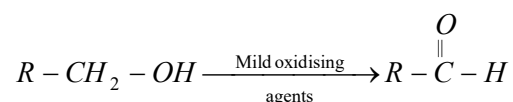
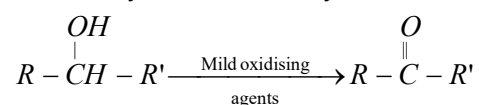


Preparation of carbonyl compounds.

Preparation of only aliphatic or aliphatic as well as aromatic carbonyl compounds.

(1) From alcohols

(i) Primary and secondary alcohols on oxidation give aldehydes and ketones respectively.



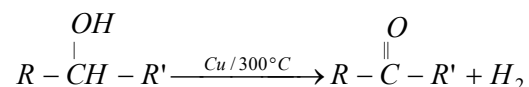
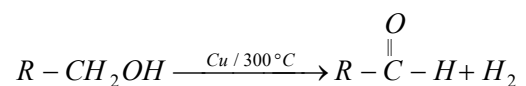
Mild oxidising agents are:

- (a) X_2 (b) Fenton reagent (c) $K_2Cr_2O_7 / H^+$ (d) Jones reagent
(e) Sarret reagent (f) MnO_2 (g) Aluminium tertiary butoxide

Note: When the secondary alcohols can be oxidised to ketones by aluminium tert-butoxide, $[(CH_3)_3CO]_3Al$ the reaction is known as oppenauer oxidation. Unsaturated secondary alcohols can also be oxidised to unsaturated ketones (without affecting double bond) by this reagent.

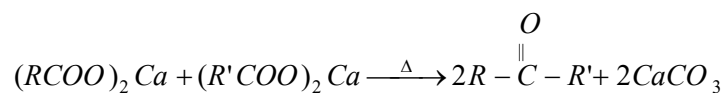
The yield of aldehydes is usually low by this methods. The alcohols can be converted to aldehydes stage by treating with oxidizing agent pyridiniumchloro-chromate ($C_5H_5NH^+CrO_3Cl^-$). It is abbreviated as PCC and is called **Collin's reagent**. This reagent is used in non-aqueous solvents like CH_2Cl_2 (dichloro methane). It is prepared by mixing pyridine, CrO_3 and HCl in dichloromethane. This is a very good reagent because it checks the further oxidation of aldehydes to carboxylic acids.

(ii) **Dehydrogenation of 1° and 2° alcohols by Cu/300° or Ag/300°C.**

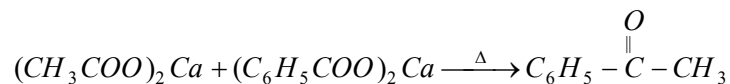
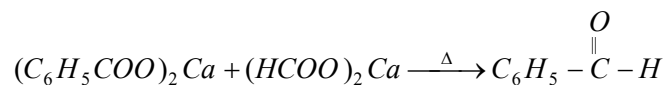
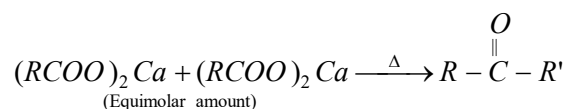
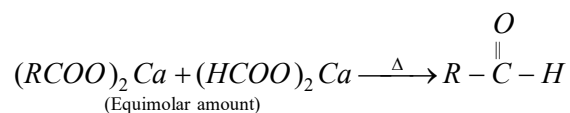
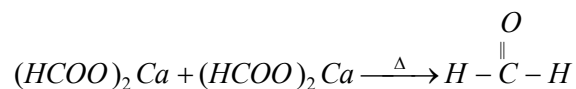


(2) From carboxylic acids

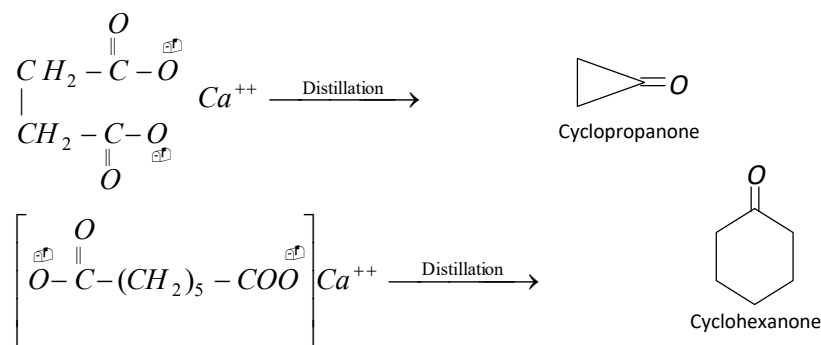
(i) **Distillation of Ca, Ba, Sr or Th salts of monobasic acids:** Salt of monobasic acids on distillation give carbonyl compounds. Reaction takes place as follows,



Thus in the product, one alkyl group comes from one carboxylic acid and other alkyl group from other carboxylic acid.



Calcium salts of dibasic acid (1, 4 and higher) on distillation give cyclic ketones.

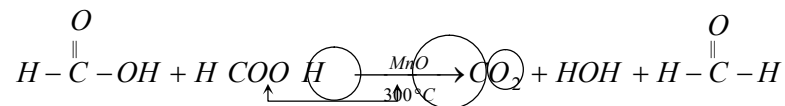


(ii) Catalytic decomposition of carboxylic acids or Decarboxylation and Dehydration of acids by MnO/ 300°C.

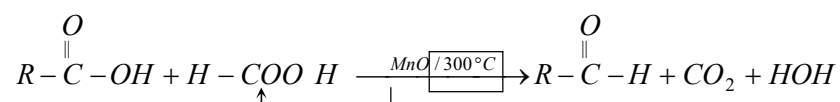
(a) This reaction takes place between two molecules of carboxylic acids. Both may be the same or different.

(b) If one of the carboxylic acids is $HCOOH$ then this acid undergoes decarboxylation because this acid is the only monobasic acid which undergoes decarboxylation even in the absence of catalyst.

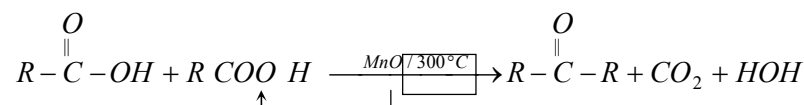
Case I: When both are $HCOOH$



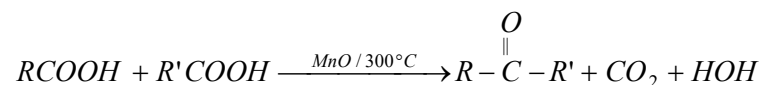
Case II: When only one is formic acid.



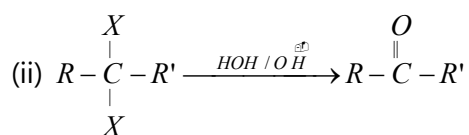
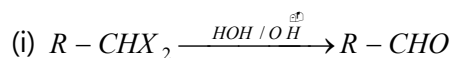
Case III: When none is formic acid.



Or



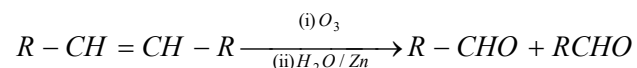
(3) **From gem dihalides:** Gem dihalides on hydrolysis give carbonyl compounds

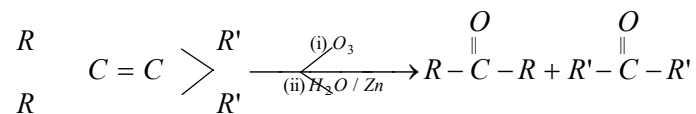


Note: This method is not used much since aldehydes are affected by alkali and dihalides are usually prepared from the carbonyl compounds.

(4) **From alkenes**

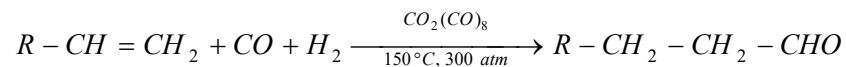
(i) **Ozonolysis:** Alkenes on reductive ozonolysis give carbonyl compounds





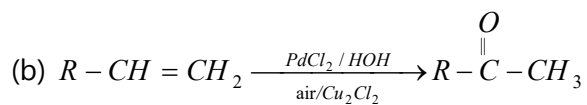
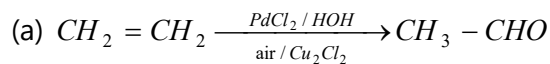
Note: This method is used only for aliphatic carbonyl compounds.

(ii) **Oxo process:** This method converts terminal alkenes into aldehydes.

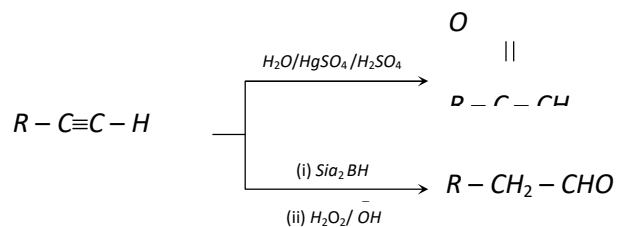


Note: Oxo process is used only for the preparation of aldehydes.

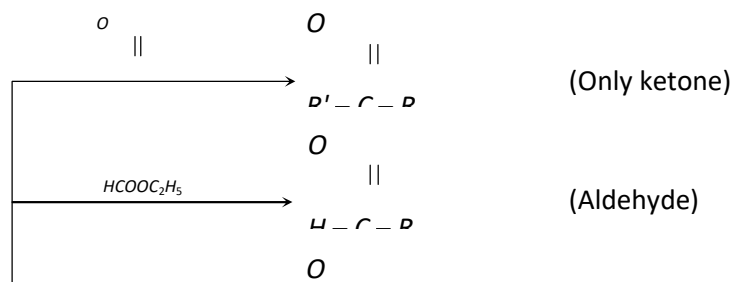
(iii) **Wacker process:** This reaction converts alkenes in carbonyl compounds.



(5) **From alkynes:** Alkynes on hydration and on boration – oxidation give carbonyl compounds.

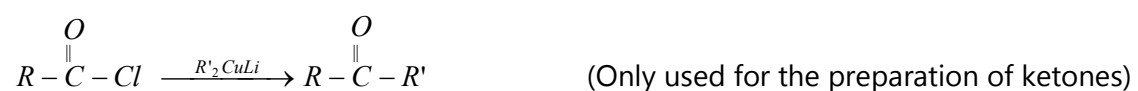
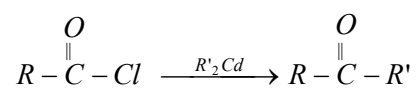


(6) **From Grignard reagents:** Carbonyl compounds can be prepared from Grignard reagents by following reactions:



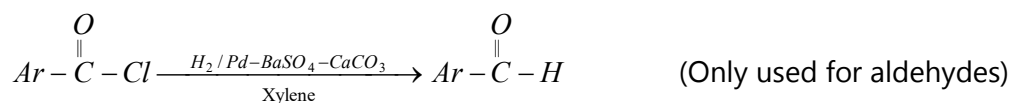
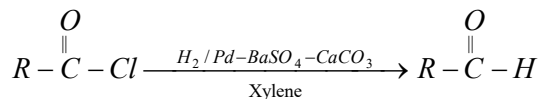
(7) From acid chloride

(i) Acid chlorides give nucleophilic substitution reaction with dialkyl cadmium and dialkyl lithium cuprate to give ketones. This is one of the most important method for the preparation of ketones from acid chlorides.



In this method product is always ketone because $R \neq H$ and also $R' \neq H$.

(ii) **Rosenmundsreduction:** Acid chlorides on partial reduction give aldehydes. This reduction takes place in the presence of Lindlars catalyst.

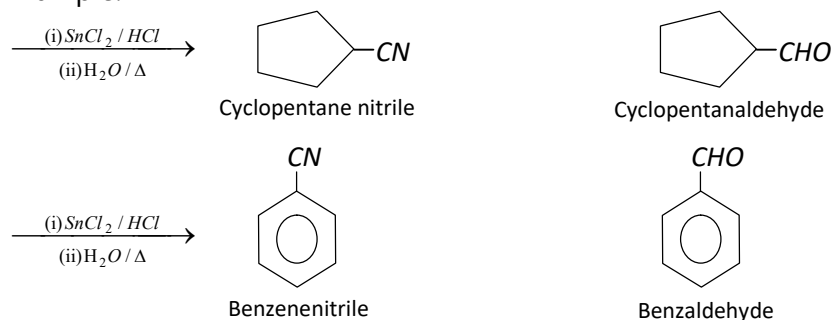


(8) From cyanides

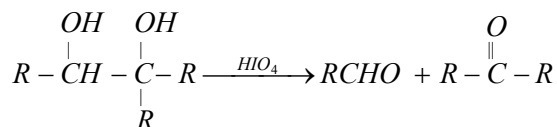
(i) **Stephen aldehyde synthesis:** Conversion of cyanides into aldehydes by partial reduction with $SnCl_2 / HCl$, followed by hydrolysis, is known as Stephen's aldehyde synthesis.



Example:

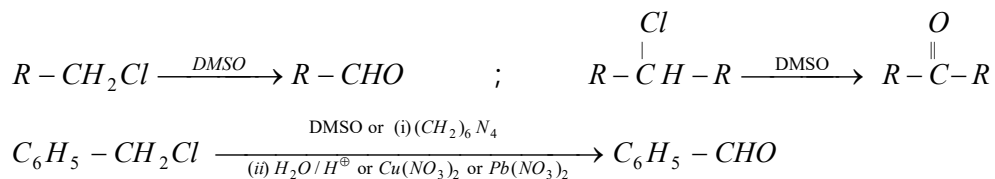


(9) **From vicdiols:** Vic diols on periodate oxidation give carbonyl compounds.

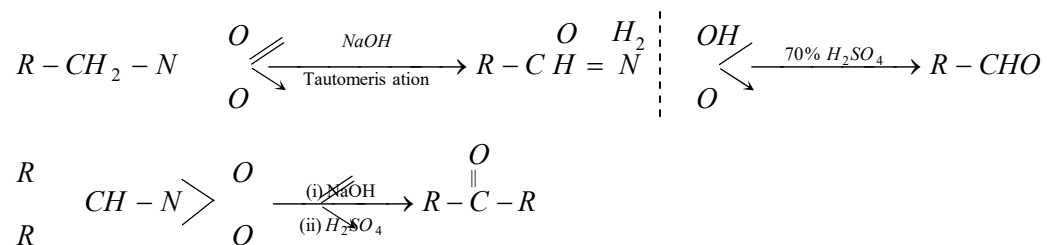


Note: $Pb(OCOCH_3)_4$ also gives similar oxidation products.

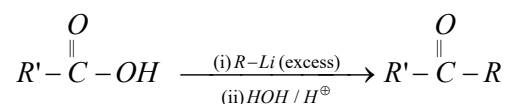
(10) **From Alkyl halides and benzyl halides:** These compounds on oxidation give carbonyl compounds.



(11) **From nitro alkanes:** Nitro alkanes having at least one α -hydrogen atom give carbonyl compounds on treatment with conc NaOH followed by 70% H_2SO_4 . The reaction is known as **Nef carbonyl synthesis**.

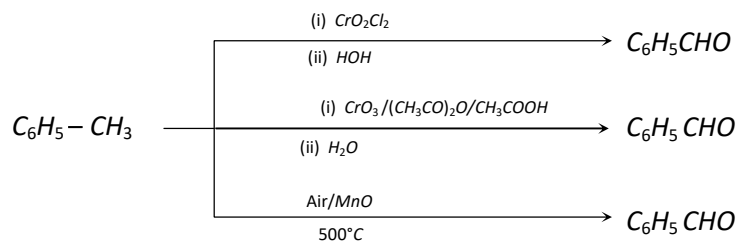


(12) **Reaction with excess alkyl lithium:** Carboxylic acids react with excess of organo lithium to give lithium salt of gem diols which on hydrolysis give ketones.

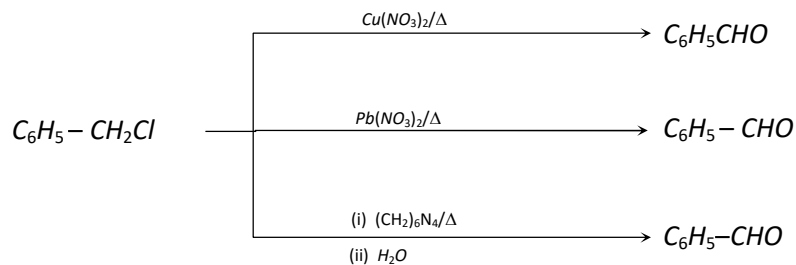


Preparation of only aromatic carbonyl compounds

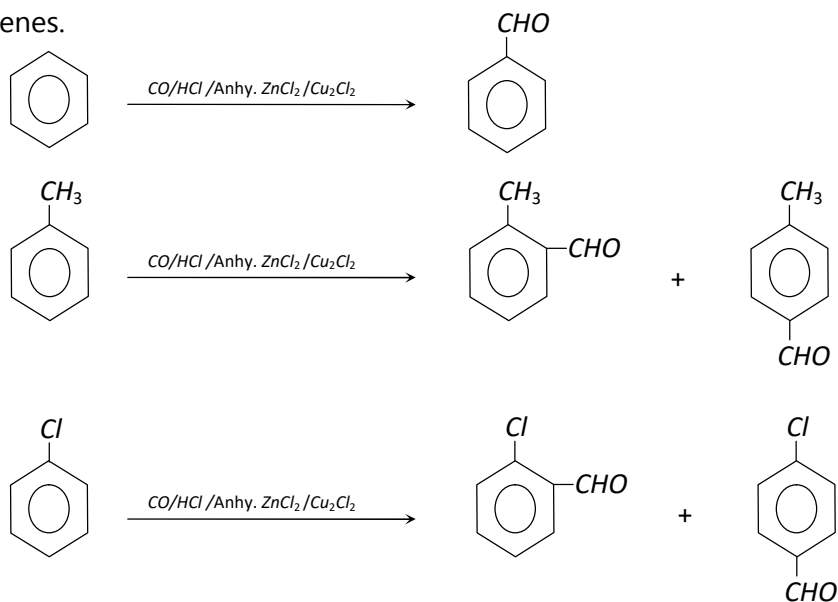
(1) **From methyl arenes:** Methyl arenes can be converted into aldehydes by the following reagents



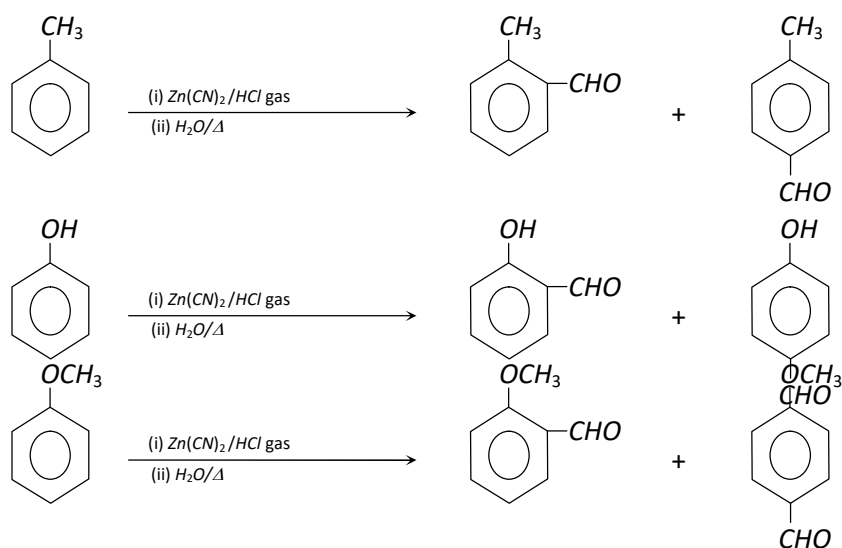
(2) **From chloro methyl arenes:** Chloromethyl arenes on oxidation give aromatic aldehydes.



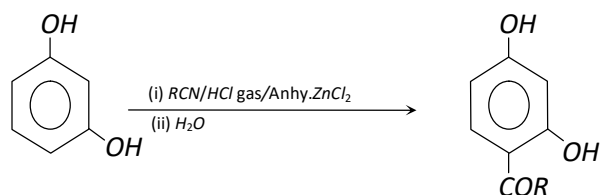
(3) **Gattermann – Koch formylation:** This reaction is mainly given by aromatic hydrocarbons and halobenzenes.

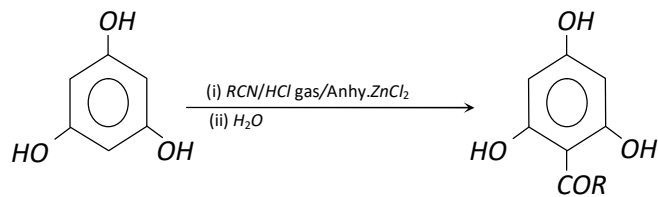


(4) **Gattermannformylation:** This reaction is mainly given by alkyl benzenes, phenols and phenolic ethers.



(5) **Houben – Hoesch reaction:** This reaction is given by di and polyhydric benzenes.





(6) **Reimer – Tiemann reaction:** Phenol gives o- and p- hydroxy benzaldehyde in this reaction.

