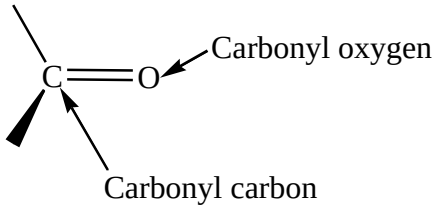
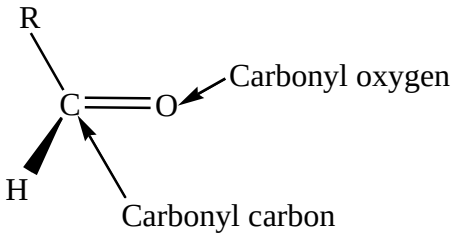
Carbony compounds

The are compounds that contain carbonyl group



Aldehydes

Thes are carbonyl compounds with the following structure.



R = alkyl group

Nomenclature of aldehydes

1. Aldehydeare named by replacing the final “e” of the names of corresponding alkanes with “al.”
2. Since the aldehyde group must be at the end of the chain its position in not indicated.
3. When other sustituents are present, the carbonyl carbon is assumed to occupy position one.

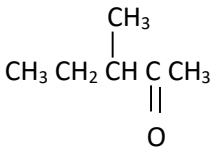
Example

HCHO	Methanal (40% solution is called formalin) or formaldehyde
CH_3CHO	Ethanal or Acetaldehyde
CH_3CH_2CHO	Propanal or propionaldehyde
$CH_3CH_2CH_2CHO$	Butanal or butyraldenhyde
$CH_3CH_2CH_2CH_2CHO$	Pentanal or veraldehyde

Nomenclature of ketones

1. Their names end in suffix “one”
2. The position of the ketone group (-CO-) is given the lowest number.

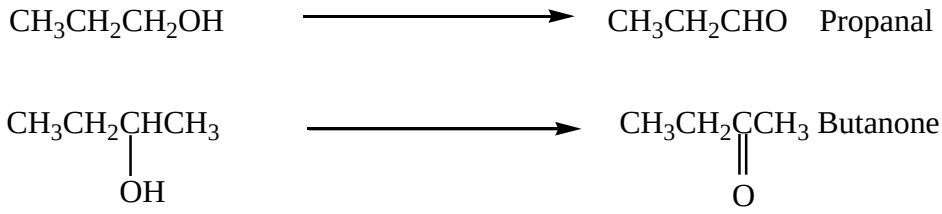
CH_3COCH_3	Propanone
$CH_3CH_2COCH_3$	Butanone



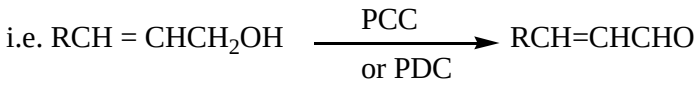
2-methylpentan-2-one

Preparation of carbonyl compounds

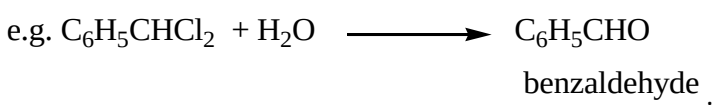
a. Oxidation of alcohol with acidified potassium dichromate, sodium dichromate or potassium permanganate. Primary alcohols give aldehydes whereas secondary alcohols give ketones.
Example



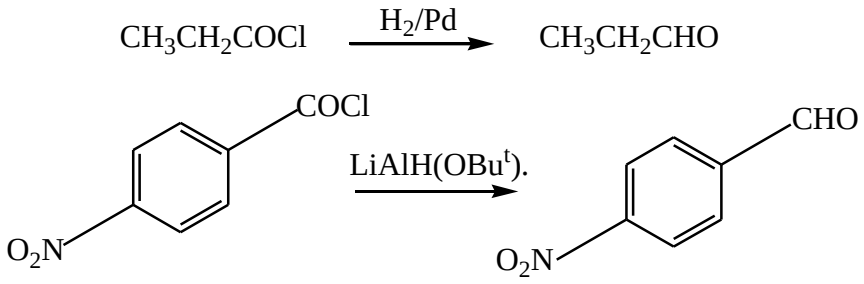
b. Oxidation of alcohols using pyridiumchlorochromate [PCC, $\{C_5H_5NH^+\}Cl.CrO_3$] and pyridinium dichromate [PDC, $\{C_5H_5NH^+\}_2Cl.Cr_2O_7^{2-}$] are currently the reagents of choice, particularly for oxidation of α,β- unsaturated primary and secondary alcohols to give aldehydes and ketones respectively.



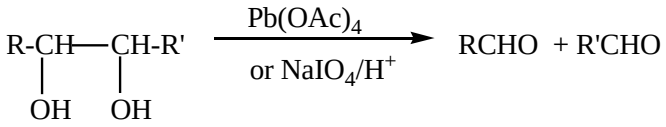
3. Hydrolysis of gem dihalide, ($RCHCl_2$, R_2CCl_2)



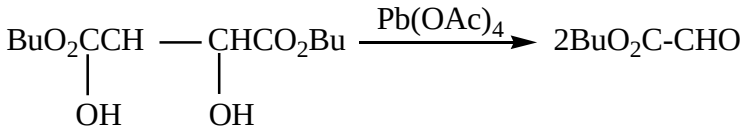
4. Reduction of acid chloride by hydrogen on palladium which is supported on barium sulphate or by using $LiAlH(OBu^t)$.



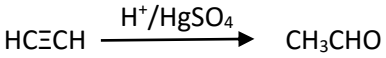
5. Cleavage of 1,2-diol using either lead tetraacetate or sodium metaperiodate



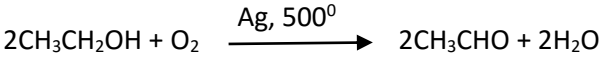
Example

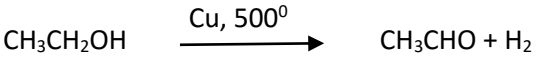


6. Preparation of ethanol
   (i) By oxidation of ethane with palladium chloride in water
   $CH_2=CH_2 + H_2O + PdCl_2 \longrightarrow CH3CHO$
   (ii) Passing ethyne through dil sulphuric acid in presence of mercury sulphate as a catalyst.



   (iii) Oxidation ethanol



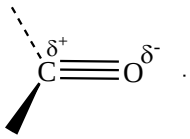


Physical properties

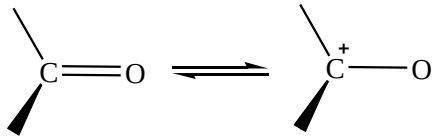
(a) The polar carbonyl group makes carbonyl compounds polar and therefore, the have melting and boiling points than non-polar compounds with similar molecular mass.
(b) Lower members are soluble in water but the solubility decreases with the increase in chain length.

Chemical properties

The structure of carbonyl compound is sp2 hybridized

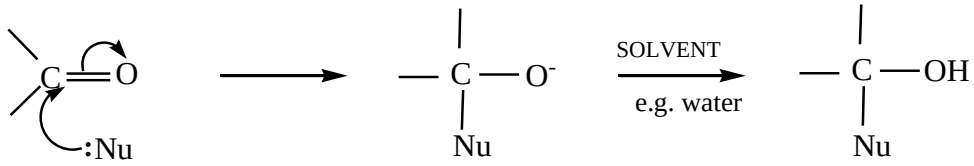


Possible structure

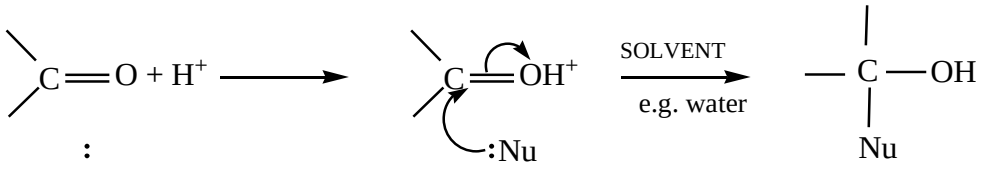


As a result of the partial positive charge, the carbonyl carbon is subjected to nucleophilic attack by a large number of nucleophiles. This results in nucleophilic addition reaction a cross the carbon-oxygen double bond. The nucleophilic addition to the carbon-oxygen double bond, can be regarede to occure in two possible ways generally.

(i) In presence of a strong nucleophile.



(ii) Weak nucleophile, the carbon oxygen bond has to be protonated first.



Generally, aldehydes undergo nucleophilic addition reaction more readily than ketones

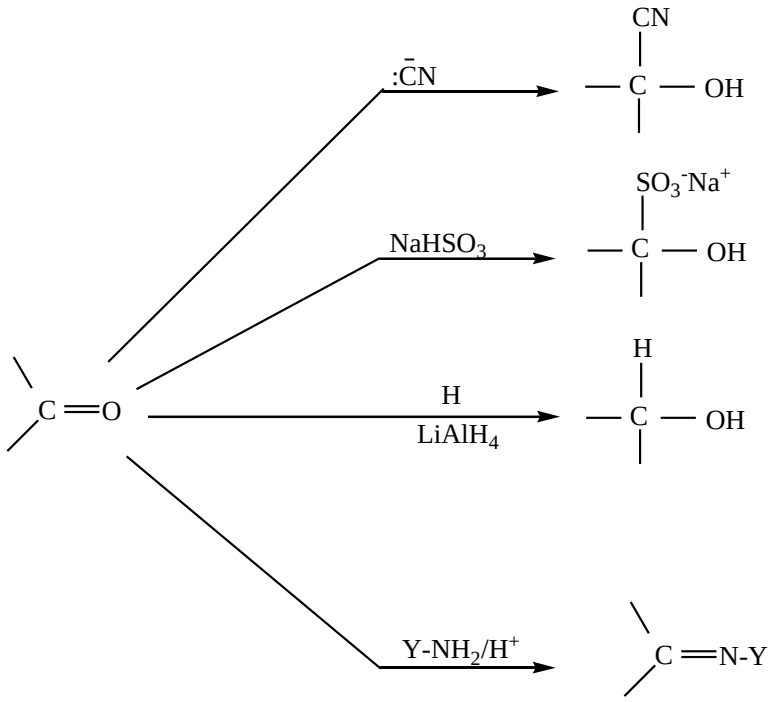
Reasons

(i) Steric effect: the bulkiness of the alkyl groups attached to the carbonyl carbon hinders the approach of nucleophile.

(ii) Inductive effect: the positive inductive effect of the alkyl groups attached to the carbonyl carbon in ketones, reduce the positivity of the carbonyl carbon thus rendering it less reactive towards nucleophiles.

NB. Presence of an electron withdrawing group on the alkyl carbon make the carbonyl carbon more reactive towards nucleophilic addition reaction. For example, CCl_3CHO is more reactive than CH_3CHO.

General scheme of nucleophilic reaction to carbonyl compounds

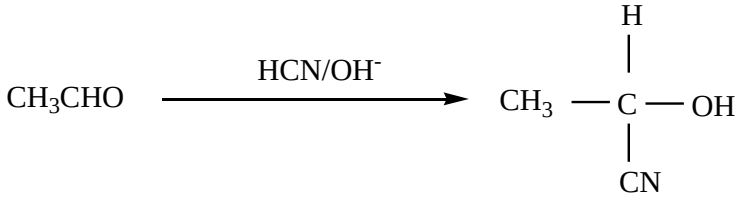


Mechanism

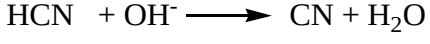
(a) Addition of HCN or KCN

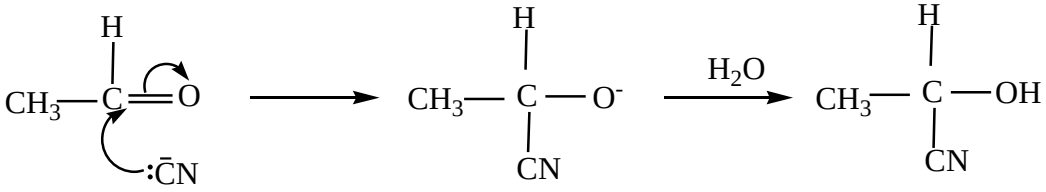
The reaction for addition of HCN is catalyzed by NaOH or KOH

Example



Mechanism

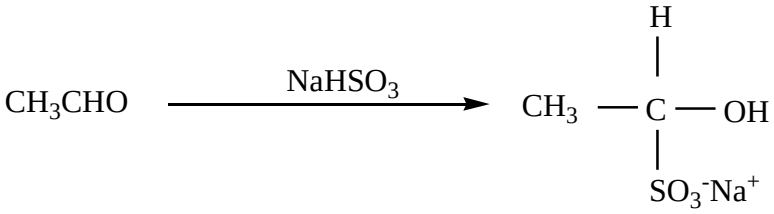




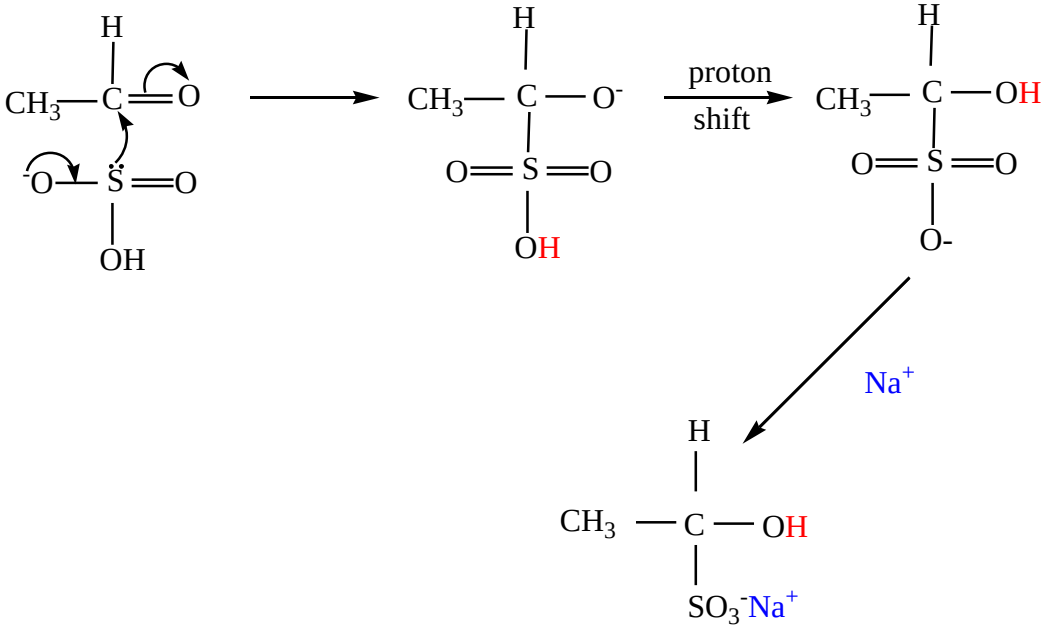
This reaction can be used to increase the carbon chain by one carbon atom

Exercise
Complete and write a mechanism
$CH_3COCH_3 + KCN \longrightarrow$

(b) Addition of sodium hydrogensulphite, $NaHSO_3$.
Example



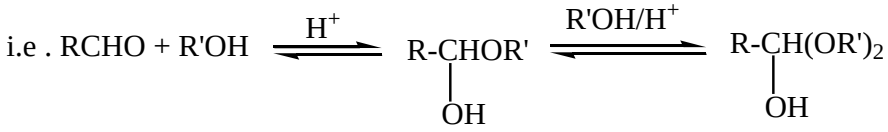
Mechanism



The reaction can be used to purify carbonyl compound since the products formed are solid. After crystallization, the can be redissolved.

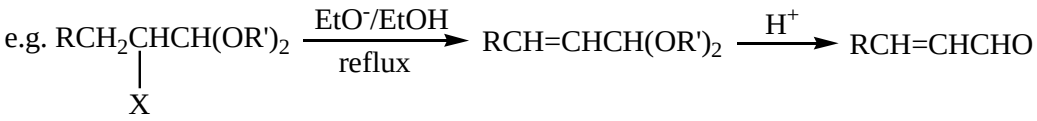
(c) Addition of alcohols

- 1mole of aldehyde + 1mole of alcohol in presence of an acid the product is hemiacetal
- 1mole of aldehyde + 2moles of alcohol in presence of an acid is acetal.

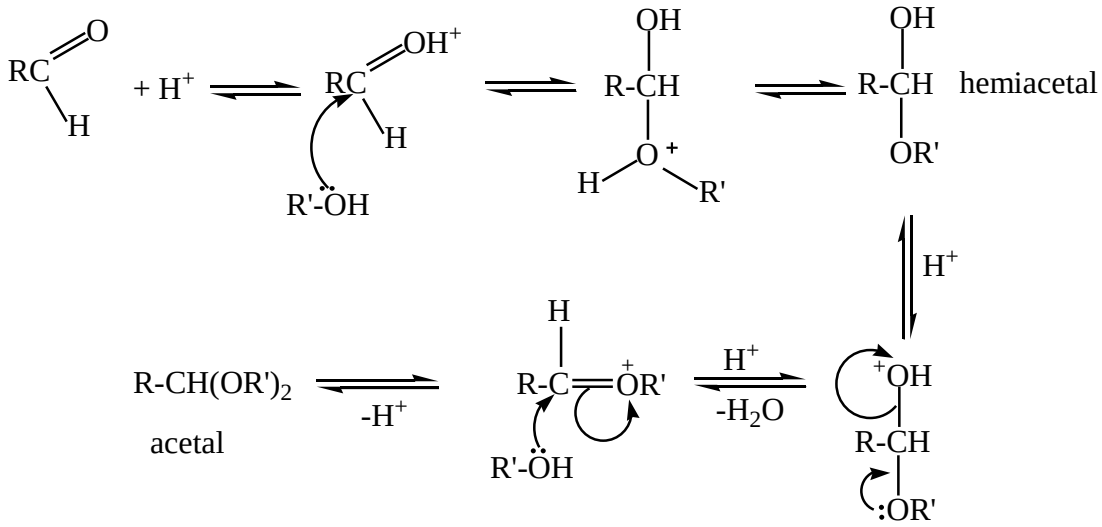


The reaction is used to protect the aldehyde group in chemical synthesis.

Example



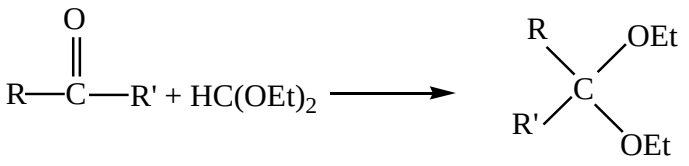
Mechanism



NB (i) Formation of acetals is sensitive to steric hindrances, i.e. depends on the size of groups attached to carbonyl carbon and the size of alcohol. Simple compounds give up to 80% yield, but the yield decrease with the increase in the size of the groups.

(ii) Reaction is reversible; therefore, it's necessary to reduce the concentration of the acid to minimize the reversibility of the reaction.

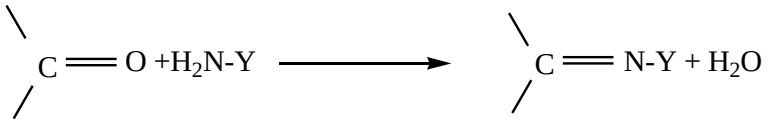
(iii) Ketals are not prepared by direct reaction between ketones and alcohol. This is because the equilibrium of the reaction lies mainly to the left. In this case **orthoformate** is used.



2. Addition of ammonia derivatives

Carbonyl compounds react with compounds of the general formula H_2N-Y with elimination of water. The reaction is catalyzed by acids. A reaction in which two molecules combine with elimination of small molecules e.g. water is called **condensation reaction**.

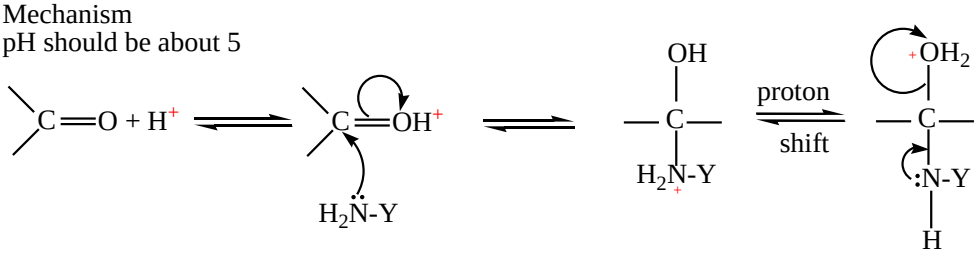
General equation

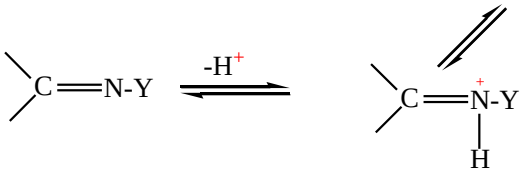


Y	REAGENTS	PRODUCTS
-OH	H_2N-OH	C=OH (Oxime)
-NH_2	H_2N-NH_2	C=N-NH_2 (Hydrazone)
NH-	NH-NH_2	C=N-NH Phenylhydrazone
O_2N NH- NO_2	O_2N NH-NH_2 NO_2	C=N-NH NO_2 NO_2 2,4-dinitrohenylhydrazone
-NH-C(=O)-NH_2	H_2N-NH-C(=O)-NH_2	C=N-NH-C(=O)-NH_2 Semicarbazone

Mechanism

pH should be about 5



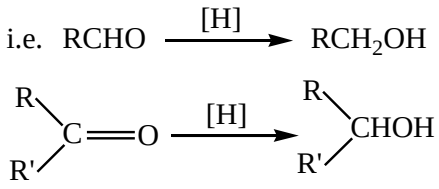


The products of these condensation reactions, i.e. oxime and hydrazones are orange crystalline solids with sharp melting points. Thus, they can be used to characterize carbonyl compounds. The most commonly used ammonia derivatives to characterize carbonyl compounds is 2,4-dinitrophenyl hydrazine (Brady's reagent). Reaction of carbonyl compounds with this reagent produces orange colored crystalline solids.

3. Reduction of carbonyl compounds

   (i) Reduction of carbonyl compounds to alcohols

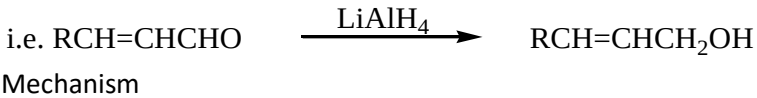
   Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols



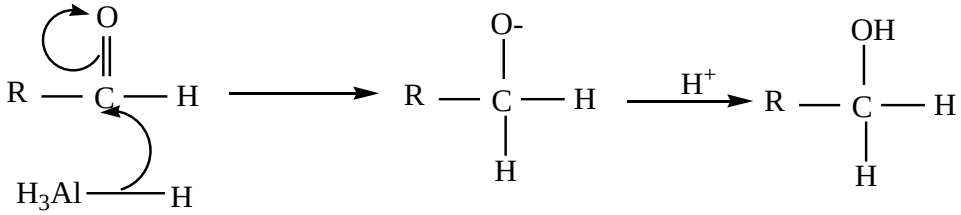
Reducing agents include

(a) H_2/catalyst (Ni, Pt, Pd): the disadvantage with this reagent is that it reduces double bonds when present.

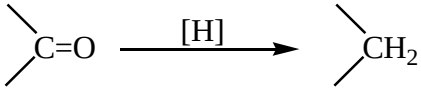
(b) LiAlH4, NaBH4 – do not reduce double bonds



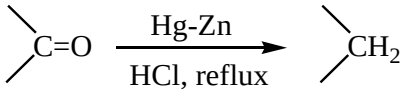
Mechanism



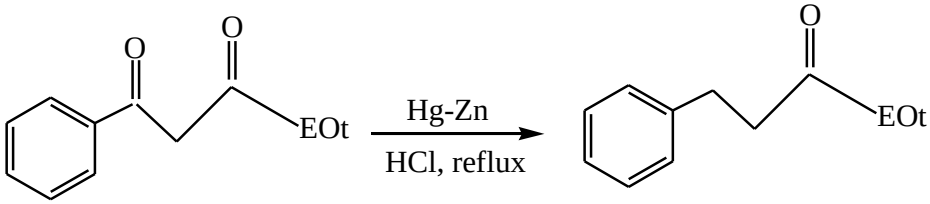
(ii) Reduction of carbonyl compounds to methylene. i.e.



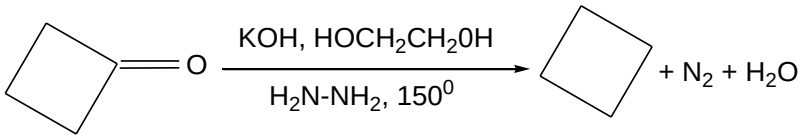
(a) Clemmensen's reduction: it is useful for compounds that are stable under acidic conditions
It is carried out by refluxing a ketone with hydrochloric acid containing amalgamated zinc. Zinc and hydrochloric acid also reduces nitro groups to amines.



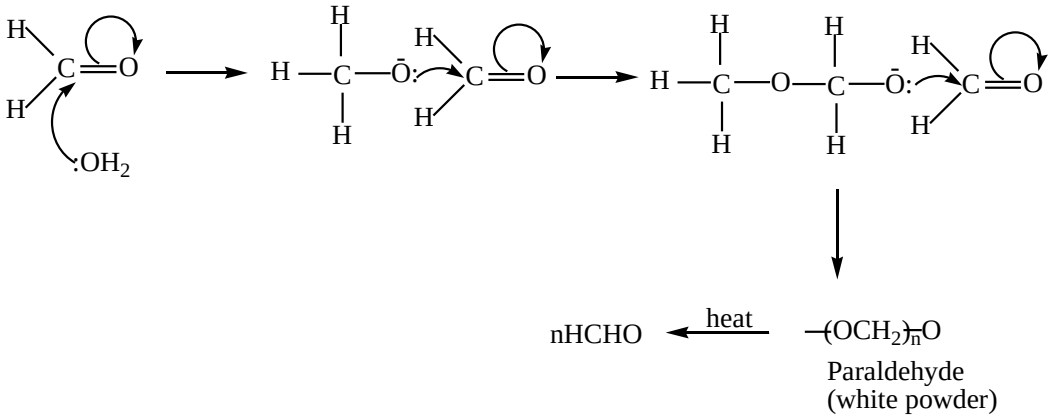
Example



(b) Hong-Mislon modification of Walf-Kishner reaction: a carbonyl compound is heated in presence of high boiling polar solvent, e.g. ethane-1,2-diol with hydrazide + KOH

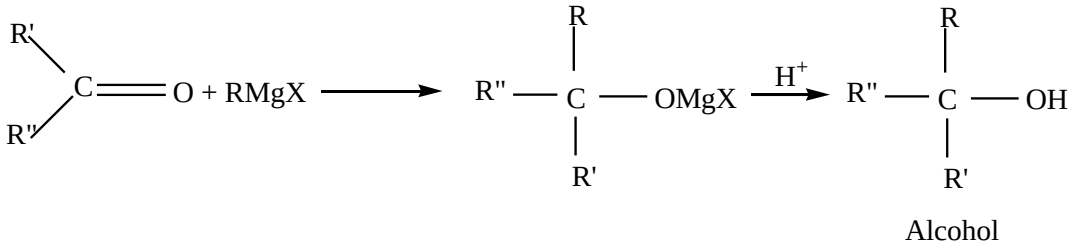


4. Polymerization of aldehyde
Aldehyde(methanol) polymerizes, mainly under basic conditions.

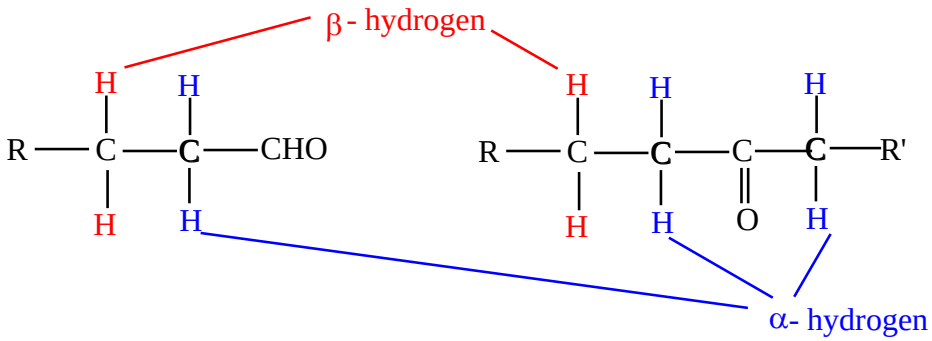


Paraformaldehyde is a useful form for transportation of methanal

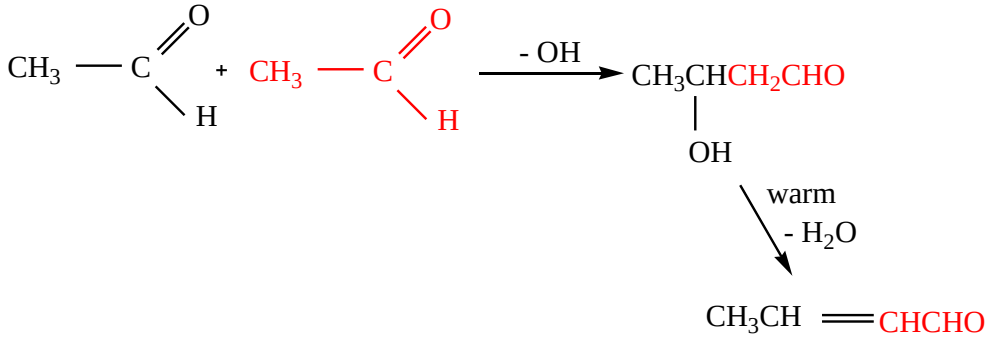
5. Reaction of Grignard's reagents
Reaction of carbonyl compounds with Grignard's reagents produces all the three types of alcohols. Thus this is an important reaction for the preparation of alcohols.



6. Aldol condensations
Carbonyl compounds which contain at least one alpha hydrogen, react in presence of alkali to form hydroxyl carbonyl compounds called Aldol



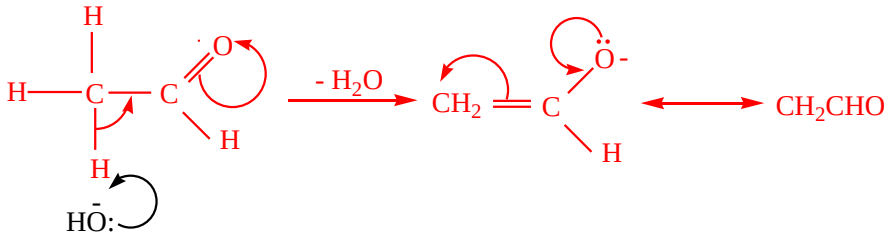
(i) Two molecules of ethanal combine to form 3-hydroxybutanal



Crotonaldehyde

Crotonaldehyde is used to calibrate spectrometer because it's absorbance is known

Mechanism



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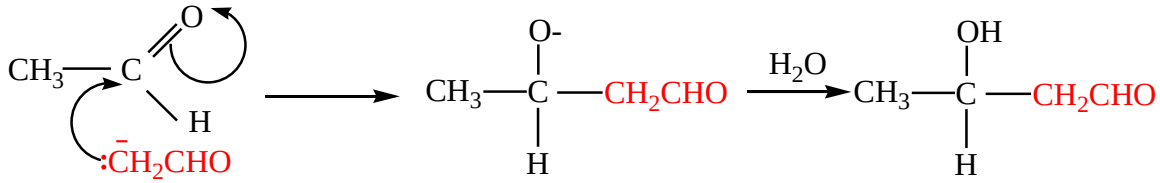
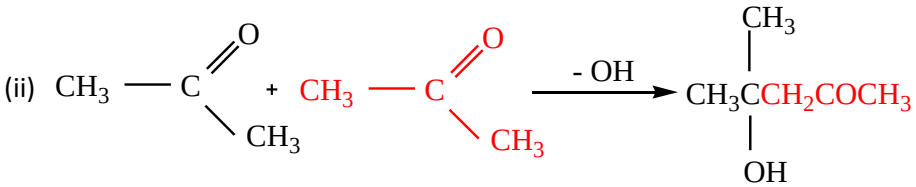
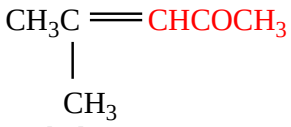
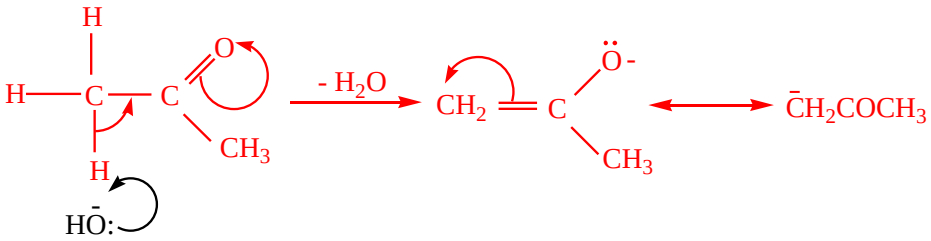


(ii) 

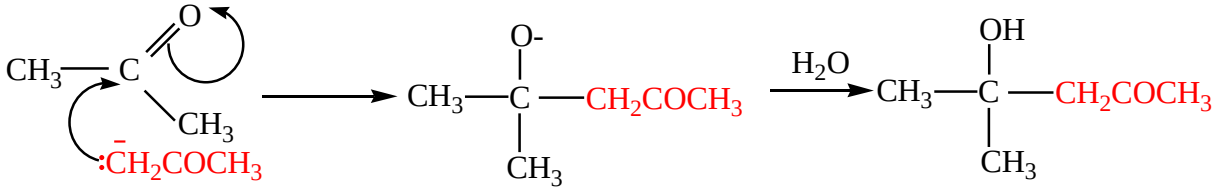


4-Methylpent-3-en-2-one

Mechanism



Then



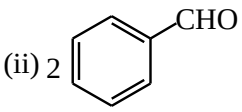
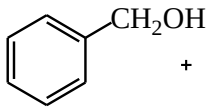
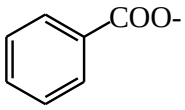
7. Cannizzaro reaction

This is a reaction between sodium hydroxide solution and aldehydes with no α-hydrogen

It's a self-oxidation – reduction reaction

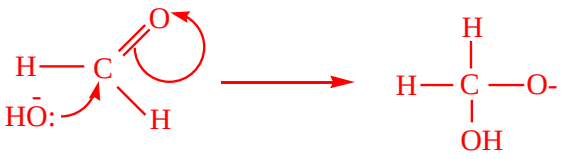
Examples

(i) $2HCHO \xrightarrow[150^0]{^-OH(aq)} HCH_2OH + HCOO^-$

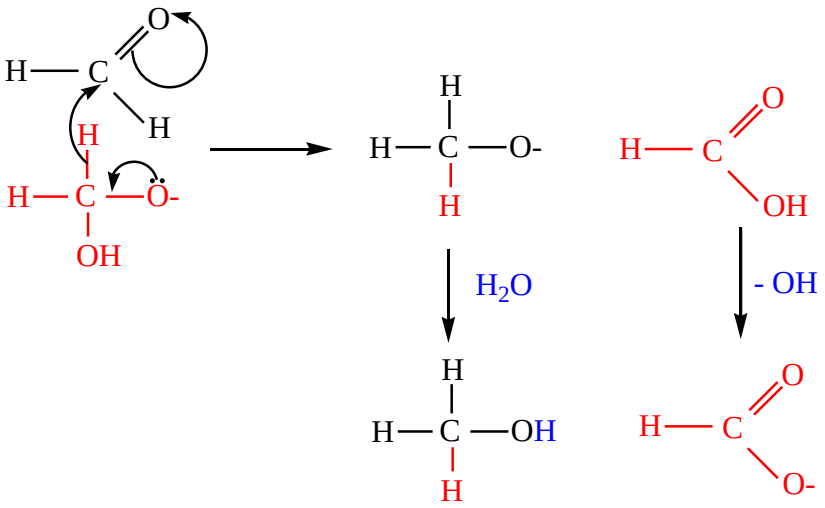
(ii) 2  $\xrightarrow[150^0]{^-OH(aq)}$  + 

Benzaldehyde Benzylalcohol Benzoate

Mechanism

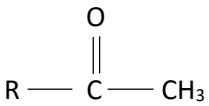


Then,



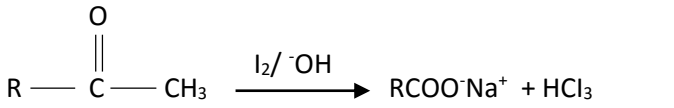
8. Iodoform reactions

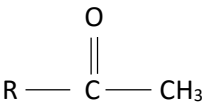
Iodine in presence of sodium hydroxide solution react with carbonyl compounds with structure



to form a yellow ppt.

i.e.



NB (i) the reaction is useful when identifying compound with the group 

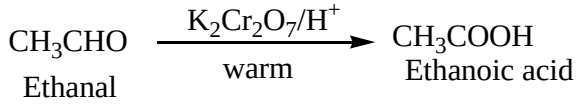
(ii) Ethanal is the only aldehyde that gives a positive iodoform test
(iii) All ketone with the structure $RCOCH_3$ give positive iodoform test
(iv) Secondary alcohols of the group $RCHOHCH_3$ give positive iodoform test
(v) Ethanol is the only primary alcohol that gives a positive iodoform test.

Exercise

Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

(i) CH_3OH and CH_3CH_2OH
(ii) HCHO and CH_3CHO
(iii) $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

9. Oxidation of carbonyl compounds
Aldehydes are easily oxidized to carboxylic acid. The oxidizing agent, normally used are $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, $KMnO_4/H^+$.
Example



Ketones are not oxidized under mild condition

Distinguishing between aldehydes and ketone

Reagent	Observation	
	Aldehydes	Ketones
Fehling's solution	Brown ppt	No observable change
Tollen's reangent or ammoniacal silver nitrate	Black ppt or silver mirror	No observable change
Acidified potassium dichromate	Orange solution turns green	No observable change

Exercise

Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

(i) CH_3CH_2CHO and CH_3COCH_3

END