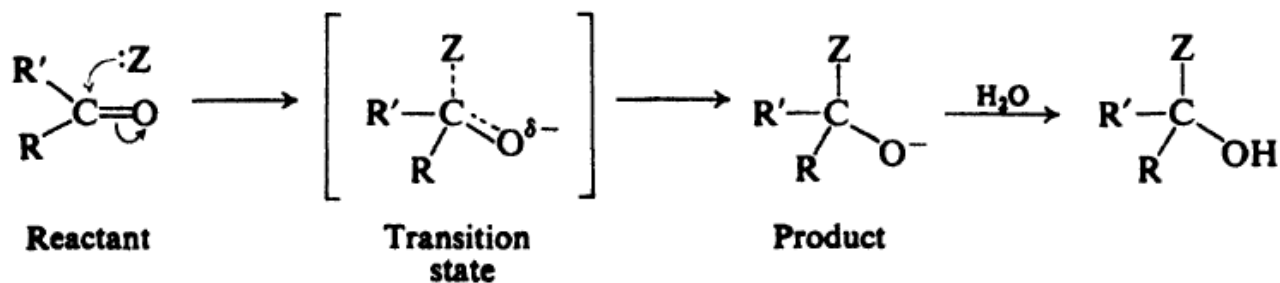


Reactions. Nucleophilic addition

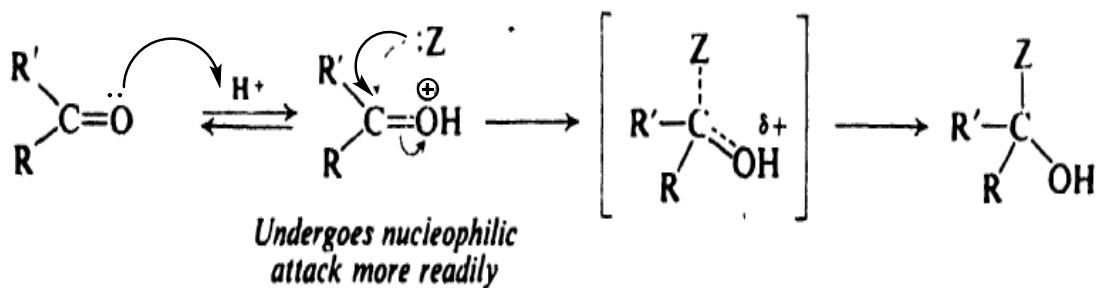
The typical reaction of aldehyde and ketones is nucleophilic addition:-

1- Without catalyst



Acid-catalyzed nucleophilic addition

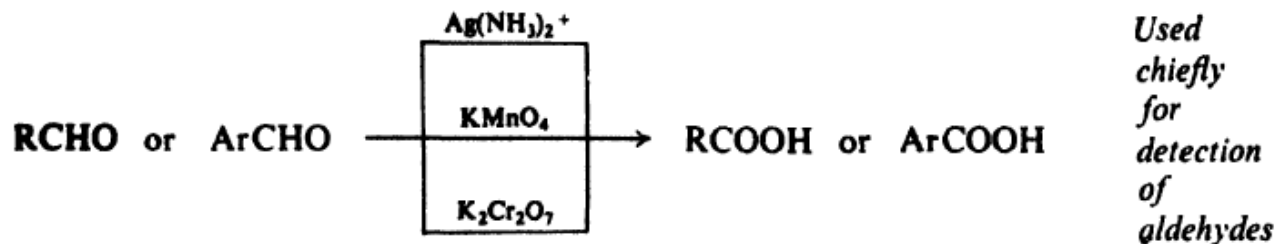
If acid is present, hydrogen ion becomes attached to carbonyl oxygen.



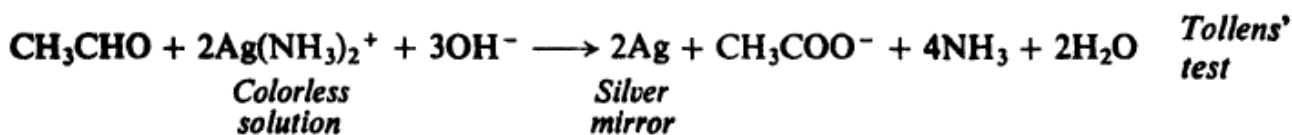
REACTIONS OF ALDEHYDES AND KETONES

1. Oxidation. Discussed in Sec. 19.9.

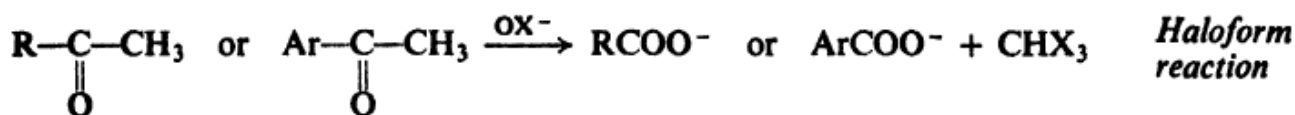
(a) Aldehydes



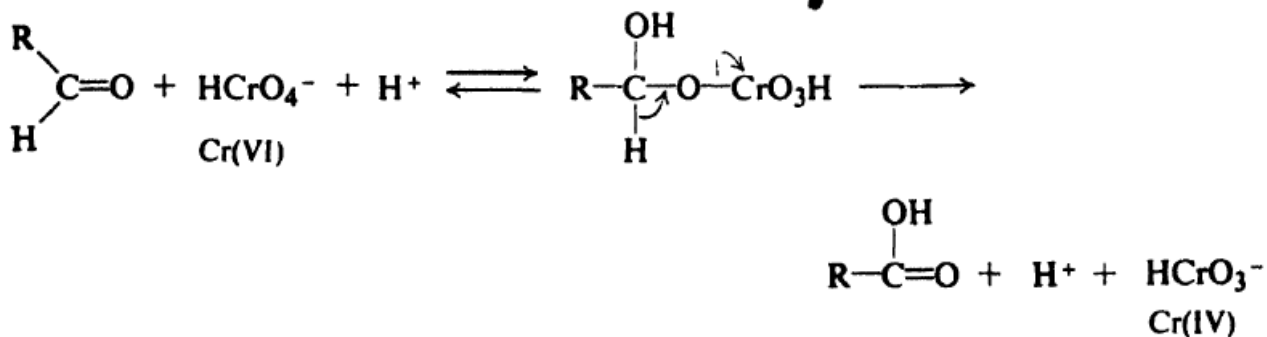
Examples:



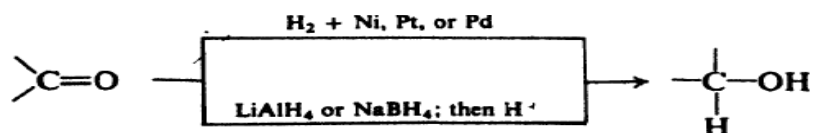
(b) Methyl ketones



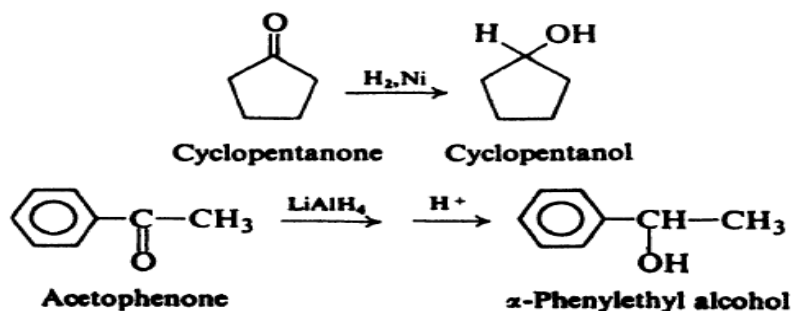
Mechanism of reaction between aldehyde and potassium dichromate



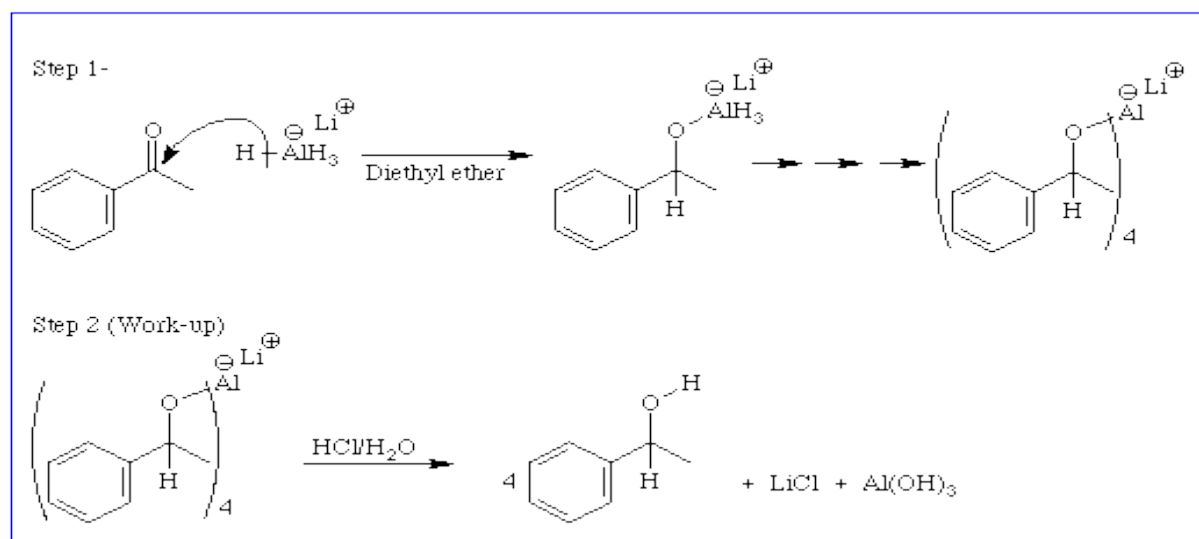
2-reduction to alcohol



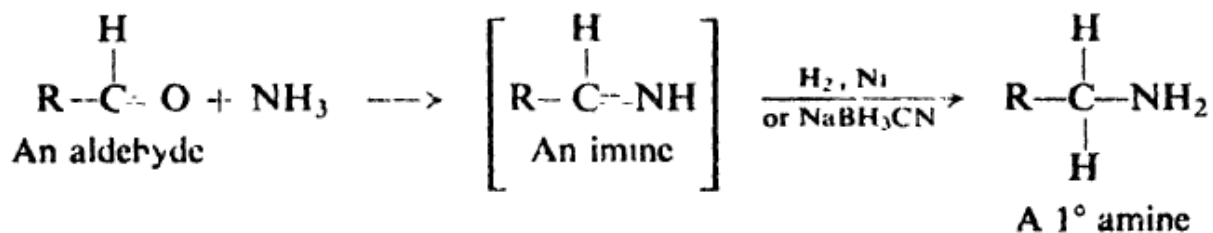
Examples:

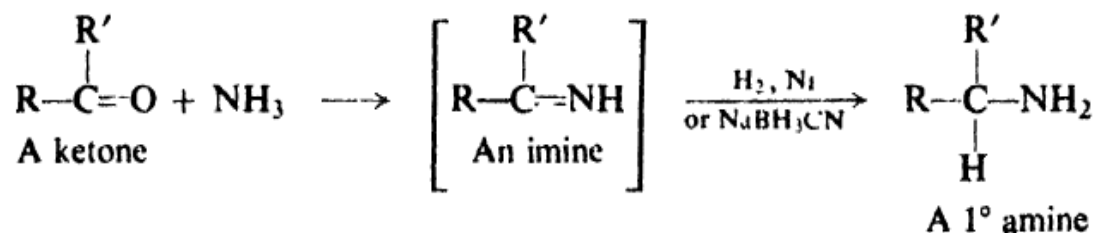


Mechanism of the reduction of acetophenone

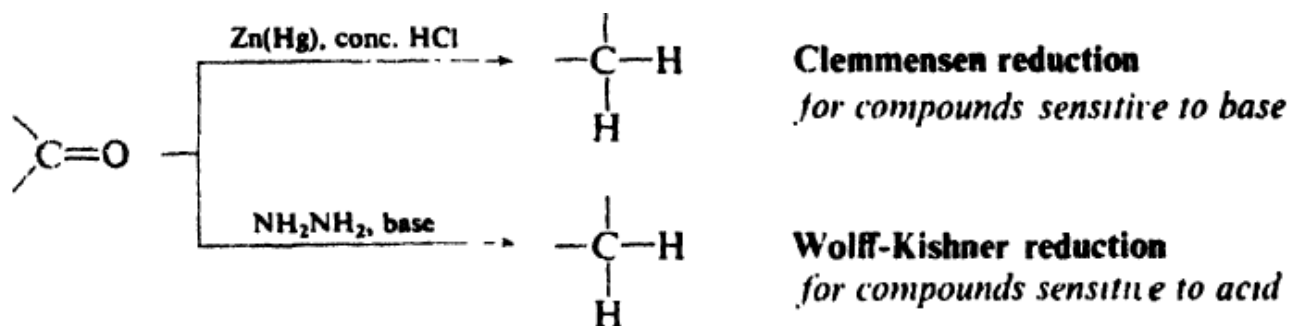


3-reduction amination

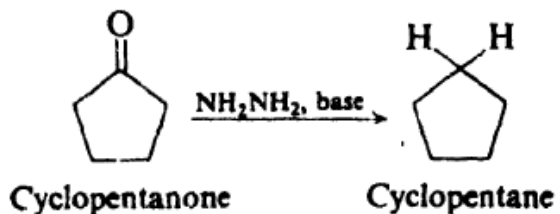
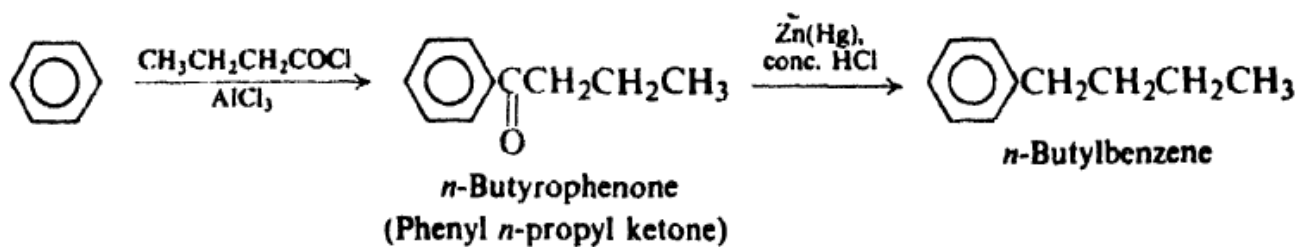




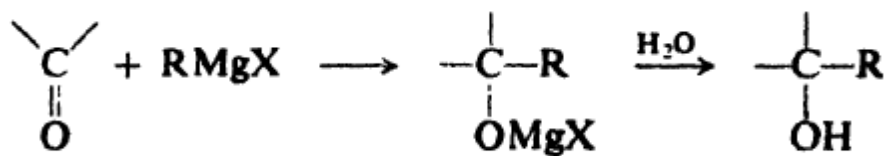
4- reduction to hydrocarbons



Examples

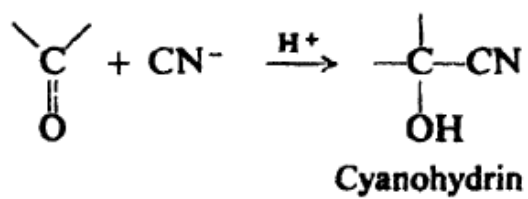
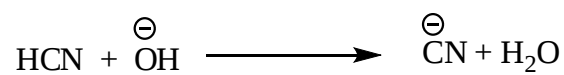


5-addition of griniard reagents

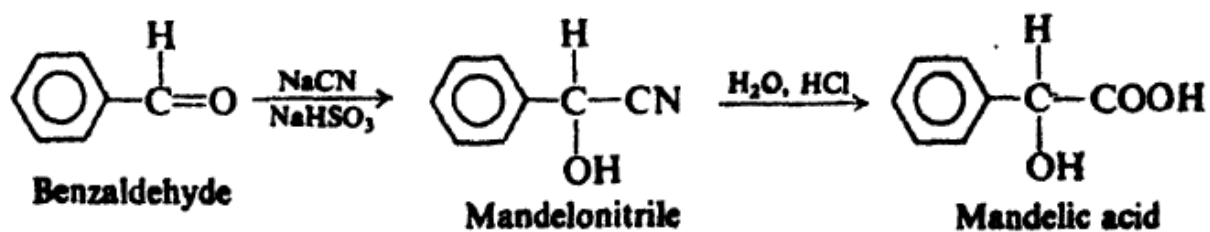


Give the mechanism of the title reaction

6-addition of cyanide to formation of cyanohydrins

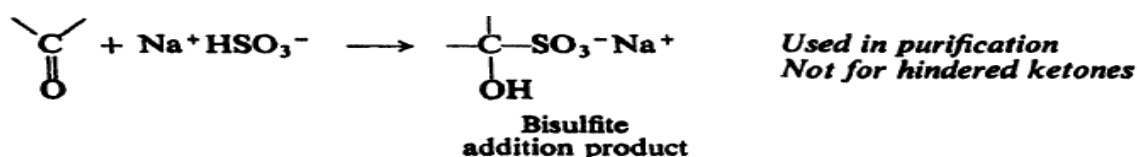


Examples:

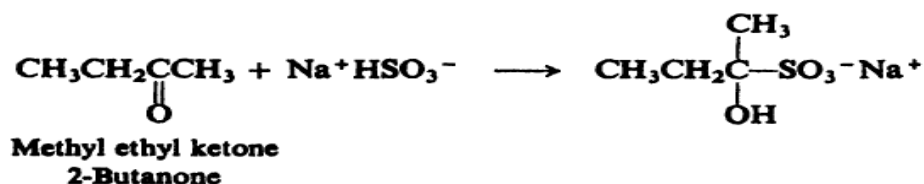
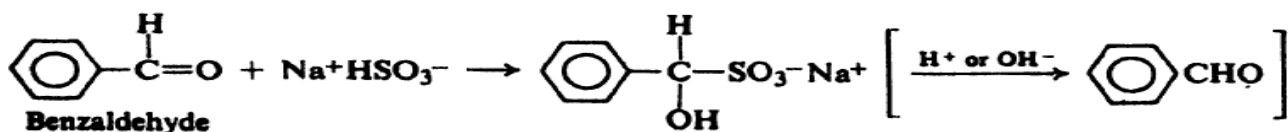


Give the mechanism

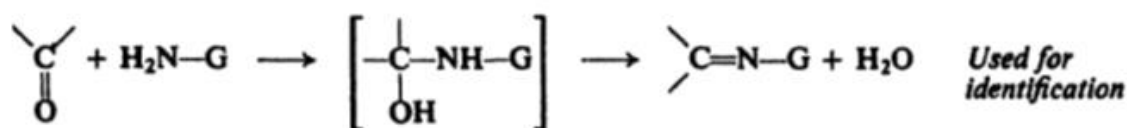
7-addition of bisulfate



Examples:

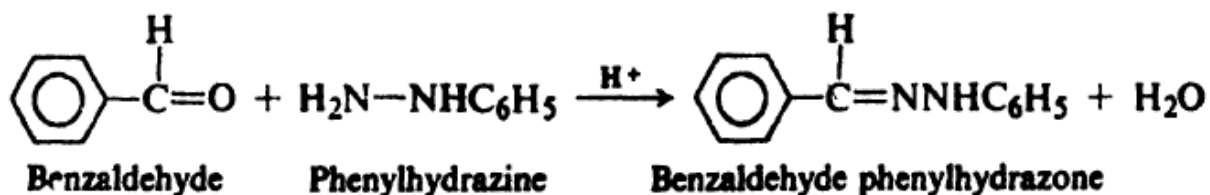
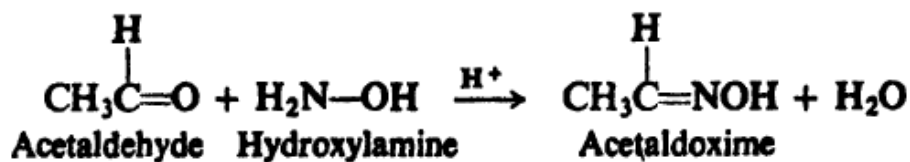


8-addition of derivatives of ammonia

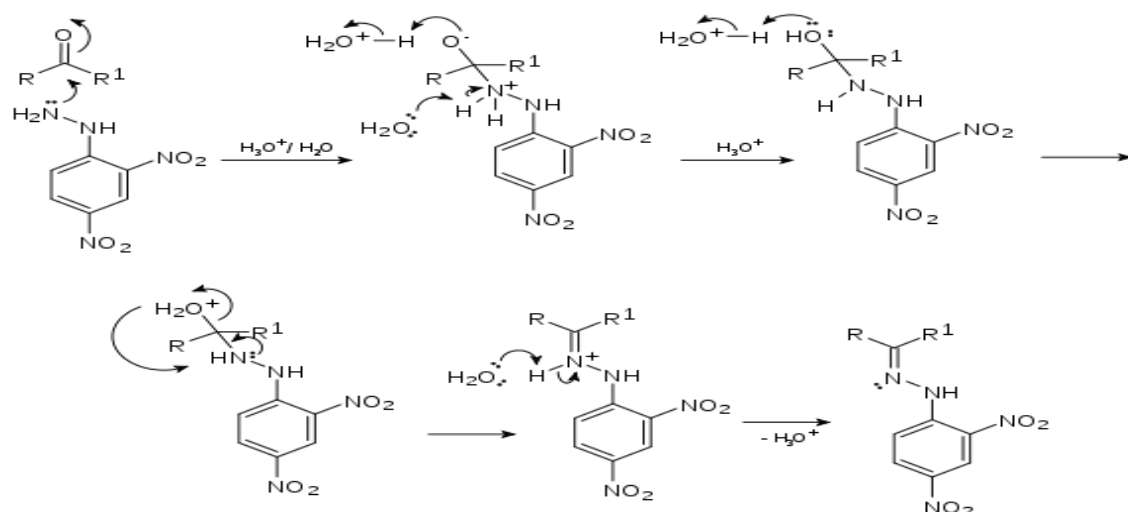


$\text{H}_2\text{N-G}$		Product	
$\text{H}_2\text{N-OH}$	Hydroxylamine	>C=NOH	Oxime
$\text{H}_2\text{N-NH}_2$	Hydrazine	>C=NNH_2	Hydrazone
$\text{H}_2\text{N-NHC}_6\text{H}_5$	Phenylhydrazine	$\text{>C=NNHC}_6\text{H}_5$	Phenylhydrazone
$\text{H}_2\text{N-NHCONH}_2$	Semicarbazide	>C=NNHCONH_2	Semicarbazone

Examples:

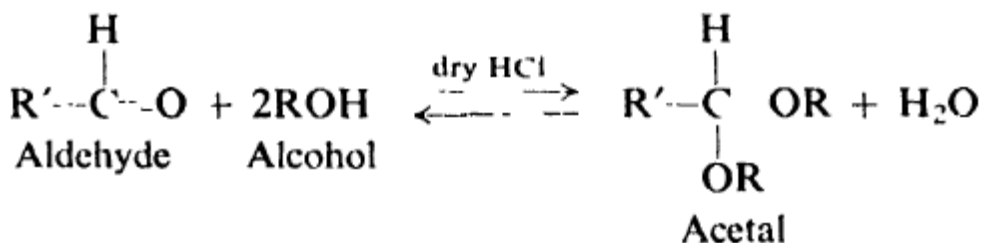


Mechanism

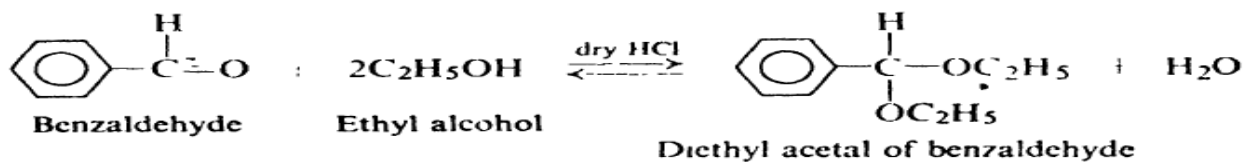


Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and ketones the product contain a carbon – nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

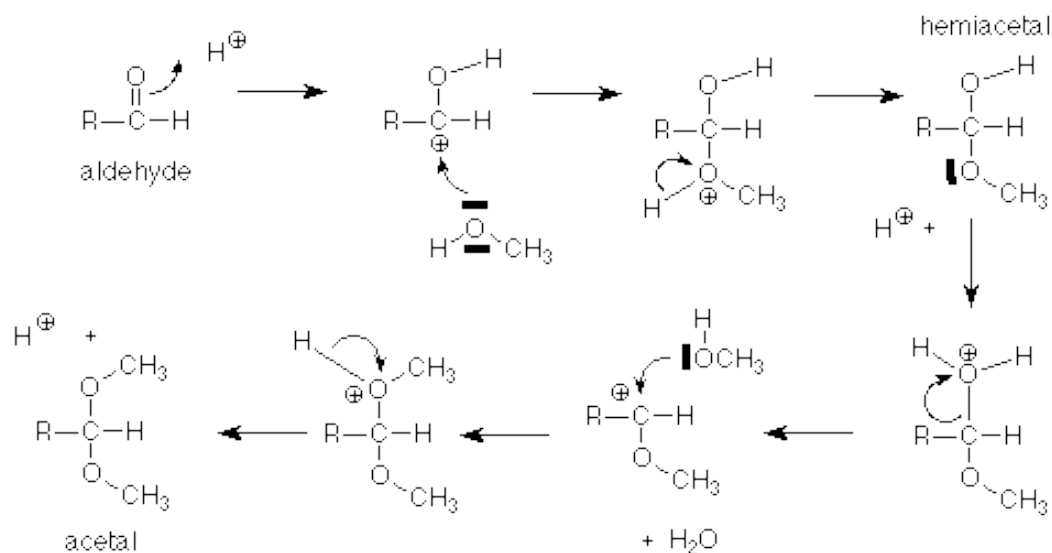
9-addition of alcohols to formation acetal and ketal



Example



Mechanism



Cannizaro reaction

The *Cannizaro* reaction represents the disproportionation of an aldehyde into a carboxylic acid and an alcohol. Alternatively, the reaction can be classified as a redox reaction because one molecule of aldehyde oxidizes another to the acid and is itself reduced to the primary alcohol. More useful is the crossed-*Cannizaro* reaction in which formaldehyde is reacted with another aldehyde. The formaldehyde reduces the aldehyde to alcohol and is itself oxidized to formic acid.

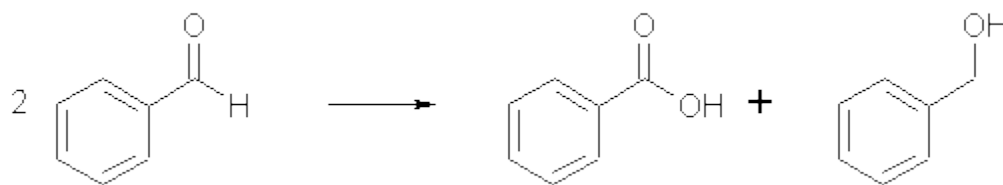


Fig.1

Disproportionation of benzaldehyde

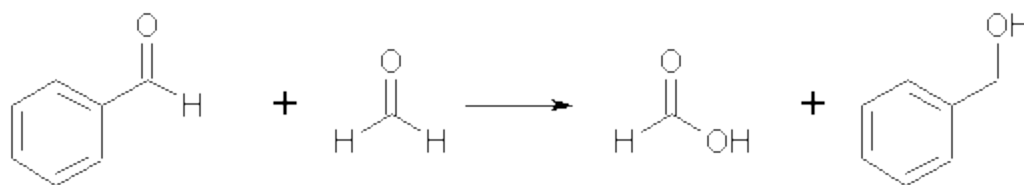
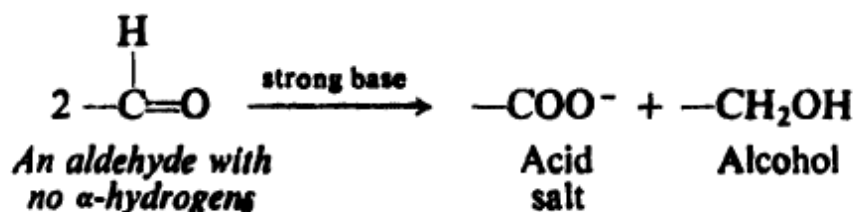
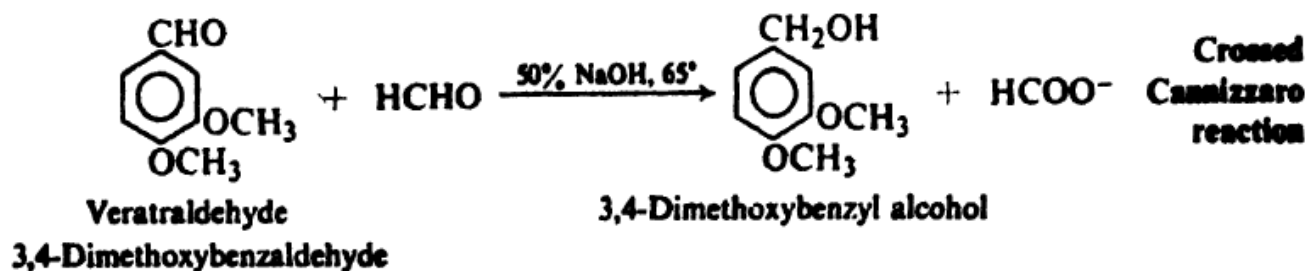
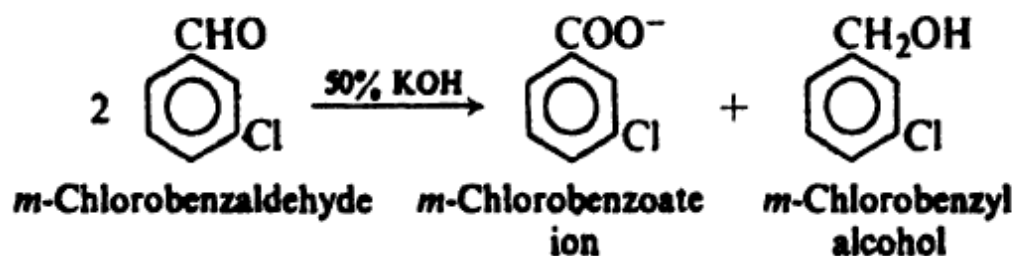
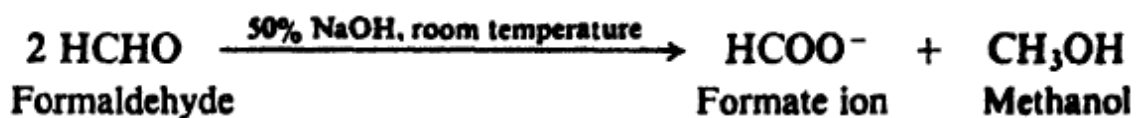


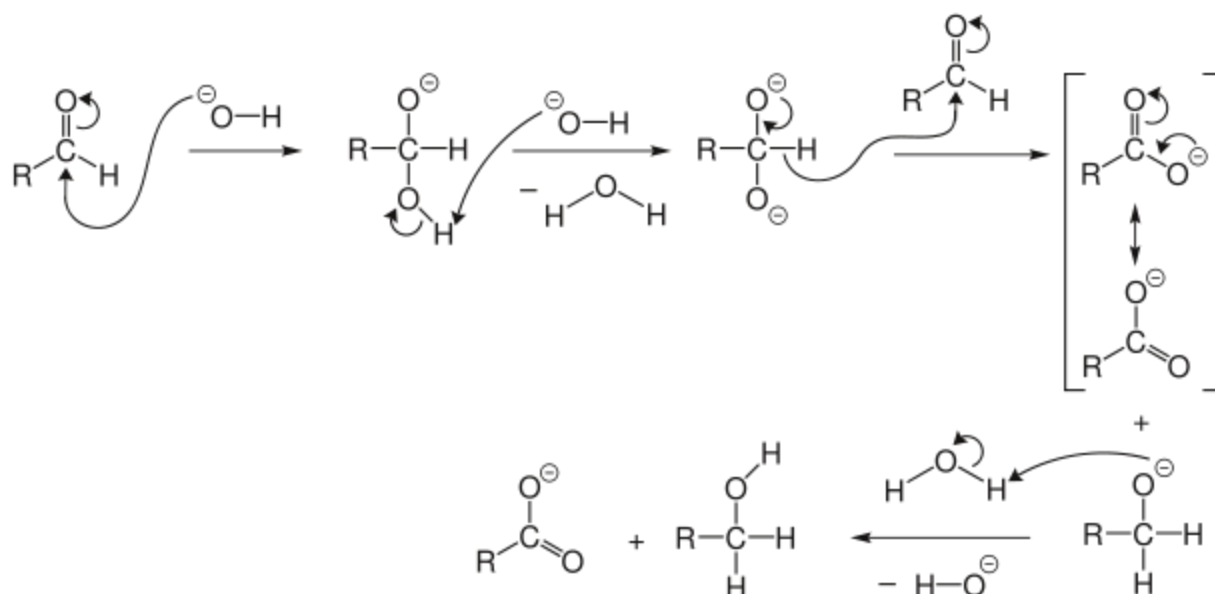
Fig.2



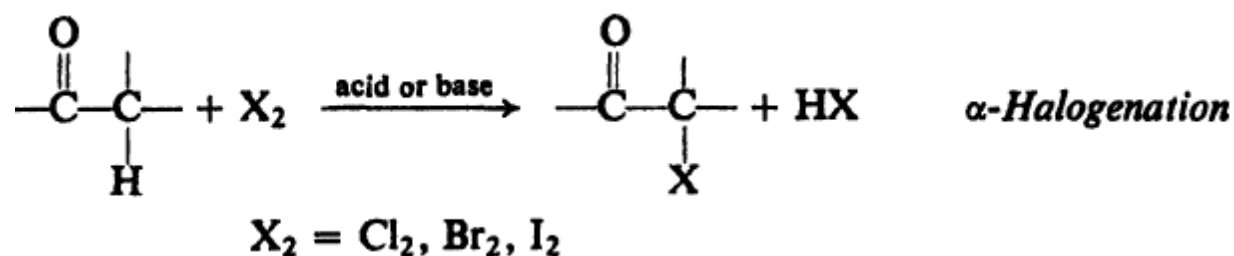
Examples:



Mechanism



10-halogenation of ketones

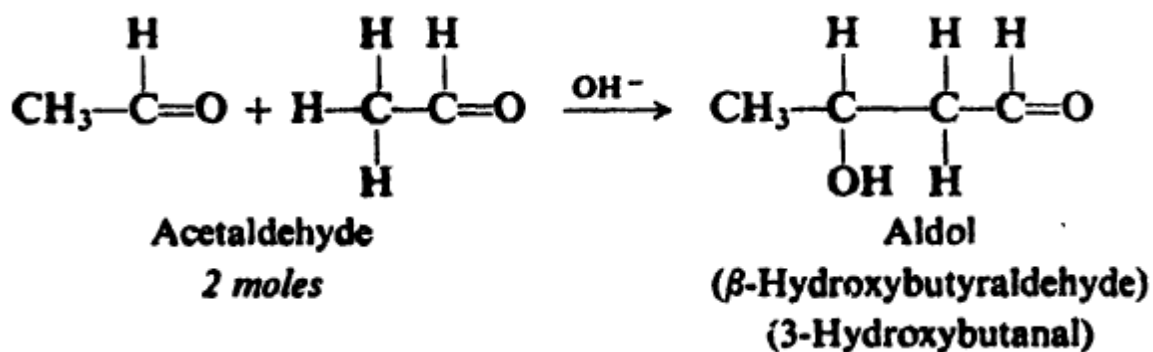


11- addition of carbanions:-

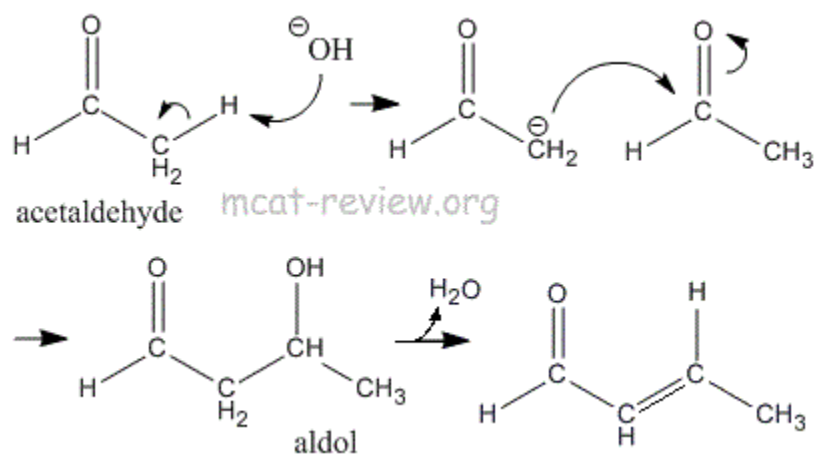
a- Aldol condensation

Under the influence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may combine to form a β-hydroxyaldehyde or β-hydroxyketone. This reaction is called the aldol condensation:-

Note :-In this reaction aldehyde or ketone should be contains α-H atom.



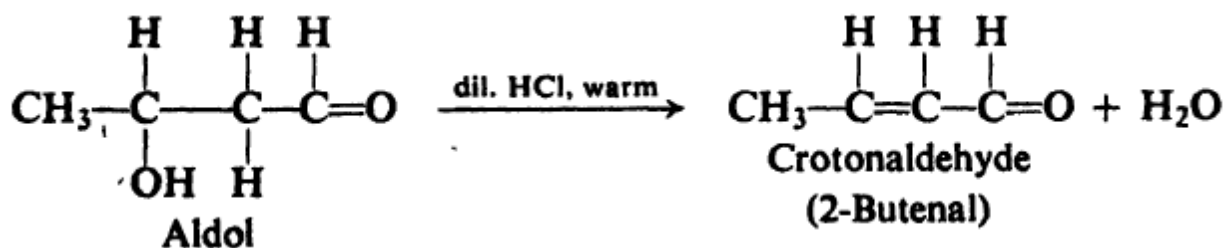
Mechanism



-give the mechanism reaction of 2 moles of acetone in alkaline medium?

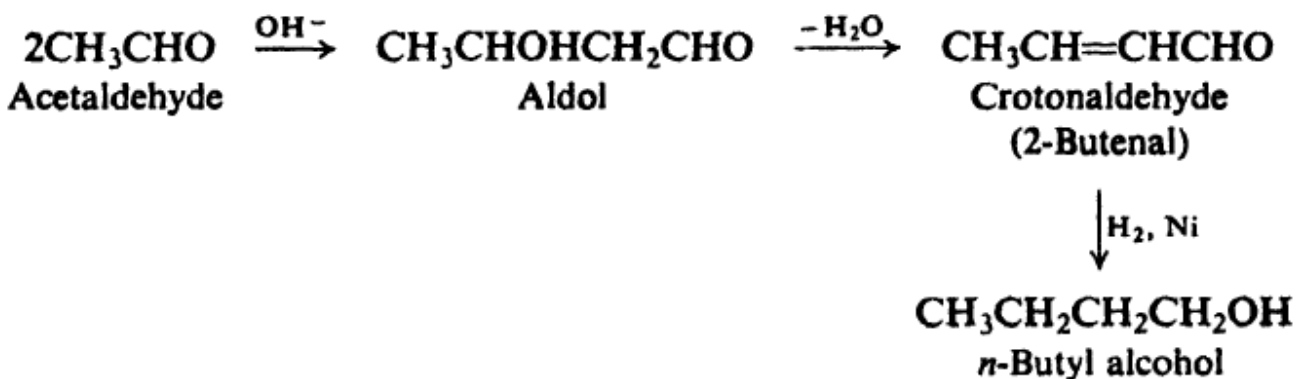
12-dehydration of aldol products

The β -hydroxyaldehydes and β -hydroxyketones obtained from aldol condensations are very easily dehydrated; the major products have the carbon-carbon double bond between the α - and β -carbon atoms. For example:

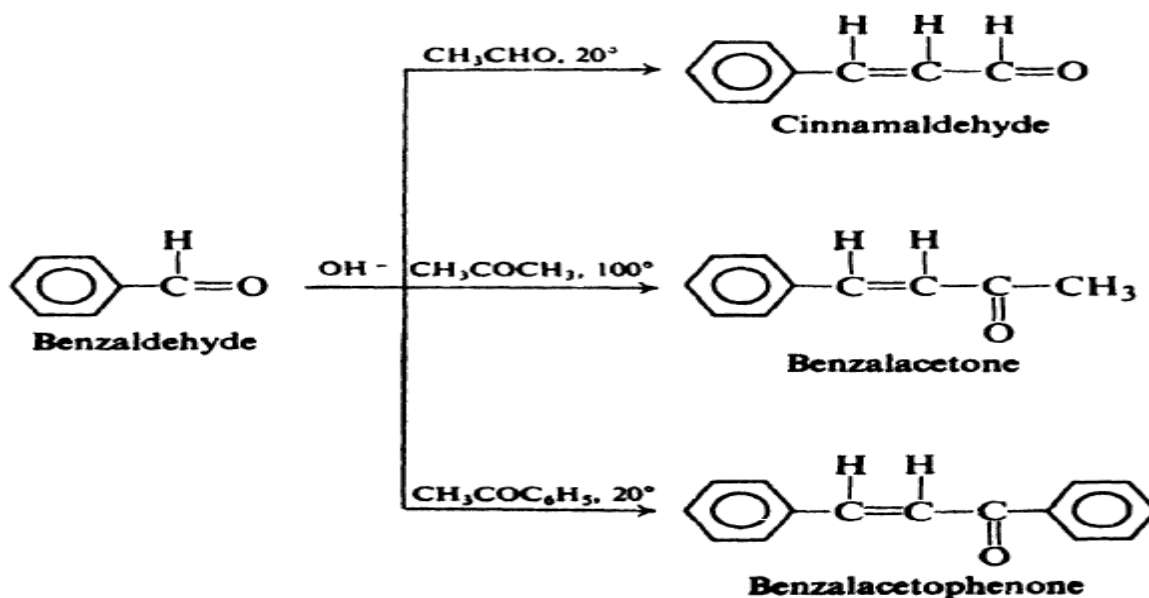


Write the mechanism of dehydration from aldol compound?

Q/ prepare the n-butyl alcohol from acetaldehyde as starting material?

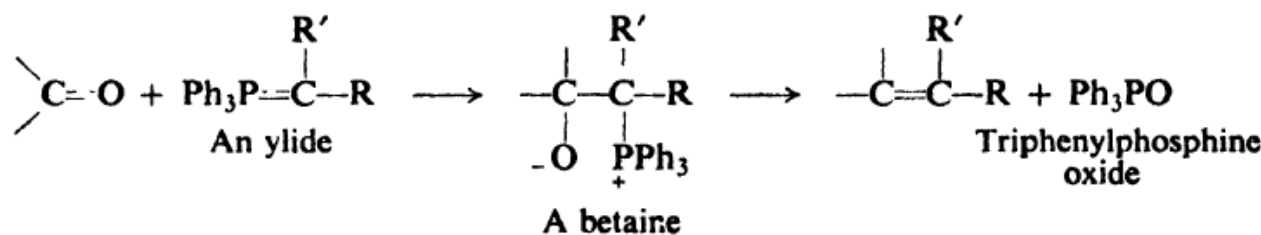


Examples

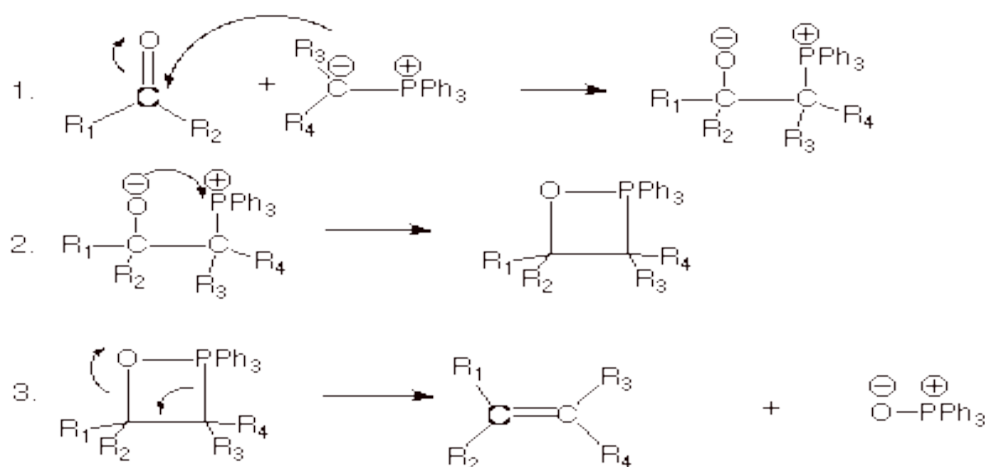


- Wittig reaction

In 1954 George Wittig reported a method of synthesizing alkenes from carbonyl compounds.

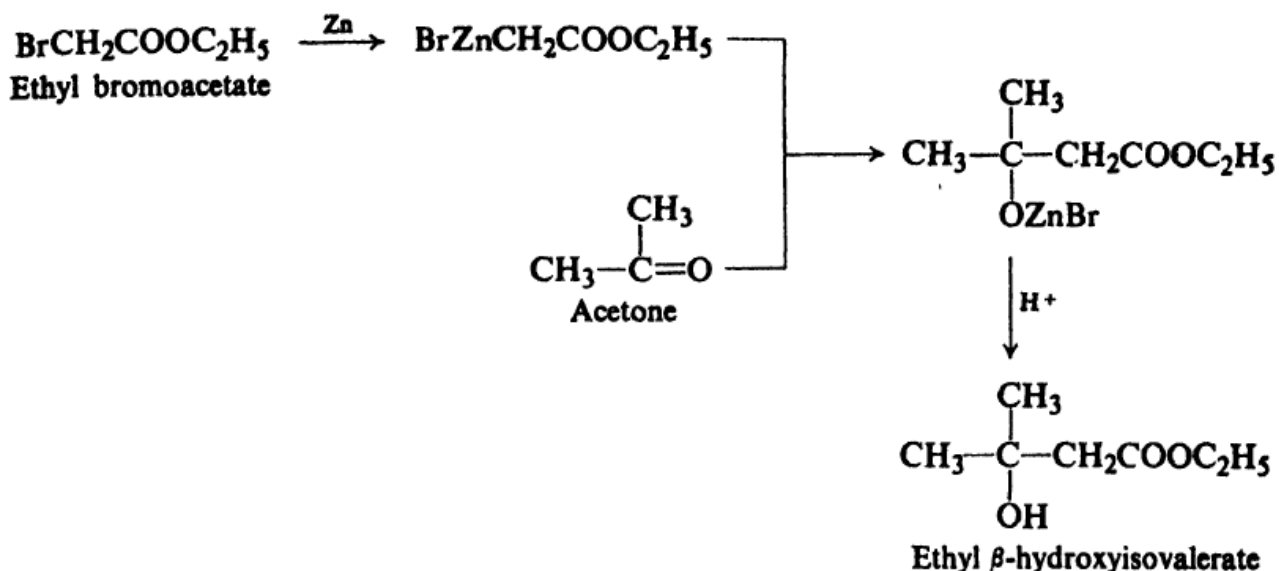


Mechanism

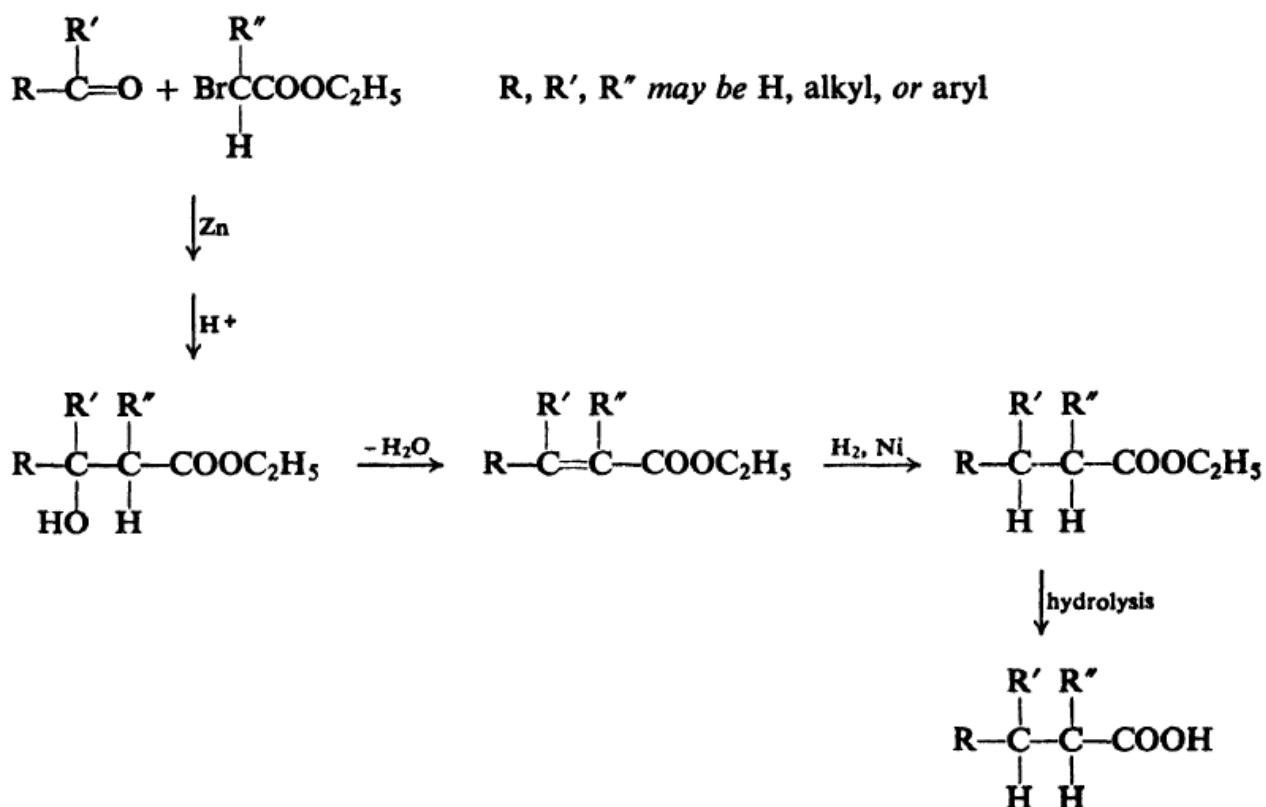


Reformatsky reaction. Preparation of β -hydroxy esters

If an α -bromo ester is treated with metallic zinc in the presence of an aldehyde or ketone, there is obtained a β -hydroxy ester. This reaction, known as the reformatisky reaction. zinc is used in place of magnesium simply because the organozinc compounds are less reactive than Grignard reagents; they do not react with the ester function but only with the aldehyde or ketone.

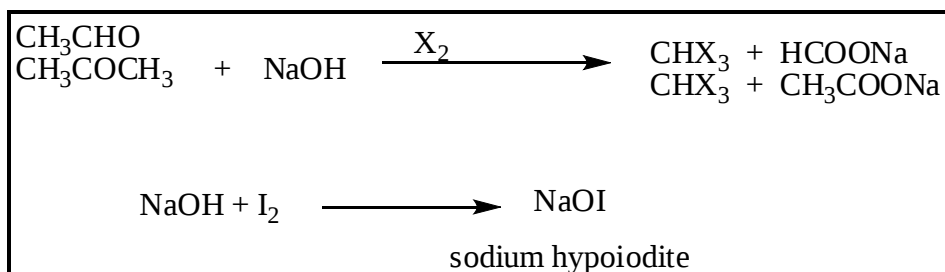


The Reformatsky reaction takes place only with esters containing bromine in the *alpha* position, and hence necessarily yields *beta*-hydroxy esters. By the proper selection of ester and carbonyl compound.



-Haloform reaction

This reaction involves oxidation, halogenations, and cleavage



mechanism

