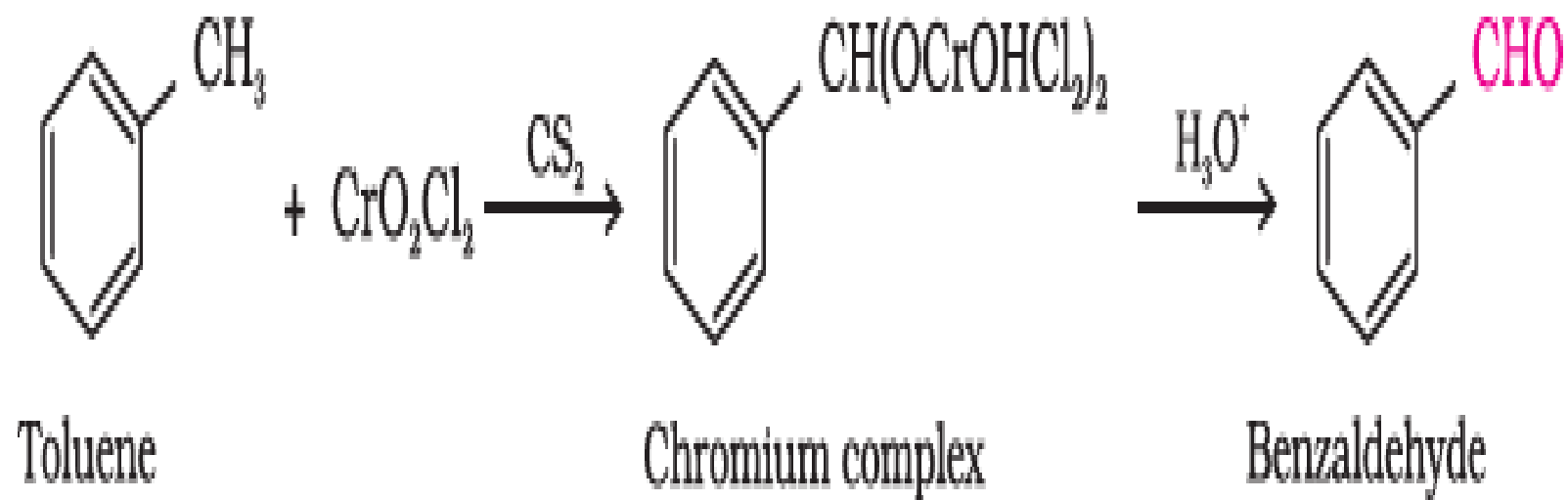


PREPARATION OF ALDEHYDES AND KETONES

CLASS XII

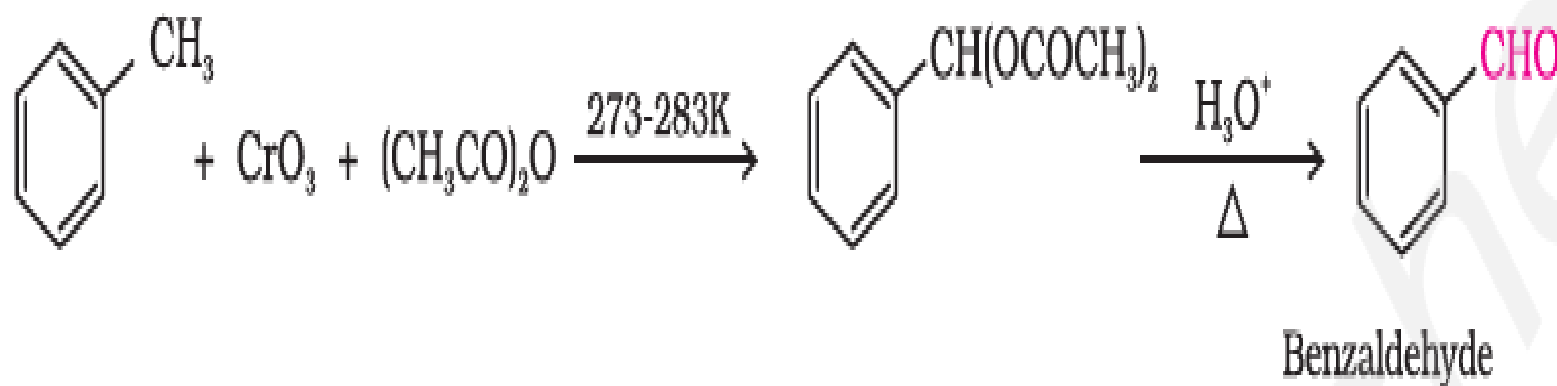
PREPARATION



This reaction is called Etard reaction.

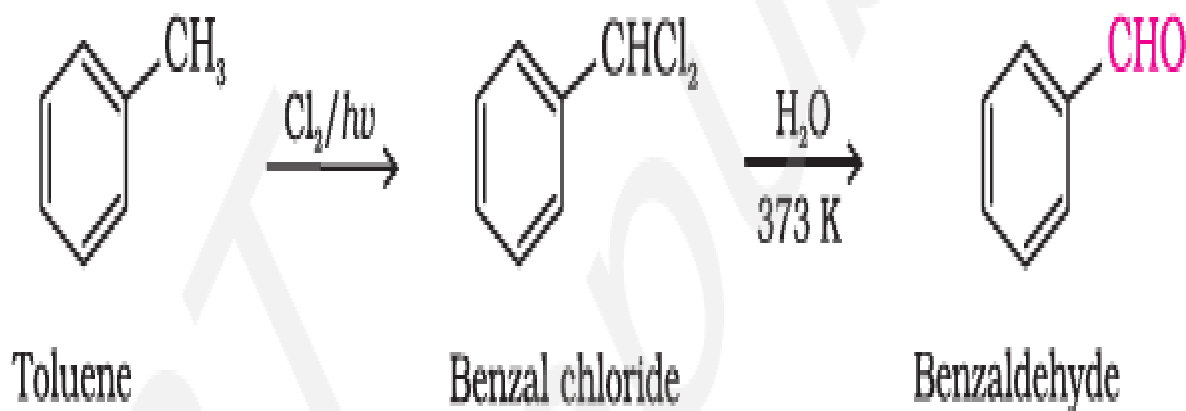
ALDEHYDE PREPARATION

(b) Use of chromic oxide (CrO_3): Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



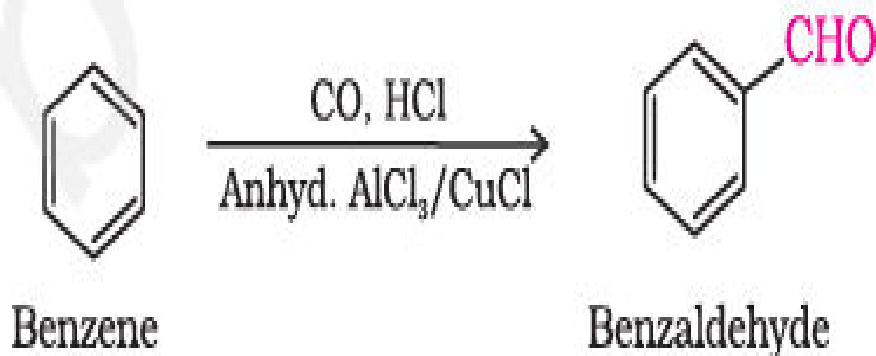
SIDE CHAIN HALOGENATIONHYDROLYSIS

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



GATTERMAN-KOCH

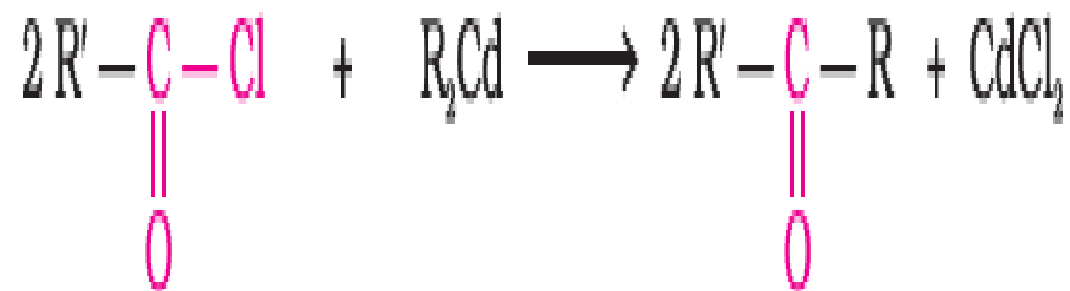
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



This reaction is known as **Gatterman-Koch** reaction.

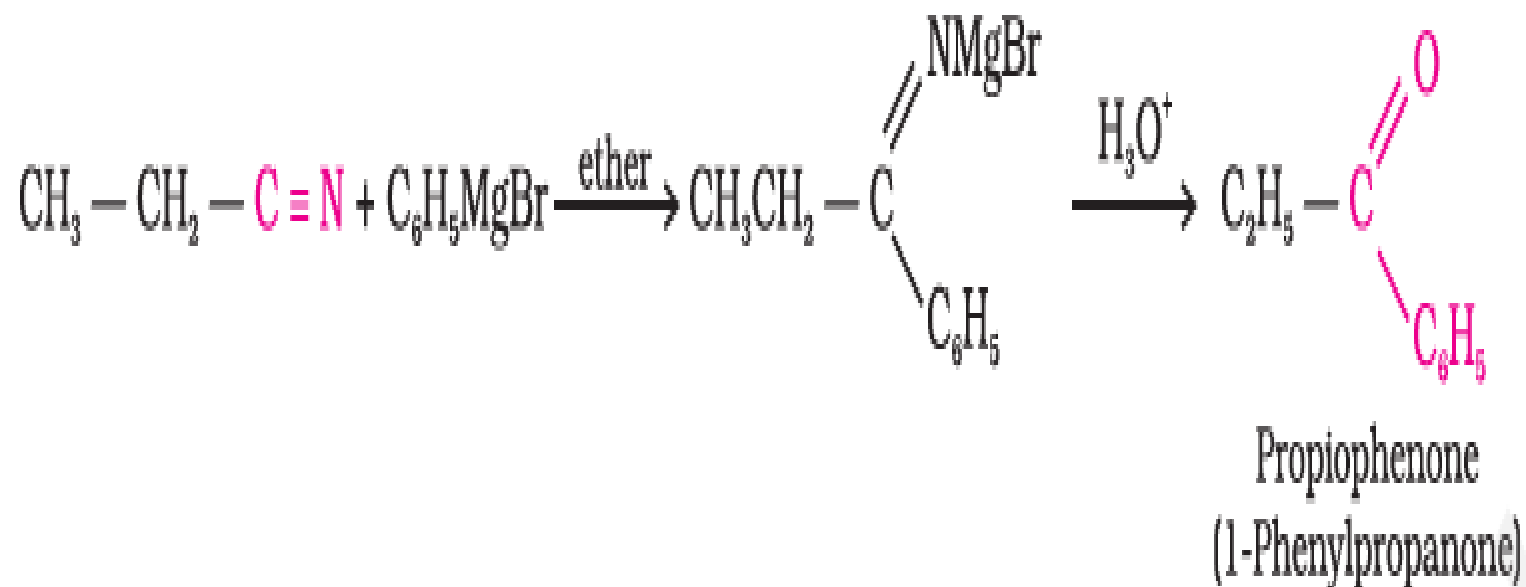
PREPARATION OF KETONE

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.



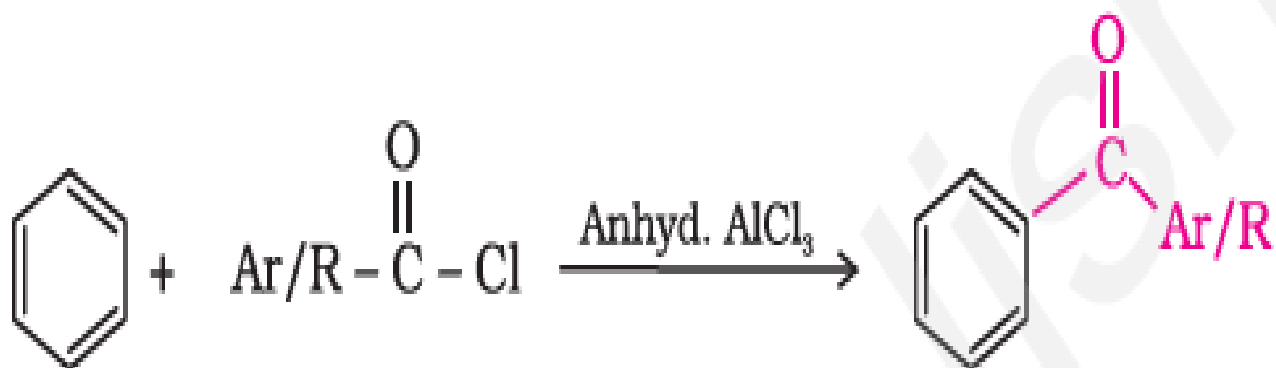
2. FROM NITRILE

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.

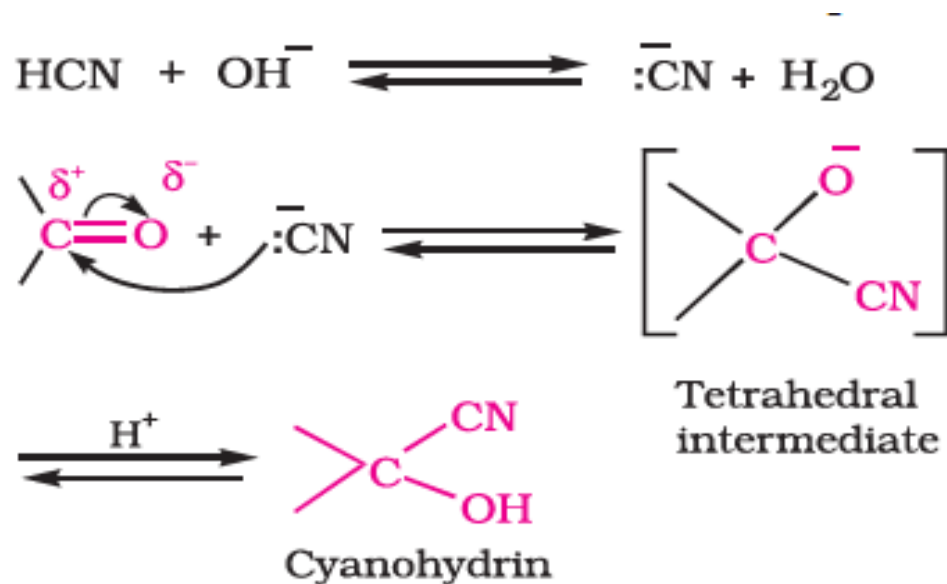


FRIEDEL-CRAFT ACYLATION

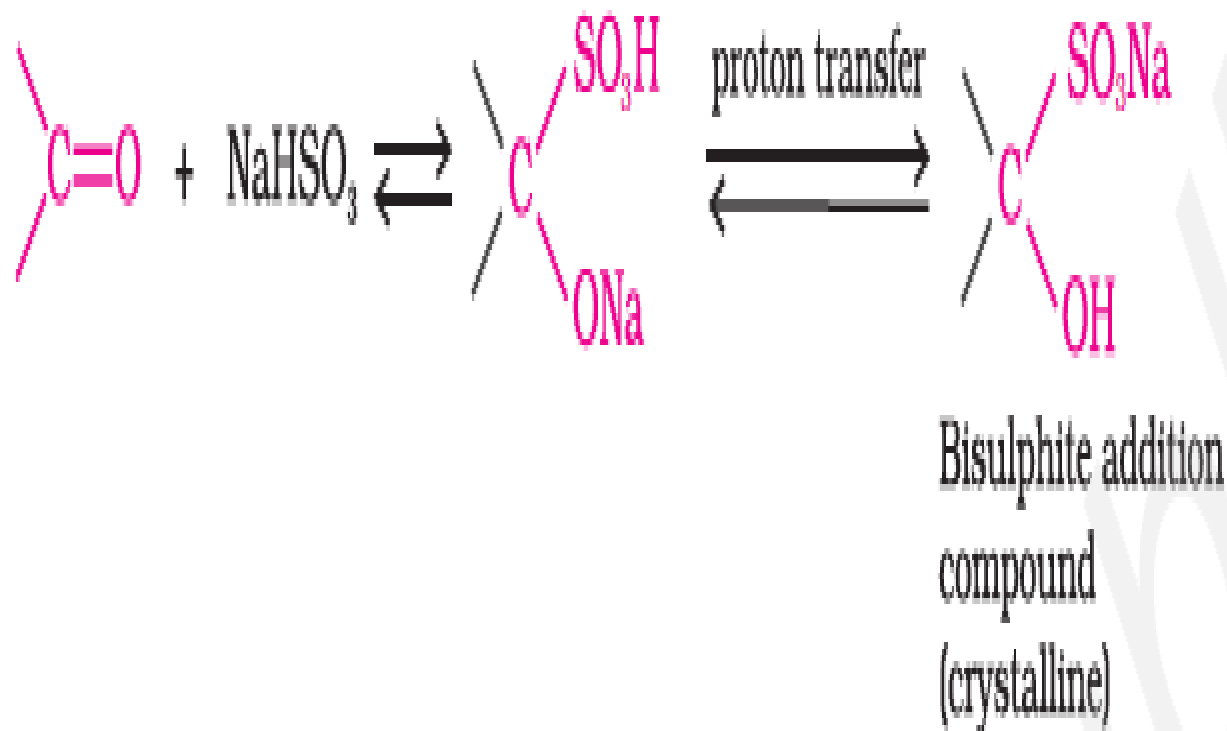
When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as Friedel-Crafts acylation reaction.



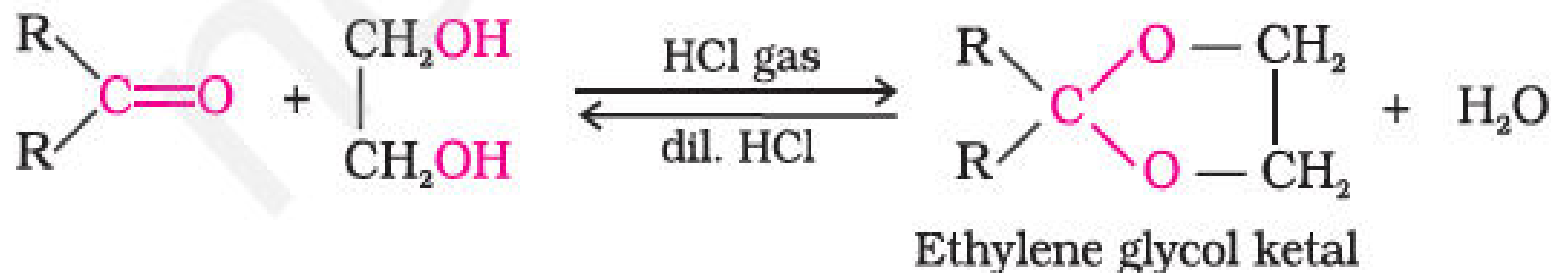
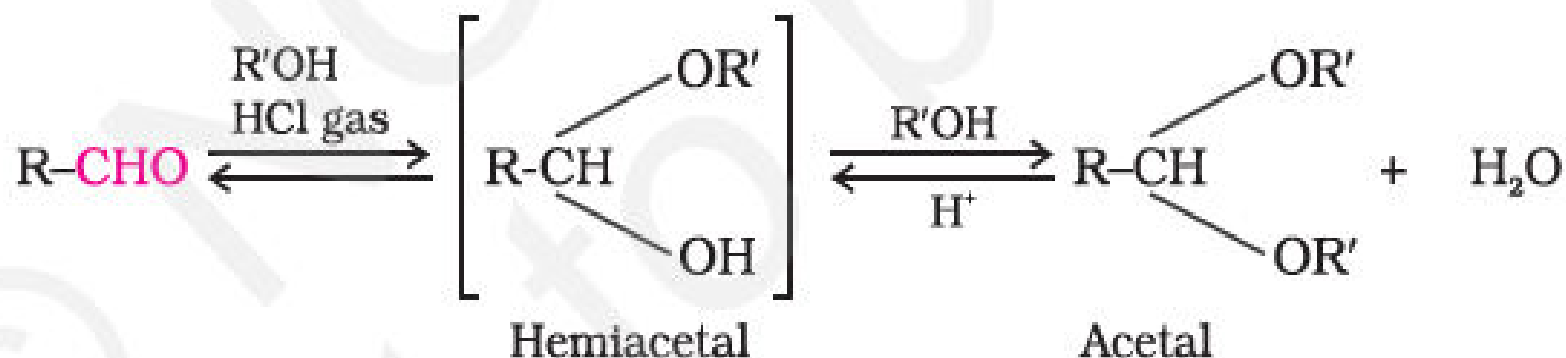
Nucleophilic addition -cyanohydrin



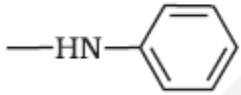
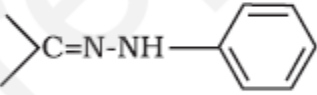
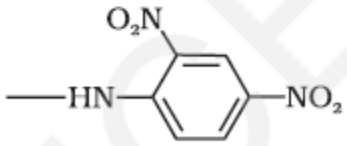
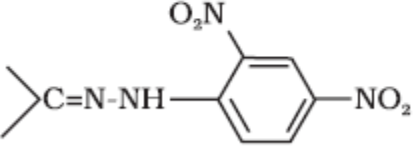
2. Addition of sodium bisulphite



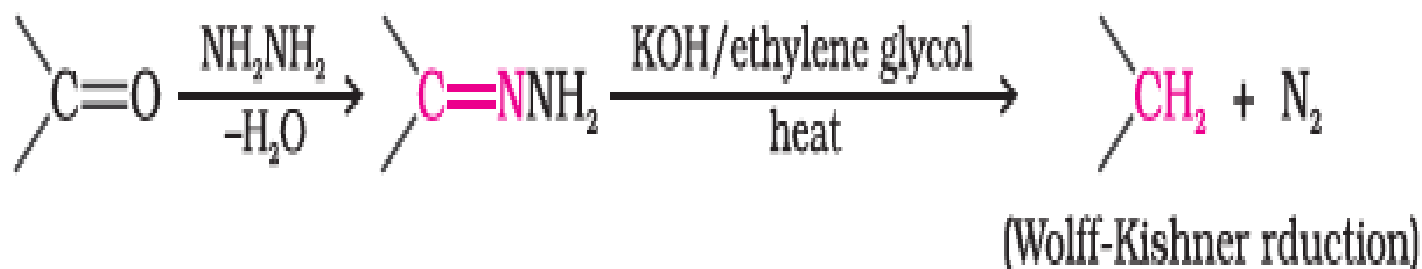
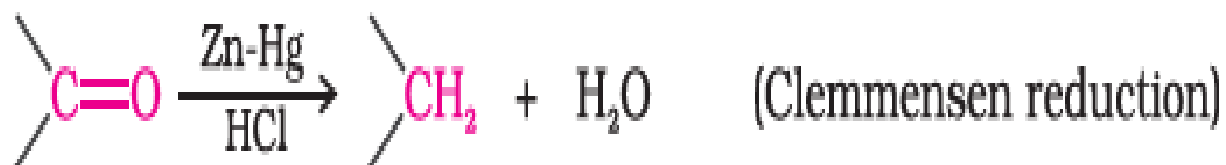
3. Addition of alcohols



Addition of ammonia derivatives

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
-OH	Hydroxylamine	>C=N-OH	Oxime
-NH ₂	Hydrazine	>C=N-NH_2	Hydrazone
-HN- 	Phenylhydrazine	>C=N-NH- 	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	>C=N-NH- 	2,4 Dinitrophenylhydrazone
-NH-C(=O)-NH ₂	Semicarbazide	$\text{>C=N-NH-C(=O)-NH}_2$	Semicarbazone

2.reduction



3.oxidation

- (i) *Tollens' test*: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

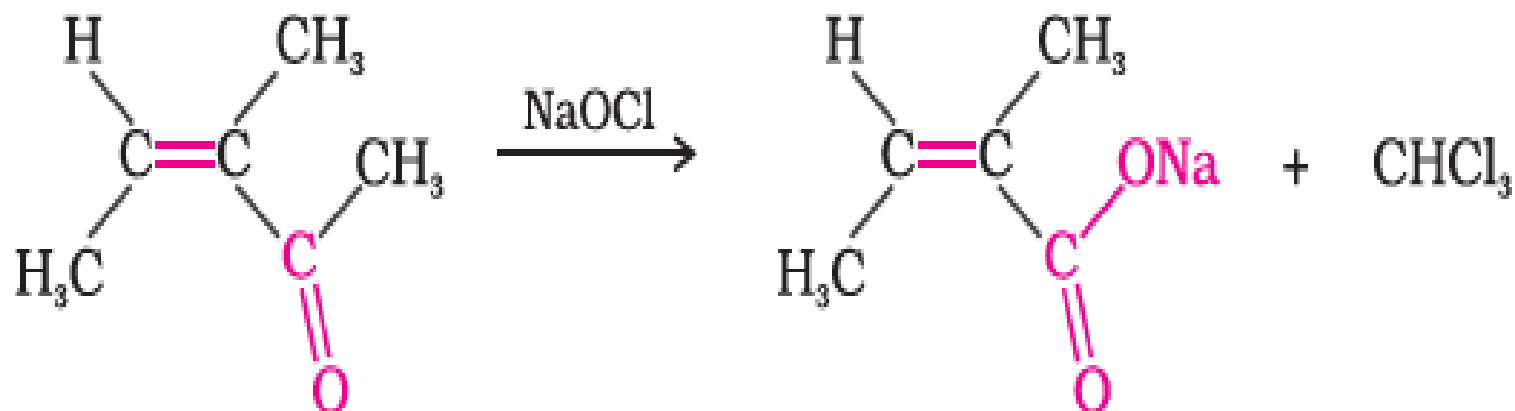
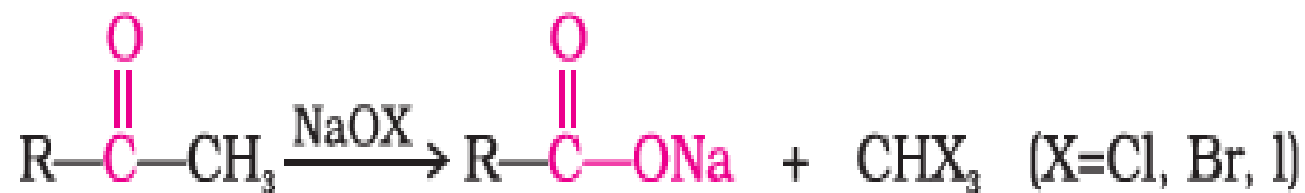


ii.Fehlings test

(ii) *Fehling's test*: Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



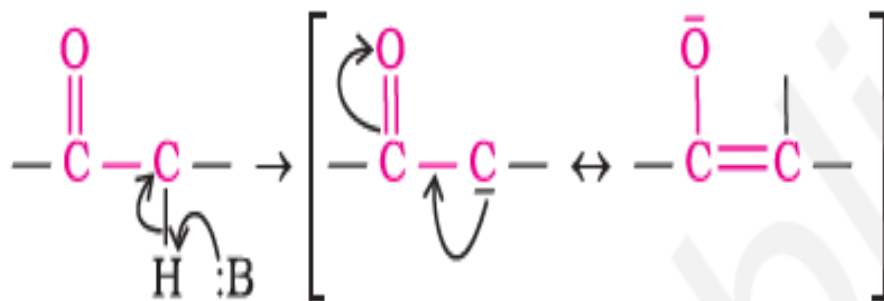
iii.haloform(iodoform)



Alpha hydrogen-acidity

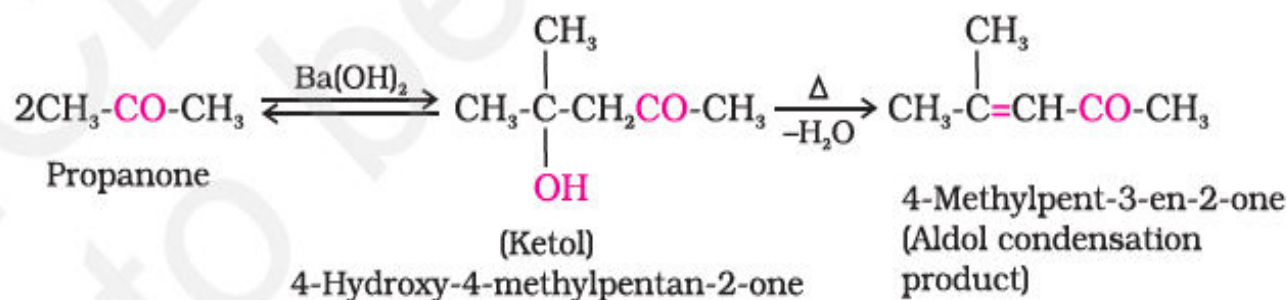
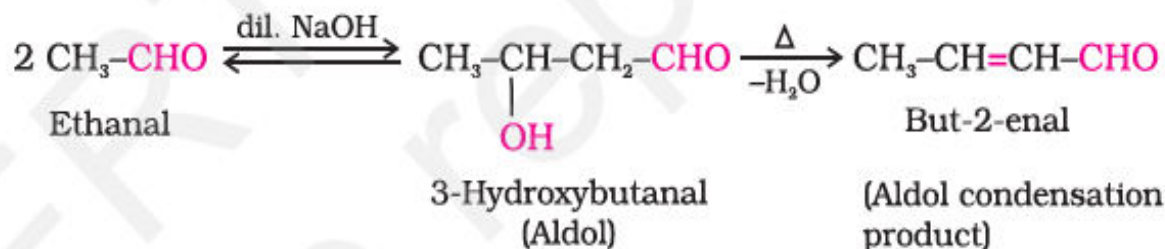
Acidity of α -hydrogens of aldehydes and ketones: The aldehydes and ketones undergo a number of reactions due to the acidic nature of α -hydrogen.

The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

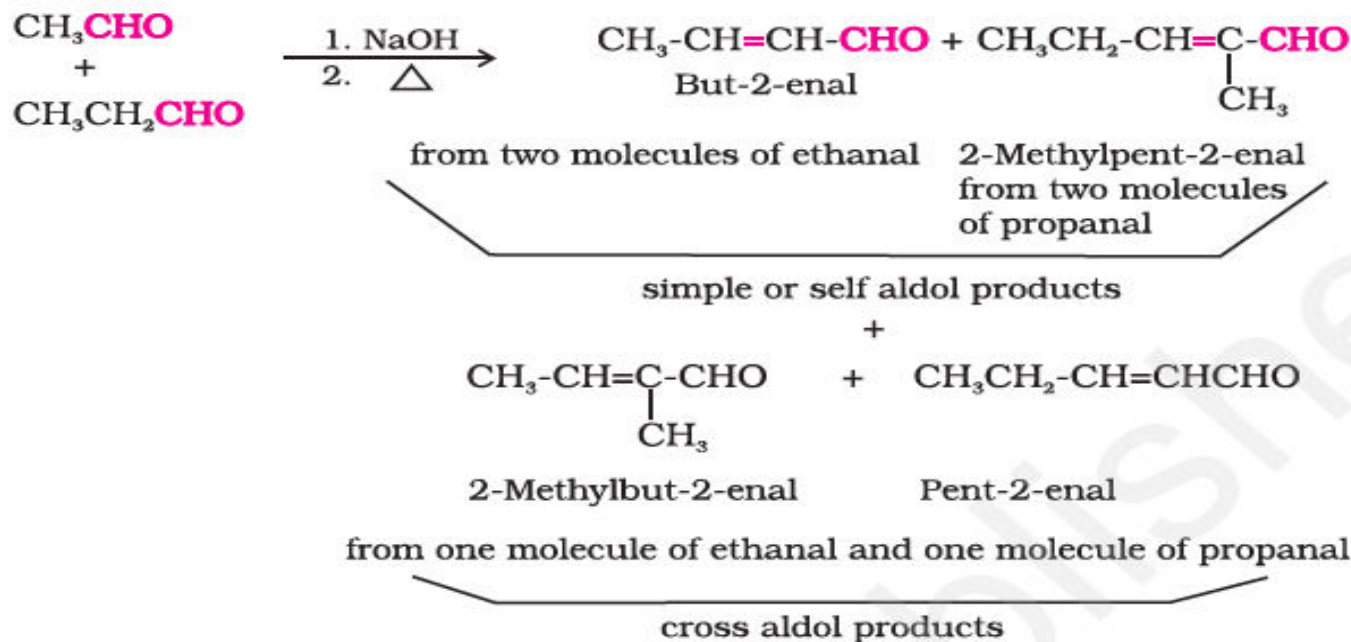


Aldol condensation

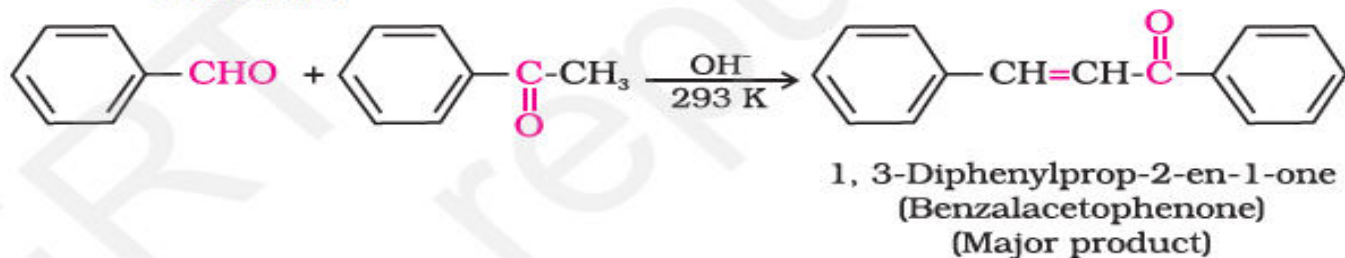
(i) *Aldol condensation:* Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.



Cross –aldol condensation

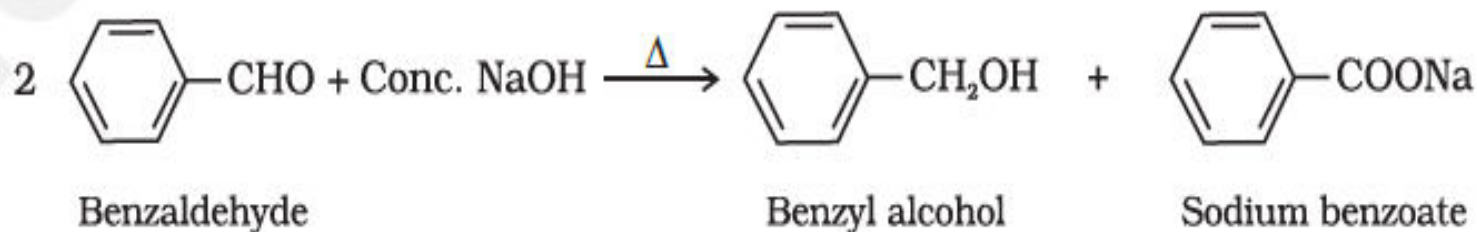
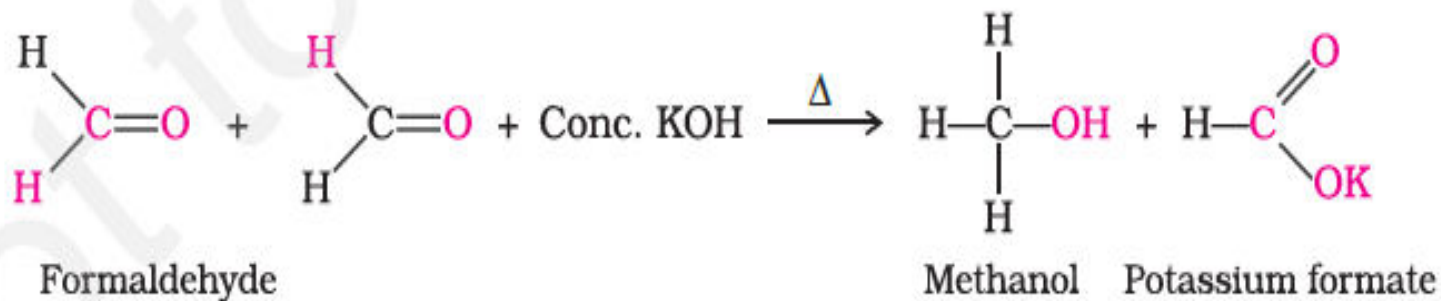


Ketones can also be used as one component in the cross aldol reactions.



Cannizaro reaction

(i) **Cannizzaro reaction:** Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



3. Electrophilic substitution

- (ii) *Electrophilic substitution reaction: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.*

