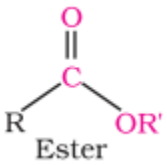
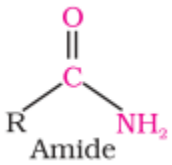
CARBONYL COMPOUNDS

Carbonyl Compounds are the organic compounds containing carbon-oxygen double bond (>C=0). It is the most important functional group of organic chemistry.

- Carbonyl compounds in which carbonyl group is bonded to a carbon and hydrogen are known as aldehydes.
- Carbonyl compounds in which carbonyl group is bonded to carbon atoms are known as ketones.
- The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides)
- Carbonyl compounds where carbon is attached to nitrogen are called amides.
- Carbonyl compounds where carbon is attached to halogen are called acid halides.



Ester



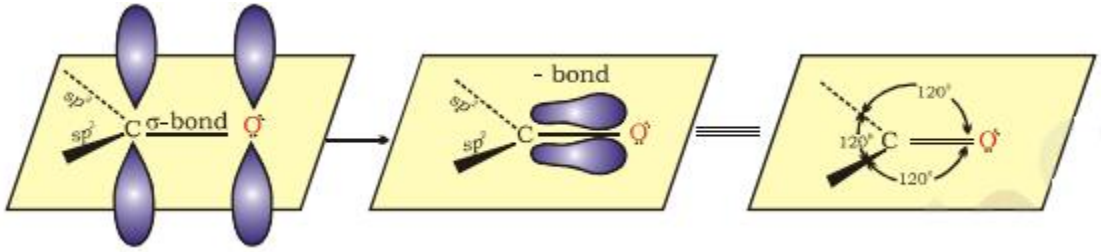
Amide

In short, carbonyl compounds can be divided into two major groups

- **Aldehydes & Ketones**
- **Carboxylic Acid & Its derivatives**

- ***Structure of Carbonyl Group***

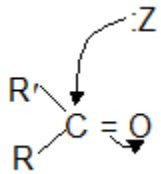
Carbonyl carbon is joined to three other atoms by s bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p-orbitals of carbon overlaps a p-orbital of oxygen to form a p bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon lies in a plane.



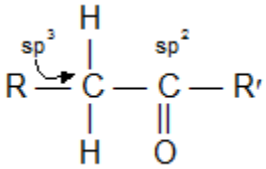
The electrons of a carbonyl double bond hold together atoms of quite different electronegativity and hence the electrons are not equally shared. Thus, the polar π-electron-cloud is pulled strongly towards the more electronegative atom, oxygen.

The carbonyl group, C = O, governs the chemistry of the aldehydes and ketones. It does this in two ways:

a) By providing a site for nucleophilic addition.



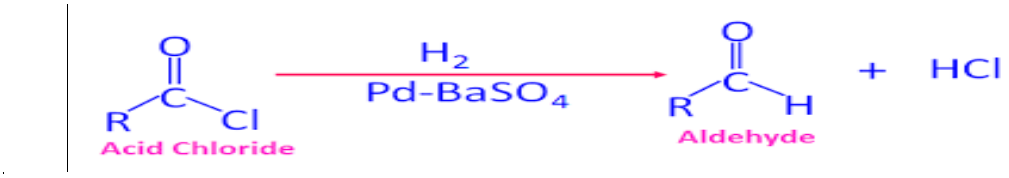
b)By increasing the acidity of hydrogen atoms attached to the alpha carbon.



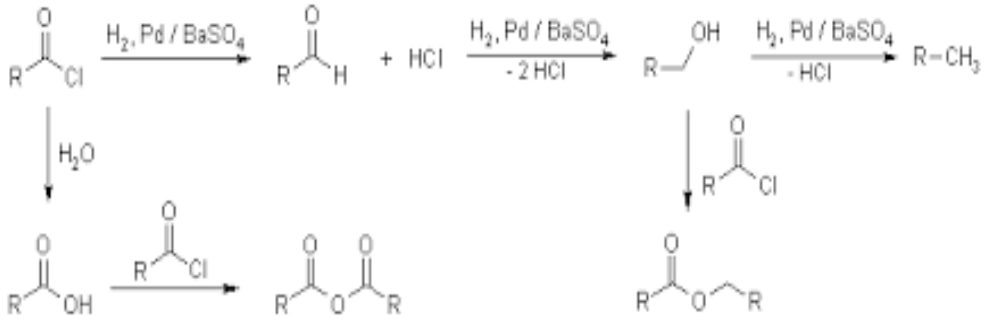
Preparation of Carbonyl compounds :

1. ***From acid chlorides (Rosenmund reduction) :***

Rosenmund reduction is the hydrogenation of an acyl chloride to an aldehyde, in presence of catalyst (Pd supported on barium sulphate). Barium sulphate partially poisons Pd metal and prevents over-reduction. Untreated Pd catalyst is too reactive. Aromatic aldehydes can also be prepared using this method.

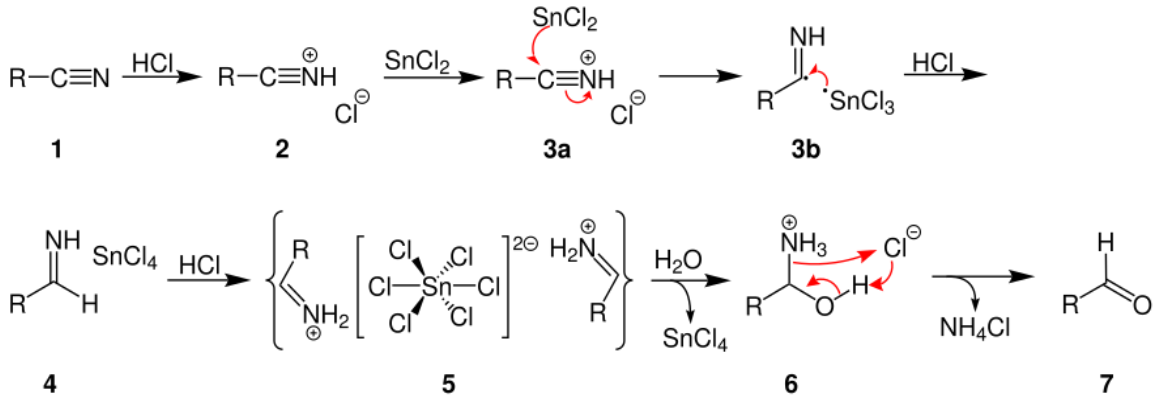


There is a wide variety of chemical transformations which involves this reaction. Some of these are-



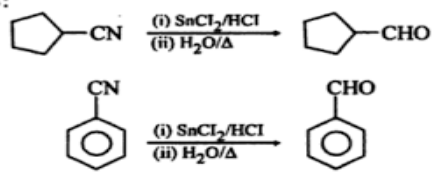
2. ***From Nitriles(Stephen Reduction) :***

Stephen reaction is also known as Stephen aldehyde synthesis or Stephen Reduction .Alkyl nitriles undergo reduction with the help of tin (II) chloride ($SnCl_2$) and hydrochloric acid and form an intermediate imine salt which undergoes hydrolysis with water, giving the final result as aldehydes. The mechanism for this reaction is given below-



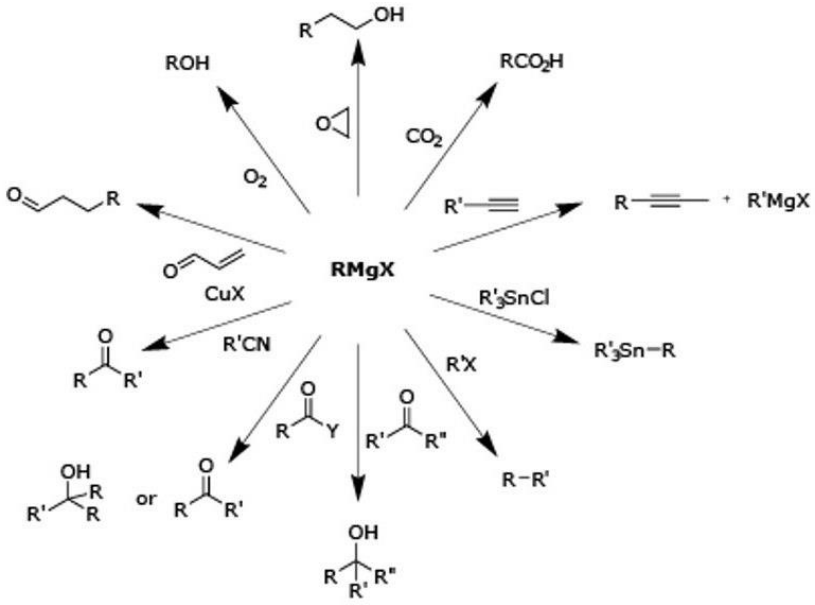
This reaction is used to prepare aldehydes from any alkyl cyanides. Some examples are-

EXAMPLES:



3. ***From Grignard reagents(RMgX) :***

Alkyl or aryl magnesium halides are called Grignard reagents. They are very widely used in the preparation of different organic compounds.

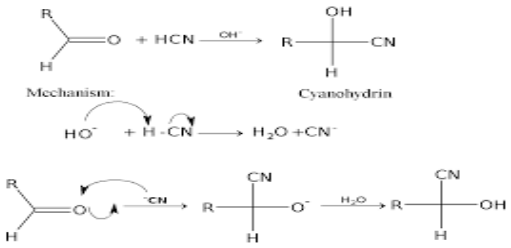


- If Grignard reagent reacts with alkyl /aryl cyanides or alkyl/aryl halides followed by hydrolysis, ketones are produced.
- If Grignard reagent reacts with carbon dioxide followed by hydrolysis, carboxylic acids are produced.
- When Grignard reagent reacts with epoxides followed by hydrolysis, a primary alcohol is produced,which on oxidation with PCC(Pyridium Chloro Chromate) gives aldehydes as a product.

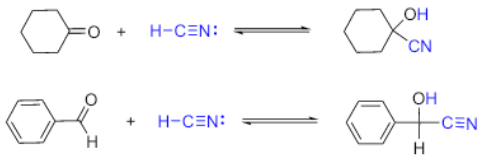
Reactions of carbonyl compounds :

Reaction with HCN:

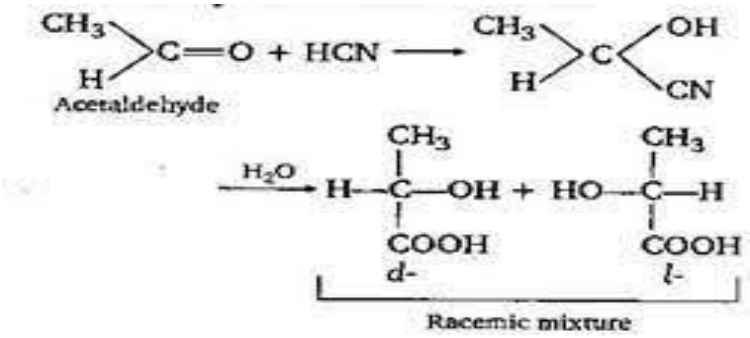
When carbonyl compounds react with HCN, cyanohydrins are produced.



Some examples are:

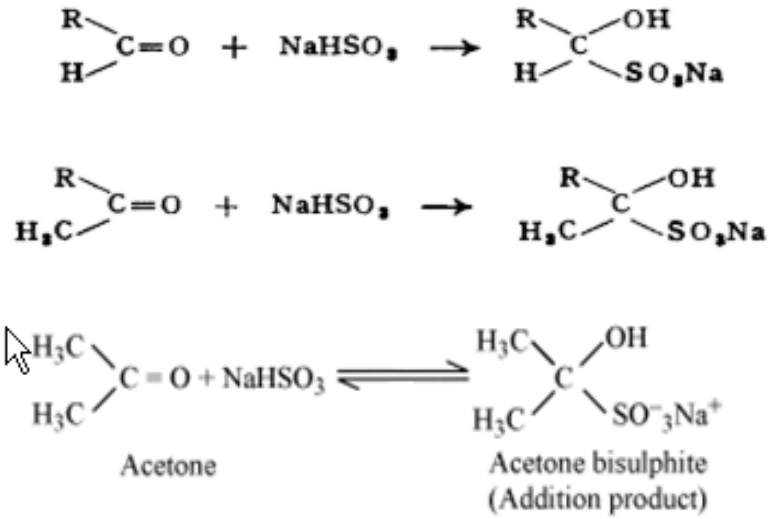


These cyanohydrins can be very useful to prepare α-hydroxy acids. For example, acetaldehyde can be converted to lactic acid by the following method-



Reaction with sodium bisulphate:

Carbonyl compounds undergo addition reaction with sodium bisulphate solution and produce a white precipitate. This reaction is useful as an identification test for carbonyls.

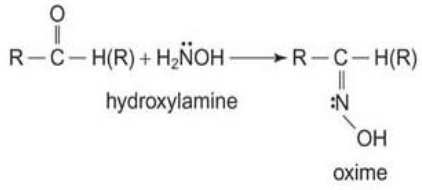


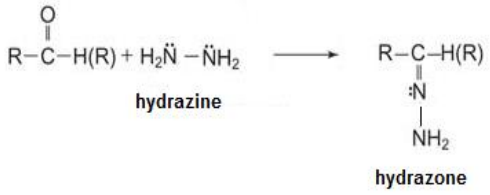
Reaction with ammonia derivatives:

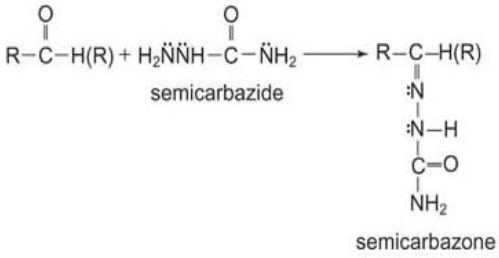
Carbonyl compounds undergo addition reactions with ammonia derivatives (NH_2 -G) to form various types of compounds. All of these reactions involves elimination of one water molecules. Hence these reactions can also be considered as condensation reactions.

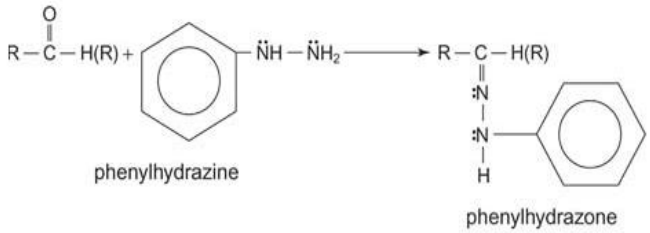
It can be noted that the reaction between carbonyls with 2,4 –DNP is very much important. When, carbonyls react with 2,4-Dinitrophenyl hydrazine (Also known as –Brady's reagent), they form orange-red/yellow-orange coloured precipitate

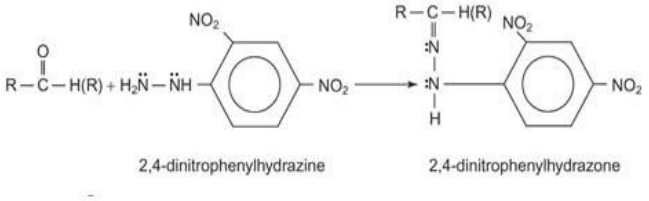
of 2,4-dinitrophenyl hydrazone. Thus this reaction is used to detect the presence of carbonyl group in an unknown organic compound.







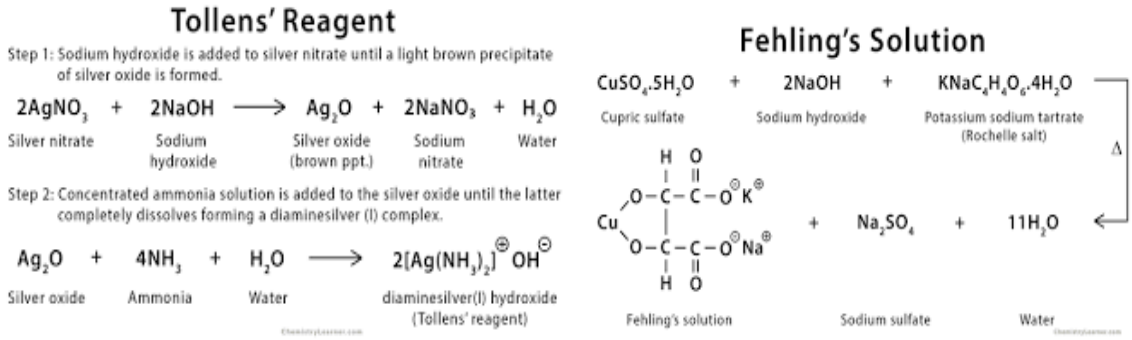




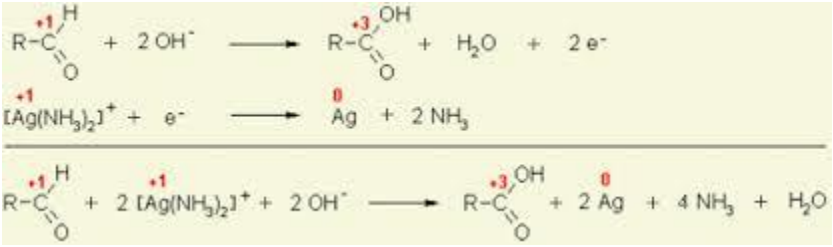
<u>Reaction with Tollen's and Fehling's reagent :</u>

Aldehydes reacts with tollens reagent to produce grayish white precipitate of metallic silver(silver-mirror test) and when aldehydes react with Fehlings reagent, they form a reddish brown precipitate of Copper(I) oxide. This are redox reactions where the Ag(I) is reduced to Ag or Cu(II) is reduced to Cu(I) and acetaldehyde is oxidized to carboxylic acid.

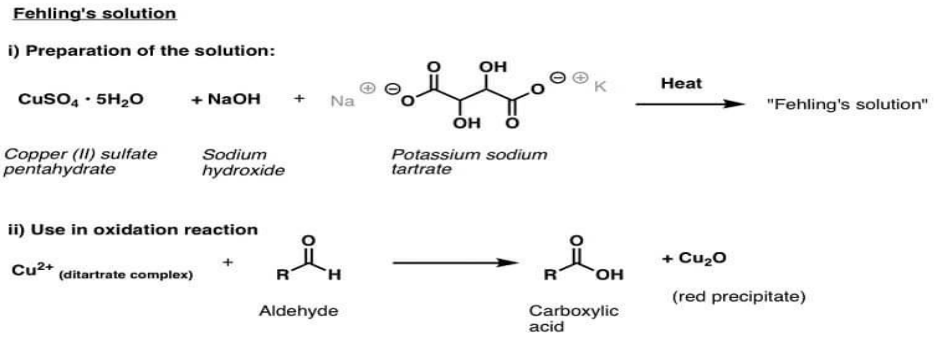
Ketones do not respond to these tests.



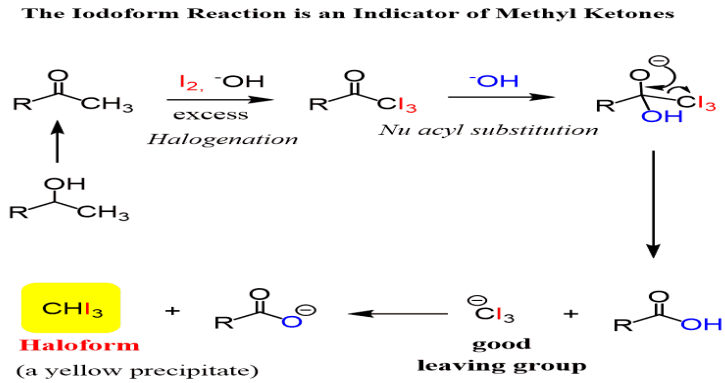
Reaction of aldehydes with Tollens reagent.:



Reaction of aldehydes with Fehling's reagent :



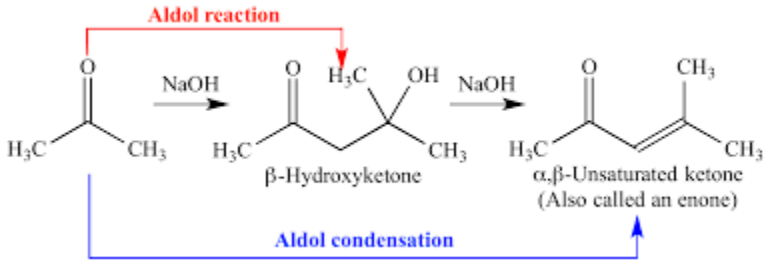
Iodoform test :Compounds containing keto-methyl group (CH_3CO) when is treated with iodine in presence of alkali (NaOH/KOH), then yellow ppt of iodoform is obtained.



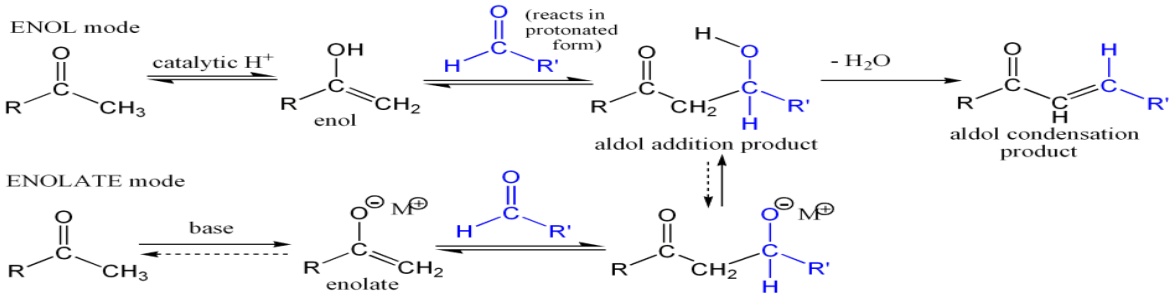
Aldol condensation :

An aldol condensation is a condensation reaction in organic chemistry in which an enol or an enolate ion reacts with a carbonyl compound to form a β-hydroxyaldehyde or β-hydroxyketone (an aldol reaction), followed by dehydration to give a conjugated enone.

It can be noted that only the carbonyl compounds containing at least one α-hydrogen can take part in this reaction.



Mechanism :



Examples :

(a) $2CH_3CHO \xrightarrow{Dil.NaOH} CH_3CHOHCH_2CHO$

(b) $2CH_3COCH_3 \xrightarrow{Dil.NaOH} CH_3COHCH_3CH_2COCH_3$

(c) $2HCHO \xrightarrow{Dil.NaOH} CH_3OH$

(d) $C_6H_5CHO + HCHO \xrightarrow{Dil.NaOH} C_6H_5CH_2OH$

Cannizzaro reaction :

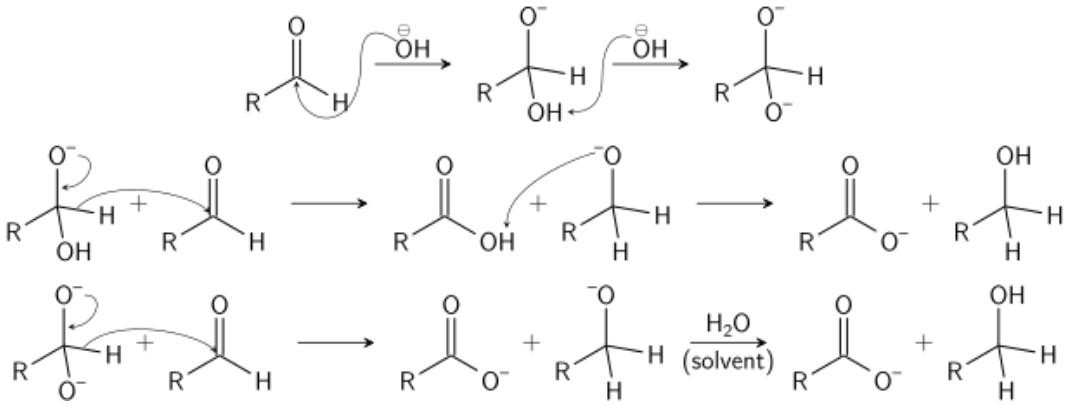
The disproportionation reaction of aldehydes without α-hydrogens in presence of a strong base to furnish an alcohol and a carboxylic acid is called Cannizzaro reaction. One molecule of aldehyde is reduced to the corresponding alcohol, while a second one is oxidized to the carboxylic acid.

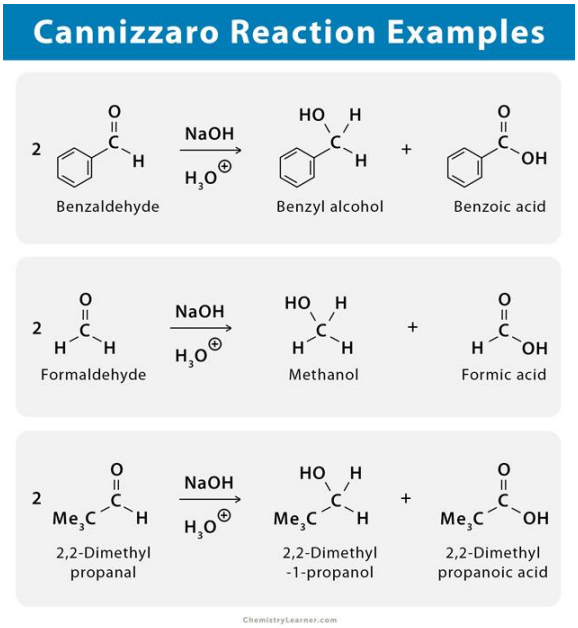
The applicability of Cannizzaro reaction in organic synthesis is limited as the yield is not more than 50% for either acid or alcohol formed.

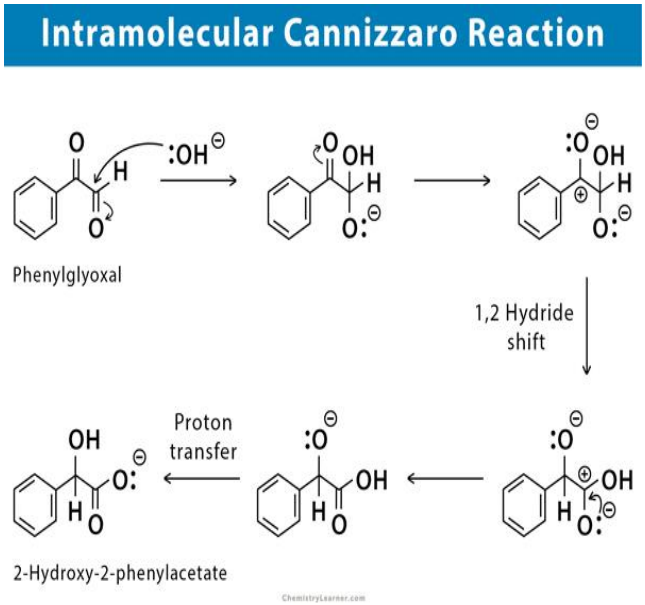
In case of aldehydes that do have α-hydrogens, the aldol condensation reaction takes place preferentially.

The α,α,α-Trihalo aldehydes undergo haloform reaction in strongly alkaline medium. e.g. Choral will give chloroform in presence of an alkali.

Mechanism :



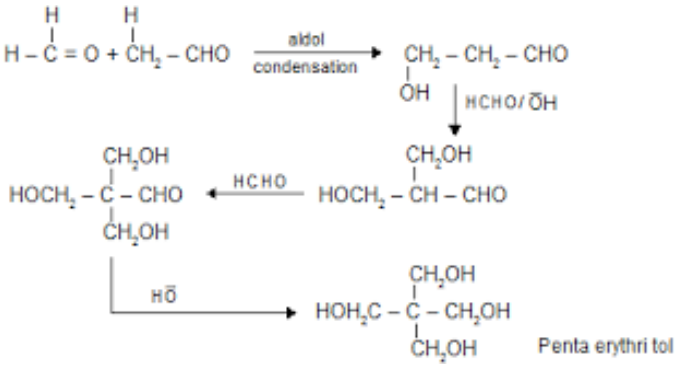




Formation of pentaerythol :

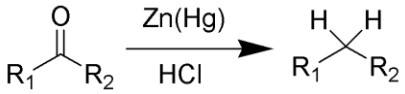
When acetaldehyde and formaldehyde reacts with each other in alkaline condition, a series of three aldol reactions and one cannizzaro reaction occurs and pentaerythol is obtained as the product.

Mechanism :



Clemmensen reduction :

When carbonyl compounds are treated with Zinc-amalgam (Zn-Hg) in the presence of conc. Hcl, the Co group gets reduced to CH_2 group. This reaction is called- Clemmensen reduction. This is a very good reaction to prepare alkanes from carbonyls.



Examples :

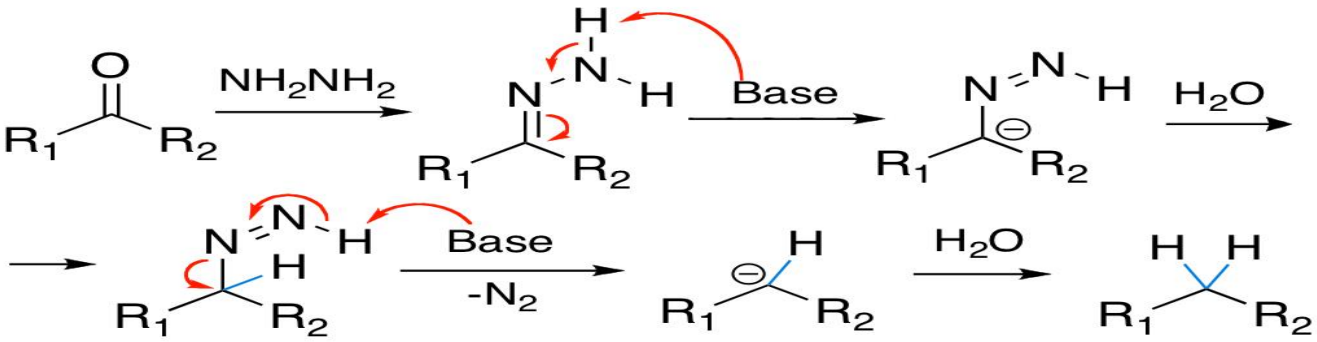
$$RCOR \xrightarrow[HCl]{Zn\text{-}Hg} RCH_2R + H_2O$$

$$CH_3CHO + 4[H] \xrightarrow[HCl]{Zn\text{-}Hg} \underset{\text{Ethane}}{CH_3{-}CH_3} + H_2O$$

$$CH_3COCH_3 + 4[H] \xrightarrow[HCl]{Zn\text{-}Hg} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

Wolff-Kishner reduction:

It is a method of reduction of aldehydes and ketones to alkanes. Condensation of the carbonyl compound with hydrazine forms the hydrazone, and treatment with base induces the reduction of the carbon coupled with oxidation of the hydrazine to gaseous nitrogen, to yield the corresponding alkane.



It can be noted that both the Clemmensen and Wolf-kishner method produces same product,but the Clemmensen reduction occurs in acid medium and Wolf-kishner reaction occurs in neutral medium. So, if the substrate gets affected by the acid medium, Clemmensen reaction is not performed but Wolf –Kishner method can be used in that case.

Wolff-Kishner Reduction Examples