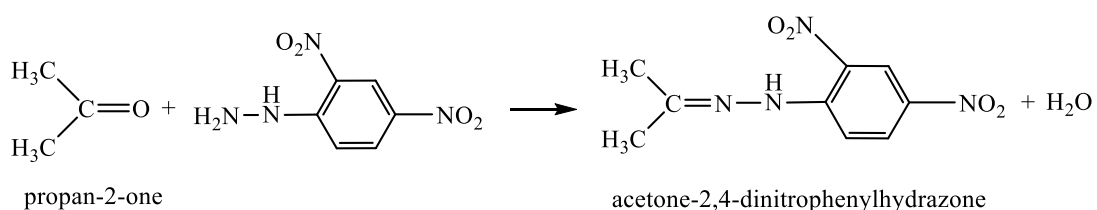
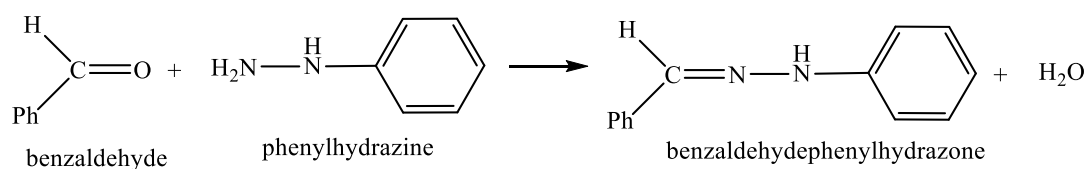
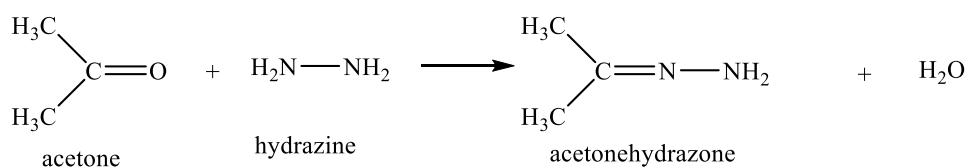
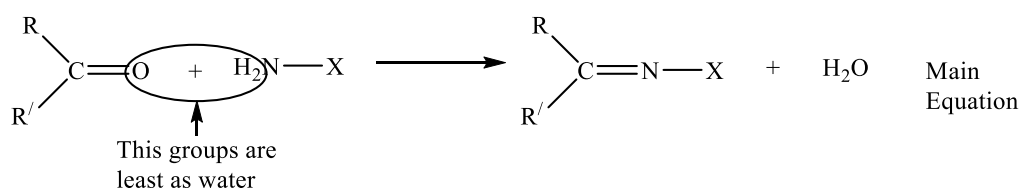
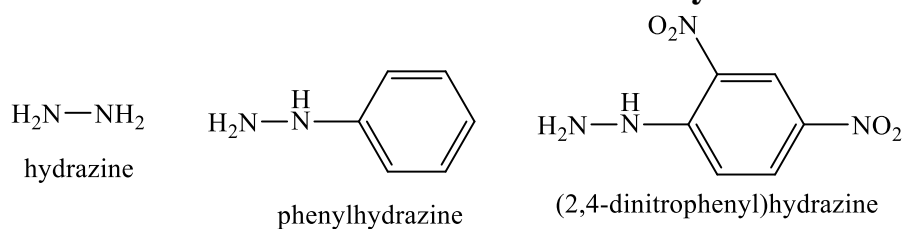
Oxidation of Aldehydes and Ketones



A laboratory test that distinguishes aldehydes from ketones takes advantage of their different ease of oxidation. In the **Tollens's silver mirror test**, the silver-ammonia complex ion is reduced by aldehydes (but not by ketones) to metallic silver. The equation for the reaction may be written as follows:

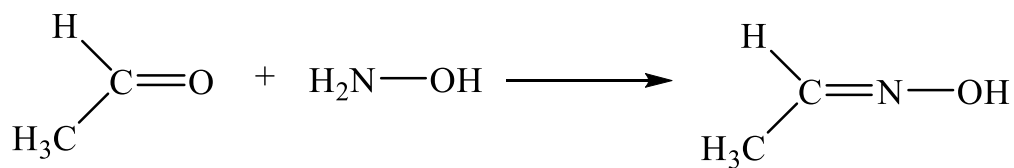


Addition – Elimination Reaction of Aldehyde and Ketone



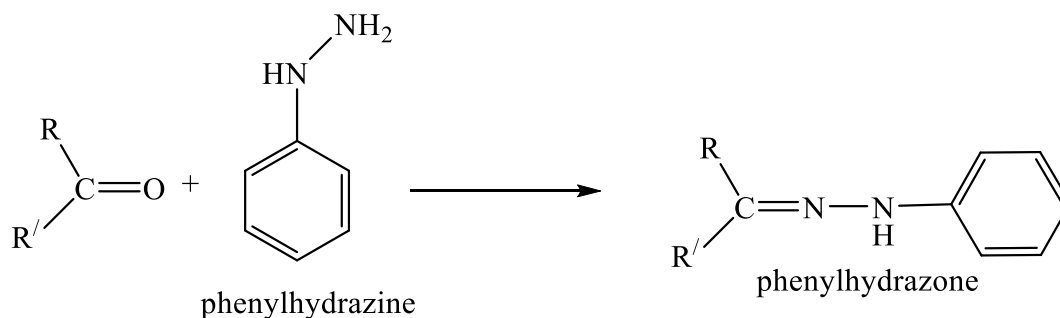
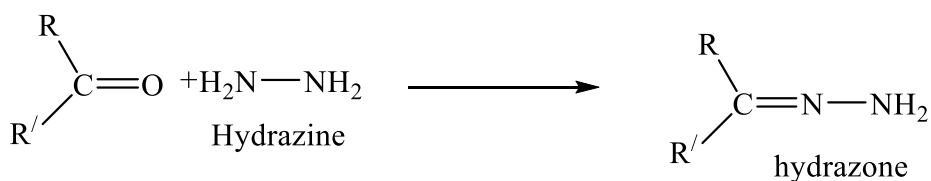
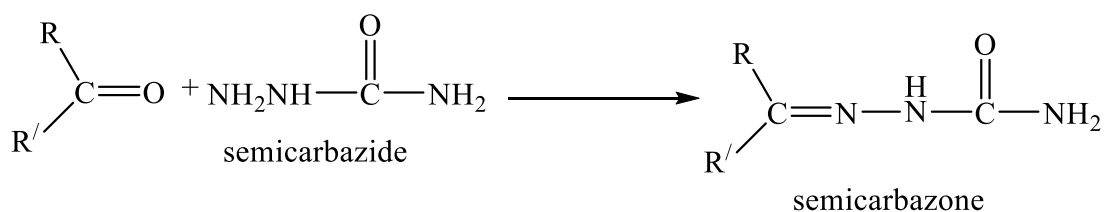
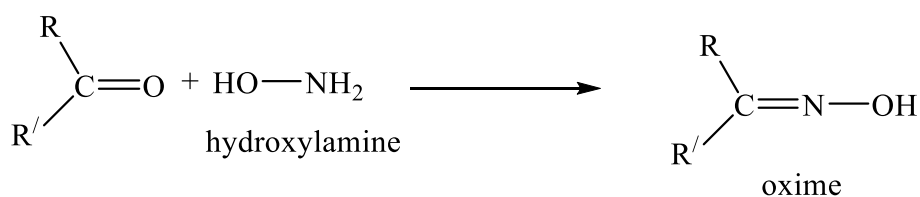
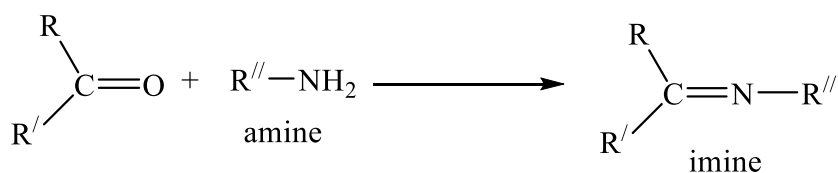
With Hydroxylamine

The product is an " oxime" for example ethanal oxime



Formation of Imines and Related compounds

The reaction of aldehydes and ketones with ammonia or 1° - amines forms imine derivatives , also known as **Schiff bases** , (Compounds having a C=N function).



Examples :-

