

Comparison between chemical reactions of aldehyde and ketone : similar reactions

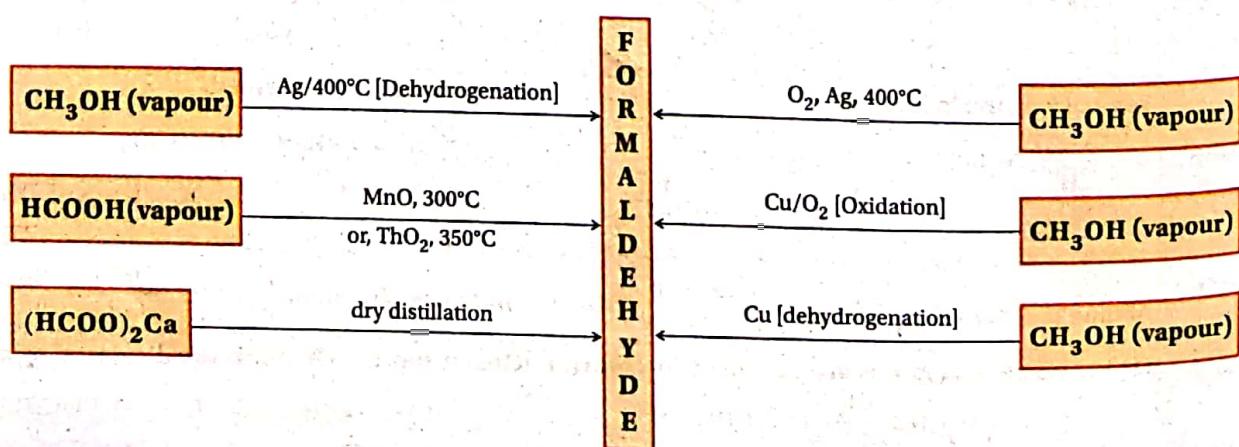
Reaction	Aldehyde	Ketone
Addition reaction with HCN	Cyanohydrin is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} + HCN \rightarrow \begin{array}{c} R \\ \\ R-C(OH)CN \end{array}$	Cyanohydrin is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} + HCN \rightarrow \begin{array}{c} R \\ \\ R-C(OH)CN \end{array}$
Addition reaction with NaHSO_3	Bisulphite addition compound is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{NaHSO}_3 \rightarrow \begin{array}{c} R \\ \\ R-C(OH)SO_3\text{Na} \end{array}$	Bisulphite addition compound is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{NaHSO}_3 \rightarrow \begin{array}{c} R \\ \\ R-C(OH)SO_3\text{Na} \end{array}$
Reaction with PCl_5	gem-dichloride is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{PCl}_5} \begin{array}{c} R \\ \\ R-C(Cl)Cl \end{array}$	gem-dichloride is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{PCl}_5} \begin{array}{c} R \\ \\ R-C(Cl)Cl \end{array}$
Reaction with NH_2OH	Aldoxime is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{NH}_2\text{OH}} \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NOH} \end{array}$	Ketoxime is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{NH}_2\text{OH}} \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NOH} \end{array}$
Reaction with NH_2NH_2	Hydrazone is obtained. $\text{R}-\text{CH}=\text{O} + \text{NH}_2\text{NH}_2 \rightarrow \text{R}-\text{CH}=\text{N}-\text{NH}_2$	Hydrazone is obtained. $\text{R}_2\text{C}=\text{O} + \text{NH}_2\text{NH}_2 \rightarrow \text{R}_2\text{C}=\text{N}-\text{NH}_2$
Reaction with phenylhydrazine	Phenylhydrazone is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{C}_6\text{H}_5\text{NNHNH}_2} \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NNHC}_6\text{H}_5 \end{array}$	Phenylhydrazone is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow{\text{C}_6\text{H}_5\text{NNHNH}_2} \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NNHC}_6\text{H}_5 \end{array}$
Reaction with 2,4-di-nitrophenylhydrazone	2,4-dinitrophenylhydrazone is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{NHNH}_2 \text{---} \text{NO}_2 \longrightarrow \text{NHNH}_2 \text{---} \begin{array}{c} R \\ \\ C=\text{O} \end{array} \text{---} \text{NO}_2$	2,4-dinitrophenylhydrazone is produced. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{NHNH}_2 \text{---} \text{NO}_2 \longrightarrow \text{NHNH}_2 \text{---} \begin{array}{c} R \\ \\ C=\text{O} \end{array} \text{---} \text{NO}_2$
Reaction with semicarbazide	Semicarbazone is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{H}_2\text{N-NHCONH}_2 \longrightarrow \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NHCONH}_2 \end{array}$	Semicarbazone is formed. $\begin{array}{c} R \\ \\ R-C=O \end{array} + \text{H}_2\text{N-NHCONH}_2 \longrightarrow \begin{array}{c} R \\ \\ R-C(=\text{O})\text{NHCONH}_2 \end{array}$
Clemmensen reduction	Alkane is obtained. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}} \begin{array}{c} R \\ \\ R-CH_2 \end{array}$	Alkane is obtained. $\begin{array}{c} R \\ \\ R-C=O \end{array} \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}} \begin{array}{c} R \\ \\ R-CH_2 \end{array}$
Reaction with Cl_2	One or more α -H atoms are displaced by chlorine. $\text{CH}_3\text{CHO} \xrightarrow{\text{Cl}_2} \text{CCl}_3\text{CHO}$	One or more α -H atoms are displaced by chlorine. $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3\text{COCH}_2\text{Cl} + \text{CH}_3\text{COCHCl}_2, \text{etc.}$

Comparison between chemical reactions of aldehyde and ketone : dissimilar reactions

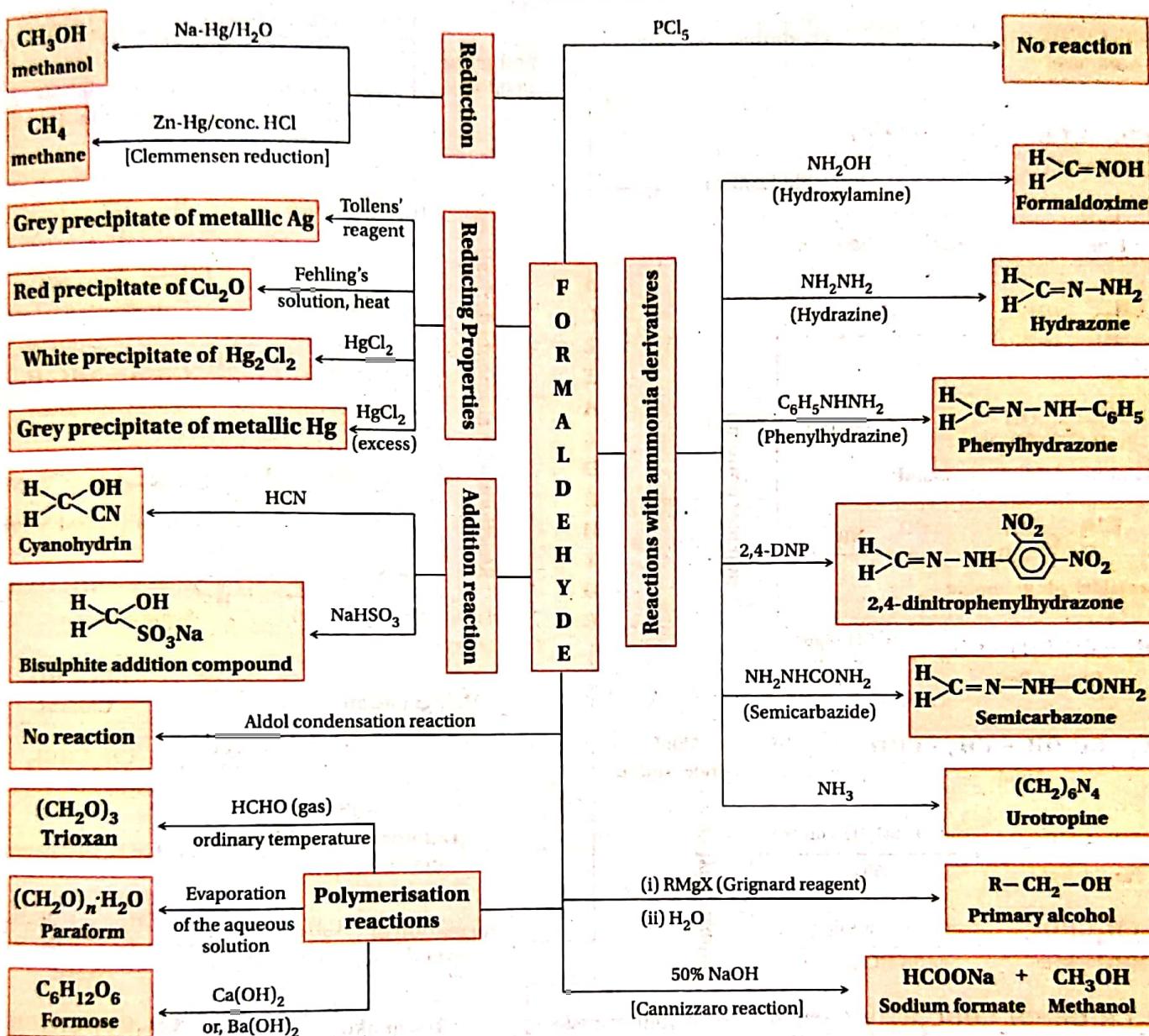
Reaction	Aldehyde	Ketone
Reaction with Tollens' reagent	Tollens' reagent is reduced and as a result, metallic silver is precipitated.	Tollens' reagent is not reduced and consequently no precipitate appears.
Reaction with Fehling's solution	Fehling's solution is reduced and red cuprous oxide (Cu_2O) is precipitated.	Fehling's solution is not reduced and no red precipitate of cuprous oxide (Cu_2O) is obtained.
Reaction with Schiff reagent	At ordinary temperature, the pink colour of the reagent is restored.	At ordinary temperature, the pink colour of the reagent is not restored.
Oxidation reaction	Easily gets oxidised and an acid with the same number of carbon atoms is produced. $\text{CH}_3\text{CHO} \xrightarrow{[O]} \text{CH}_3\text{COOH}$	Does not get oxidised easily. Strong oxidising agents produce acids with lesser number of carbon atoms. $\text{CH}_3\text{COCH}_2\text{CH}_3 \xrightarrow{[O]} 2\text{CH}_3\text{COOH}$
Reduction reaction	Primary alcohol is obtained as a result of reduction. $\text{R}-\text{CHO} \xrightarrow[\text{[H]}]{\text{LiAlH}_4} \text{R}-\text{CH}_2\text{OH}$	Secondary alcohol is obtained as a result of reduction. $\text{R}_2\text{C}=\text{O} \xrightarrow[\text{[H]}]{\text{LiAlH}_4} \text{R}_2\text{CHOH}$
Reaction with Grignard reagents	Secondary alcohol is obtained. $\text{CH}_3-\overset{\text{H}}{\underset{\text{R}}{\text{C}}}=\text{O} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) RMgX}} \text{CH}_3-\overset{\text{H}}{\underset{\text{R}}{\text{C}}}-\text{OH}$ (HCHO forms 1° alcohol)	Tertiary alcohol is obtained. $\text{H}_3\text{C}-\overset{\text{H}_3\text{C}}{\underset{\text{H}_3\text{C}}{\text{C}}}=\text{O} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) RMgX}} \text{H}_3\text{C}-\overset{\text{R}}{\underset{\text{H}_3\text{C}}{\text{C}}}-\text{OH}$
Reaction with monohydric alcohol	Acetal is produced in the presence of dry HCl gas. $\text{R}_2\text{C}=\text{O} + \text{CH}_3\text{OH} \xrightarrow{\text{dry HCl}} \text{R}_2\text{C}(\text{OCH}_3)_2$	Does not react with monohydric alcohol. But reacts with dihydric alcohol in the presence of dry HCl gas to form cyclic ketal.

Preparation & Reactions of Aldehydes & Ketones

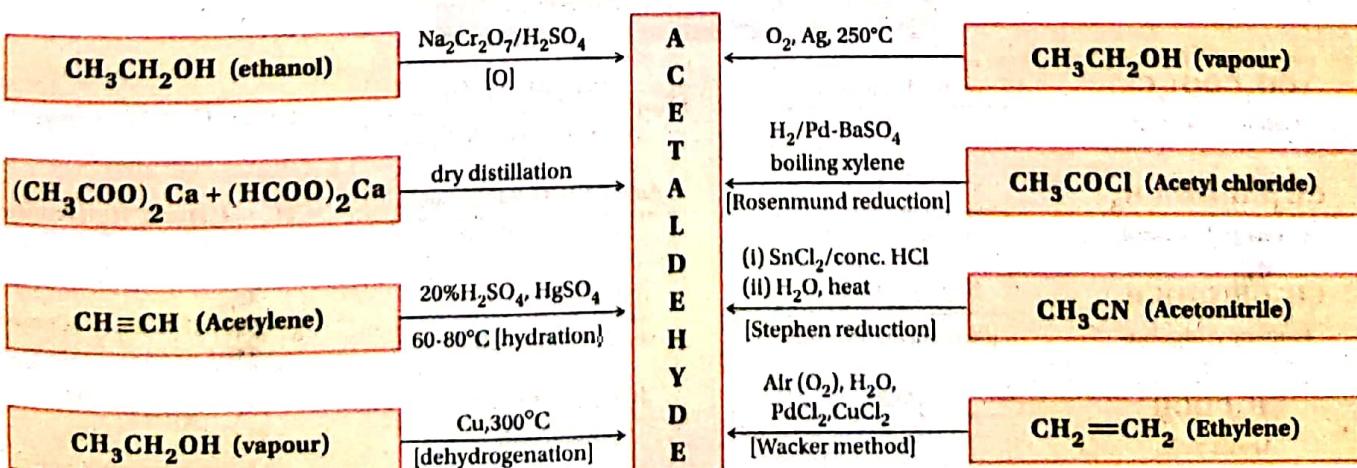
Preparation of Formaldehyde (HCHO)



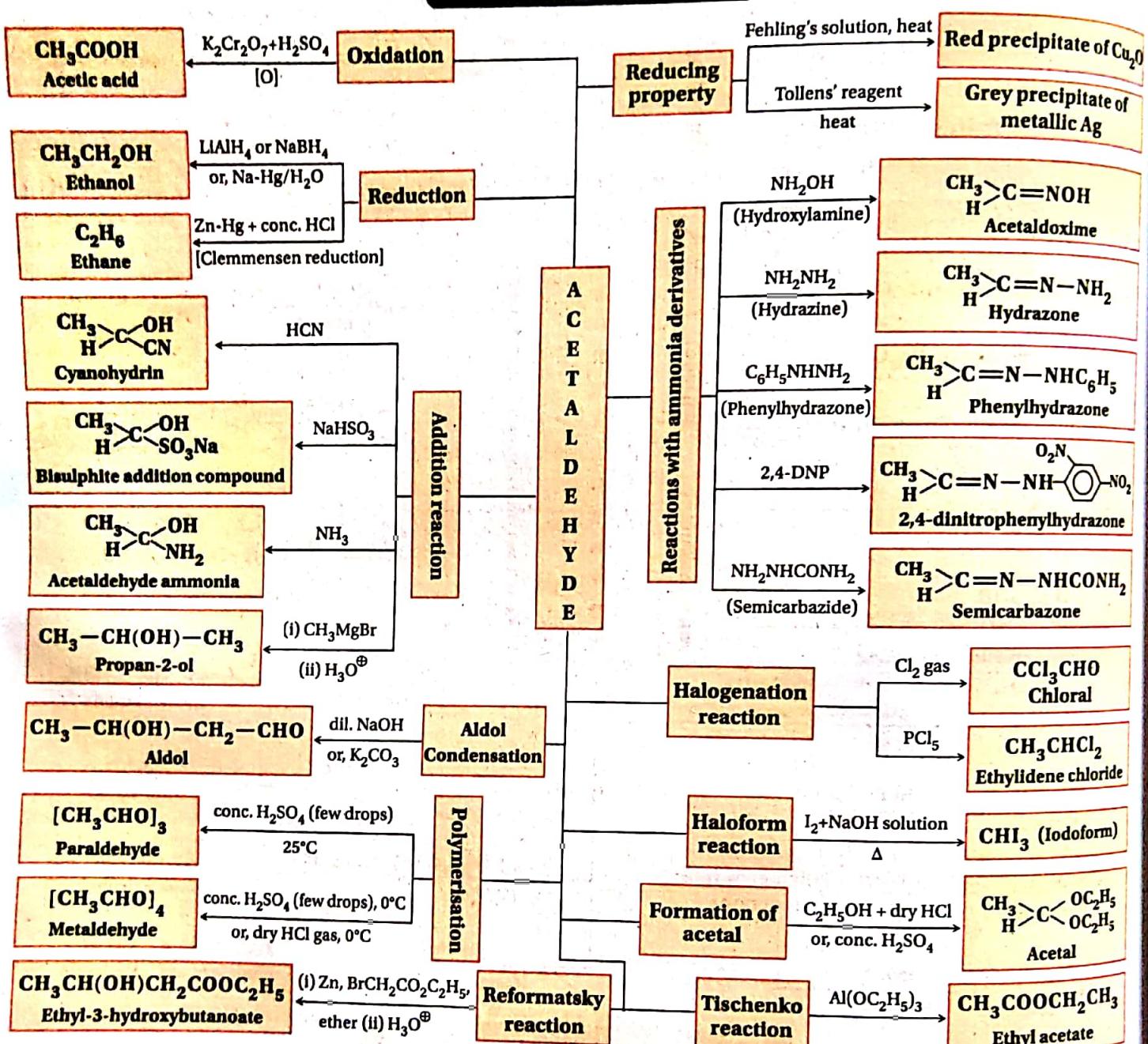
Reactions of Formaldehyde



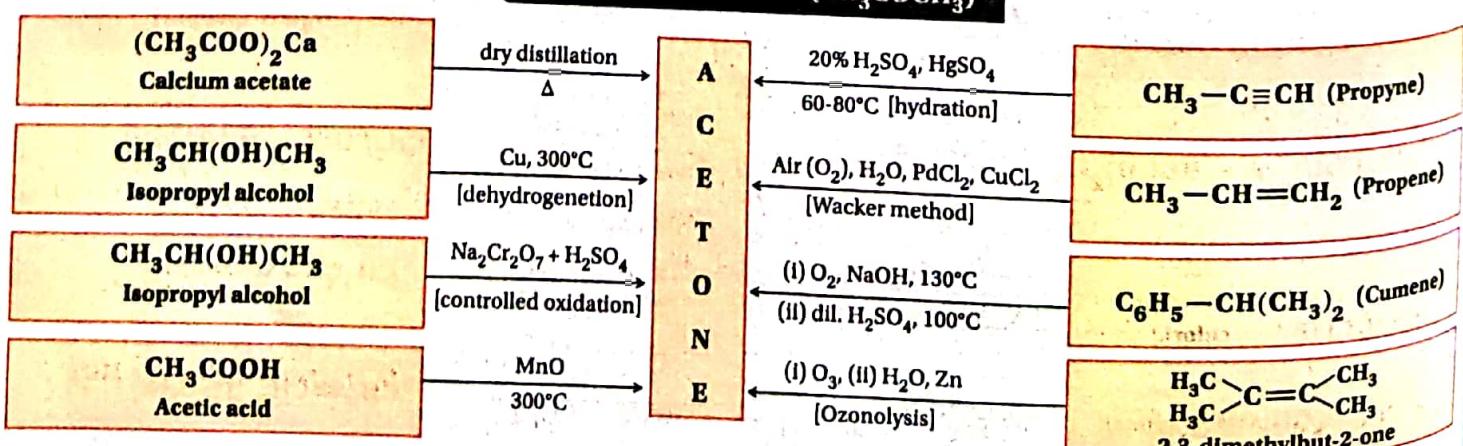
Preparation of Acetaldehyde (CH_3CHO)



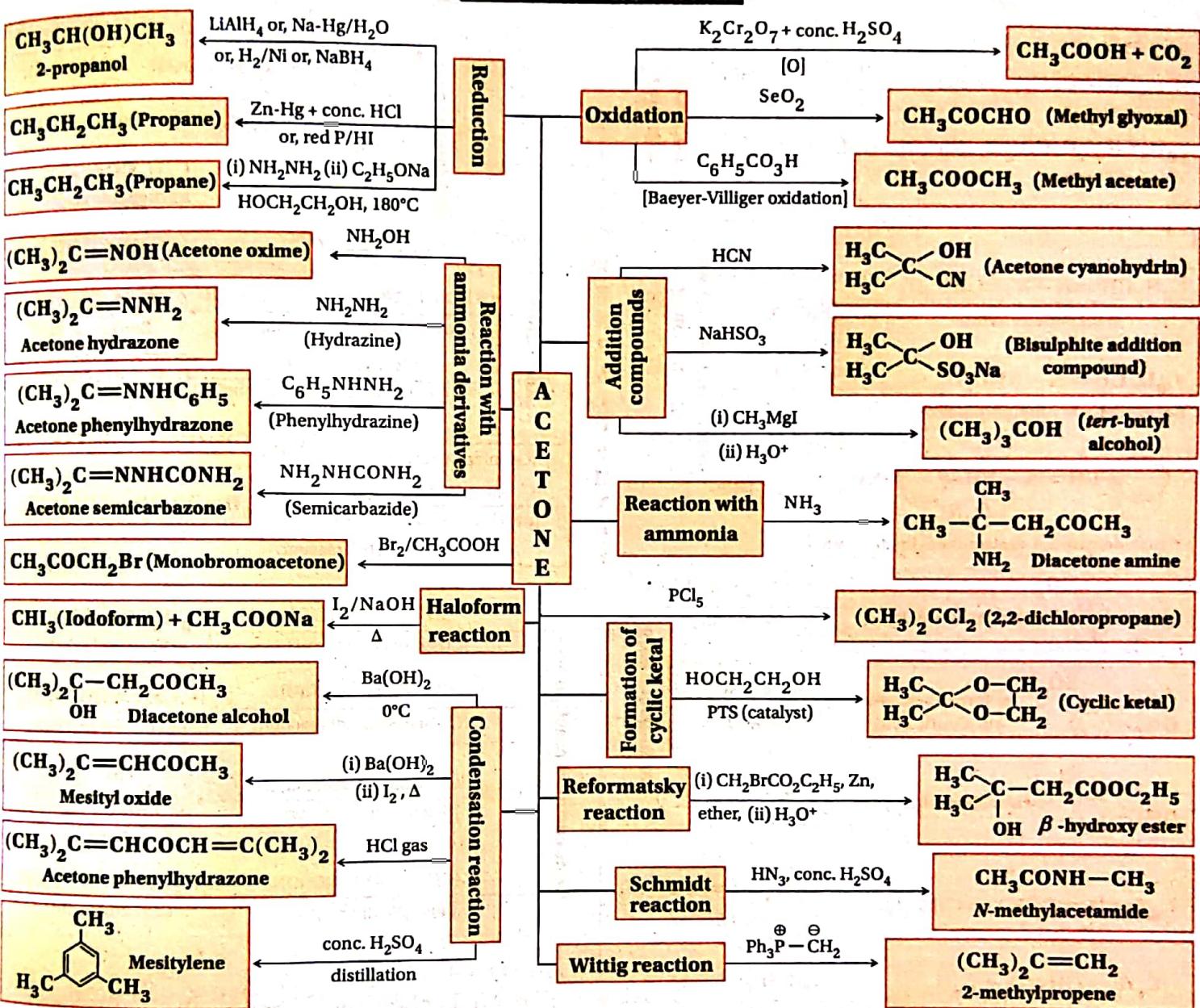
Reactions of Acetaldehyde



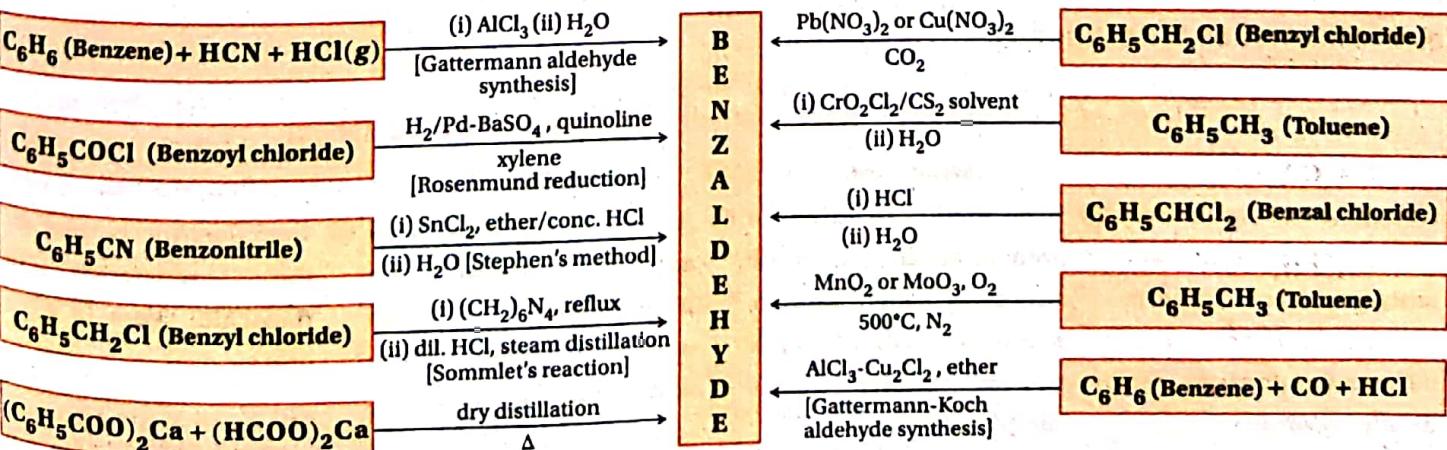
Preparation of Acetone (CH_3COCH_3)



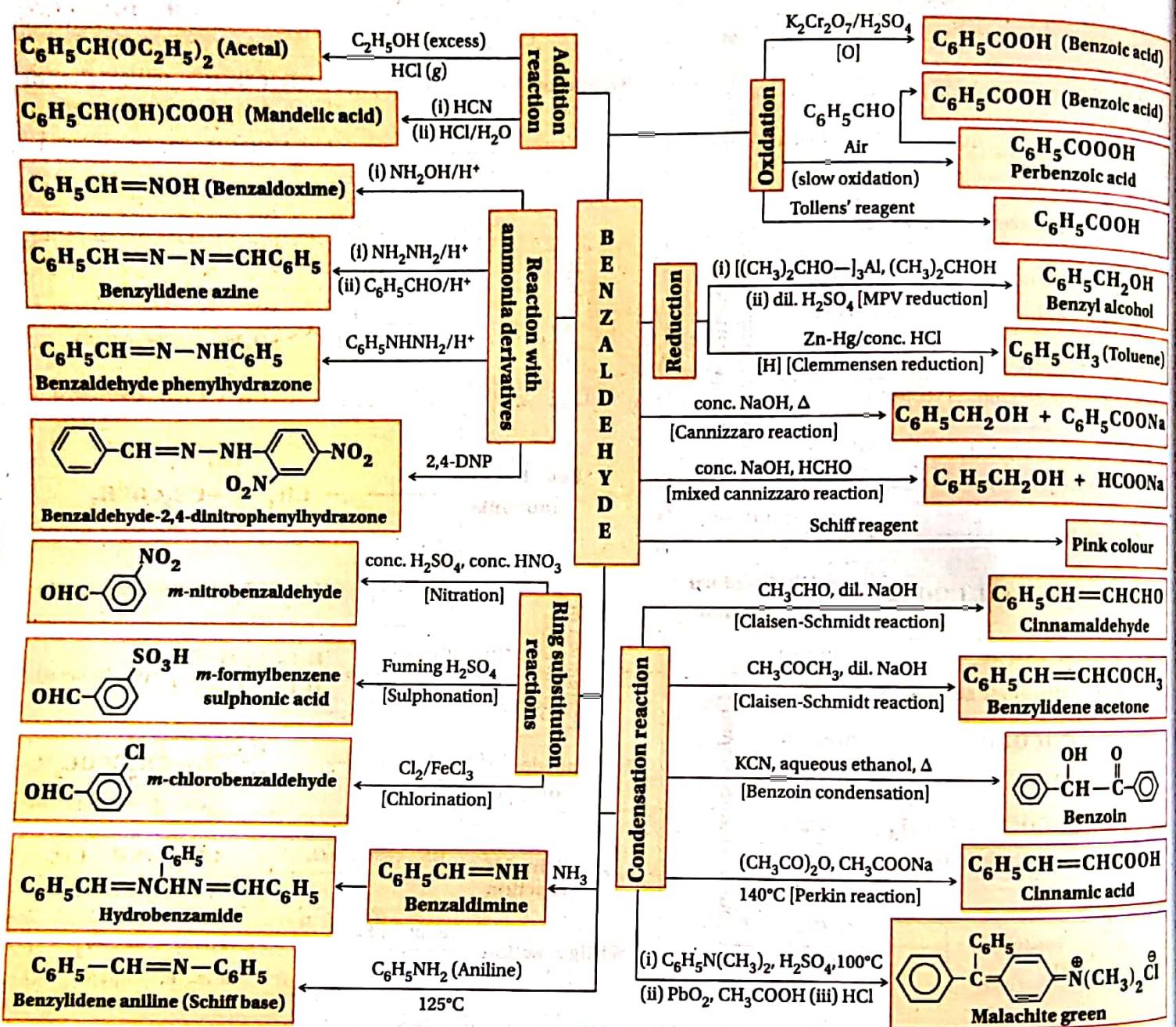
Reactions of Acetone



Preparation of Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$)



Reactions of Benzaldehyde



Uses of Formaldehyde, Acetaldehyde, Acetone and Benzaldehyde

Formaldehyde	Acetaldehyde	Acetone	Benzaldehyde
<p>① Formaldehyde is a very strong disinfectant and antiseptic. Rooms used by patients suffering from infectious diseases are disinfected by it.</p>	<p>① It is extensively used to prepare acetic acid, acetic anhydride, ethyl acetate, n-butanol (solvent & raw material of other organic compounds).</p>	<p>① Acetone is extensively used as a solvent for nitrocellulose, cellulose acetate, acetylene, varnish and lacquer, etc.</p>	<p>① Benzaldehyde is used for the preparation of malachite green (a green organic dye).</p>

Formaldehyde	Acetaldehyde	Acetone	Benzaldehyde
② Biological or anatomical specimens are preserved by 40% aq. solution of HCHO. Formalin protects these species from putrefaction.	② It is used in the preparation of dyes.	② It is used for the preparation of plexiglass (unbreakable glass).	② It is used for the preparation of benzoyl chloride, cinnamic acid, cinnamaldehyde, etc.
③ It is extensively used in the manufacture of bakelite and urea-formaldehyde resin, the basic raw materials for plastic.	③ Paraldehyde (trimer of CH_3CHO) is used as hypnotic agent. Metaldehyde (tetramer of CH_3CHO) is used as fuel.	③ It is widely used for the preparation of chloroform, iodoform, medicines, e.g., chloritone, sulphonal, etc.	③ It is widely used as a flavouring agent in perfume industry.
④ Hexamethylene tetraamine (urotropine), obtained when formaldehyde reacts with ammonia, is used in the treatment of urinary infection.	④ It is used for the preparation of butadiene (a constituent of Buna rubber).	④ It is used in the preparation of smokeless gun-powder.	
⑤ Explosives (RDX or cyclonite) are prepared by controlled nitration of urotropine.		⑤ It is used for preparing nail-polish, artificial flavouring agents, synthetic rubber, etc.	

Identification of Aldehydes & Ketones

Identification of Formaldehyde, Acetaldehyde, Acetone and Benzaldehyde

Formaldehyde	Acetaldehyde	Acetone	Benzaldehyde
① Formaldehyde can be identified by its characteristic pungent smell.	① When acetaldehyde is mixed with colourless Schiff reagent and the mixture is shaken, it restores the pink colour of the Schiff reagent.	① When acetone is heated with NH_4OH in the presence of iodine, yellow crystals of iodoform having characteristic odour is precipitated.	① Schiff reagent test : When 2-3 drops of benzaldehyde are added to Schiff reagent, the pink colour of the reagent is restored.
② Schryver's test : Few drops of phenylhydrazine and 1mL dilute potassium ferrocyanide (5%) are added to 2mL of dilute formaldehyde solution (1%). When resulting solution is acidified with conc. HCl, a pink colour develops.	② When warmed with the Fehling's solution, acetaldehyde reduces it to give a red precipitate of Cu_2O .	② If NaOH solution is added drop wise to acetone mixed with freshly prepared sodium nitroprusside solution, the solution turns orange. After some time, the colour of the solution changes to yellow.	② Tollens' reagent test : When 2-3 drops of benzaldehyde are added to Tollens' reagent and the mixture is warmed in a water bath, a silver mirror is formed on the inner walls of the test tube.

Formaldehyde	Acetaldehyde	Acetone	Benzaldehyde
<p>③ Formaldehyde can also be identified by determining the melting point of its 2,4-dinitrophenylhydrazone (167°C) derivative by its action on 2,4-DNP.</p>	<p>③ Acetaldehyde reduces Tollens' reagent with the formation of metallic silver or silver mirror.</p>	<p>③ Acetone reacts with 2,4-dinitrophenylhydrazine to form orange crystalline precipitate having melting point of 126°C.</p>	<p>③ Malachite green test : 1mL of dimethyl-aniline is added to 2 drops of benzal-dehyde and heated with a small amount of conc. H_2SO_4 or ZnCl_2. Acetic acid & PbO_2 are then added to it. If resulting solution is treated with excess conc. HCl, deep green colour is produced.</p>

Distinctive Chemical Tests

Acetaldehyde and Acetone

Test	Acetaldehyde	Acetone
① Schiff reagent is added and shaken in the cold condition.	① At ordinary temperature, pink colour appears.	① No change in colour at ordinary temperature.
② Heated with Tollens' reagent.	② Metallic silver is deposited.	② No precipitation of metallic silver occurs.
③ Heated with Fehling's solution.	③ Red precipitate of Cu_2O is obtained.	③ Red precipitate of Cu_2O is not obtained.

Ethyl alcohol and Acetone

Test	Ethyl alcohol	Acetone
① Heated with iodine (in KI solution) and NH_4OH .	① No yellow crystals of iodoform are produced.	① Yellow crystals of iodoform with characteristic smell are produced.
② Heated with Brady's reagent (2,4-DNP).	② Orange or yellow crystals are not obtained.	② Orange crystals (m. p. 126°C) are produced.
③ Heated with glacial acetic acid in the presence of conc. H_2SO_4 .	③ Ethyl acetate having characteristic smell is obtained.	③ No compound with any characteristic smell is produced.

Ethyl alcohol and Acetaldehyde

Test	Ethyl alcohol	Acetaldehyde
① Heated with Tollens' reagent.	① Metallic silver is not precipitated.	① Metallic silver is precipitated.
② Heated with Fehling's solution.	② No red precipitate of Cu_2O is produced.	② Red precipitate of Cu_2O is produced.

Formaldehyde and Acetaldehyde

Test	Formaldehyde	Acetaldehyde
Heated with conc. NaOH solution and KI solution containing dissolved iodine.	No yellow crystals of iodoform are produced.	Yellow crystals of iodoform having characteristic smell are obtained.

Formaldehyde and Acetone

Test	Formaldehyde	Acetone
① Heated with conc. NaOH solution and KI solution containing dissolved iodine.	① Iodoform is not obtained.	① Yellow crystals of iodoform having characteristic smell are produced.

Test	Formaldehyde	Acetone
② Heated with Tollens' reagent.	② Metallic silver is precipitated.	② Metallic silver is not precipitated.

Ethyl alcohol and Formaldehyde

Test	Ethyl alcohol	Formaldehyde
① Heated with Tollens' reagent.	① Metallic silver is not precipitated.	① Metallic silver is precipitated.
② Heated with Fehling's solution.	② No red precipitate of Cu_2O is obtained.	② Red precipitate of Cu_2O is produced.
③ Heated with conc. NaOH and Iodine dissolved in KI solution.	③ Yellow crystals of iodoform having characteristic odour are formed.	③ Yellow crystals of iodoform are not obtained.

Pentan-2-one and Pentan-3-one

Test	Pentan-2-one	Pentan-3-one
Heated with conc. NaOH solution and iodine dissolved in KI solution.	Yellow crystals of iodoform having characteristic odour are produced.	Yellow crystals of iodoform are not produced.

Acetophenone and Benzophenone

Test	Acetophenone	Benzophenone
Heated with conc. NaOH solution and iodine dissolved in KI solution.	Yellow crystals of iodoform having characteristic smell are produced.	Yellow crystals of iodoform are not obtained.

Acetaldehyde and Benzaldehyde

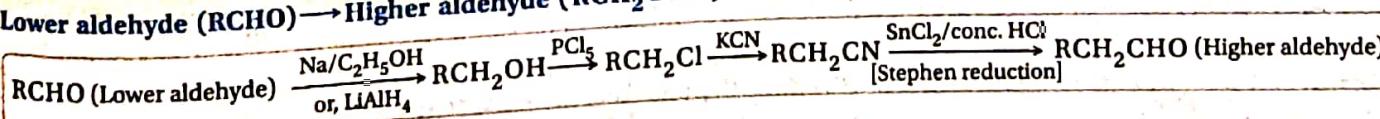
Test	Acetaldehyde	Benzaldehyde
① Heated with conc. NaOH solution and iodine dissolved in KI solution.	① Yellow crystals of iodoform having characteristic odour are obtained.	① Yellow crystals of iodoform are not produced.
② Heated with Fehling's solution.	② Red precipitate of Cu_2O is obtained.	② No red precipitate of Cu_2O is obtained.
③ Oxidised with alkaline $KMnO_4$ solution and then acidified with HCl.	③ No white precipitate is obtained.	③ White crystalline precipitate of benzoic acid is obtained.

Benzaldehyde and Acetophenone

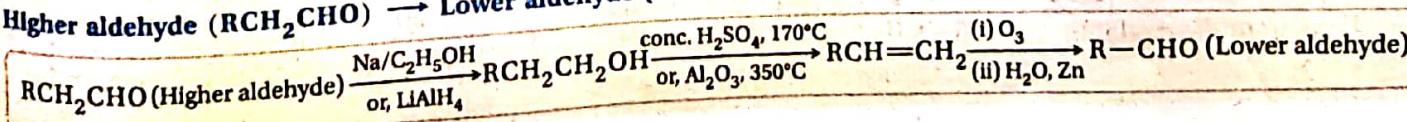
Test	Benzaldehyde	Acetophenone
Heated with conc. NaOH solution and iodine dissolved in KI solution.	Yellow crystals of iodoform are not obtained.	Yellow crystals of iodoform having characteristic odour are produced.

Transformations

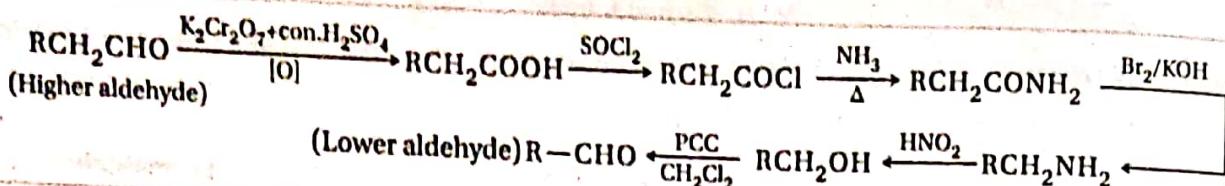
1. Lower aldehyde ($RCHO$) → Higher aldehyde (RCH_2CHO):



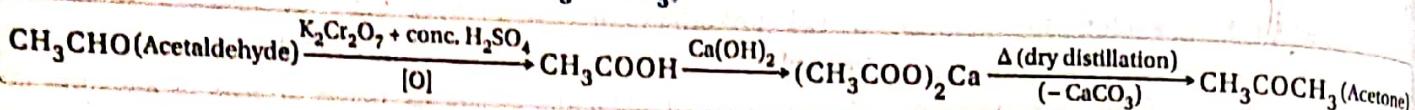
2. Higher aldehyde (RCH_2CHO) → Lower aldehyde ($RCHO$):



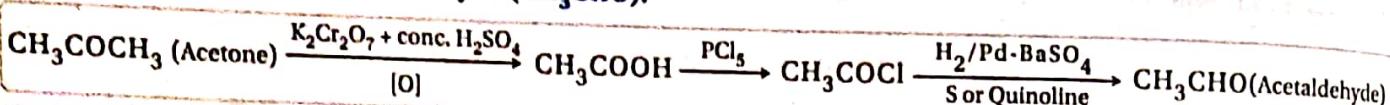
Alternative method:



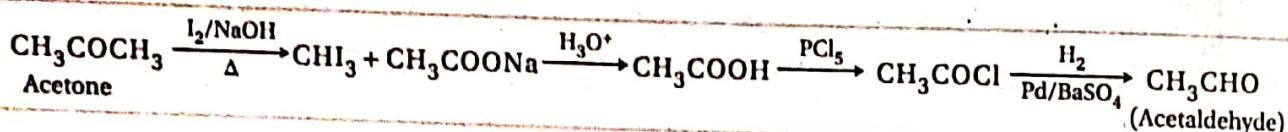
3. Acetaldehyde (CH_3CHO) → Acetone (CH_3COCH_3):



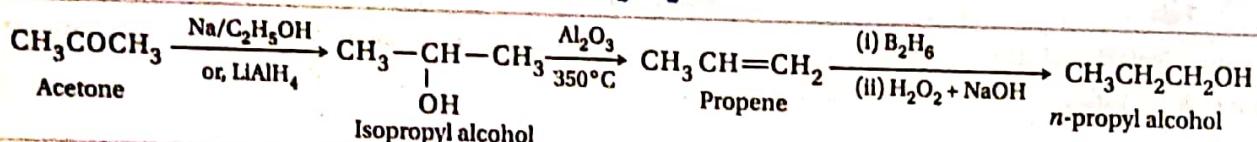
4. Acetone (CH_3COCH_3) → Acetaldehyde (CH_3CHO):



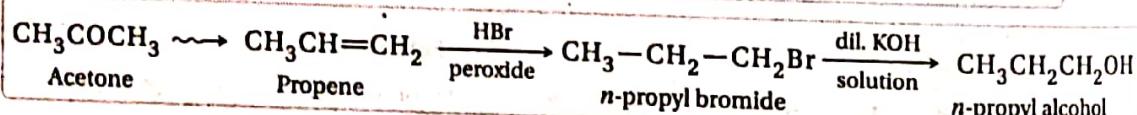
Alternative methods



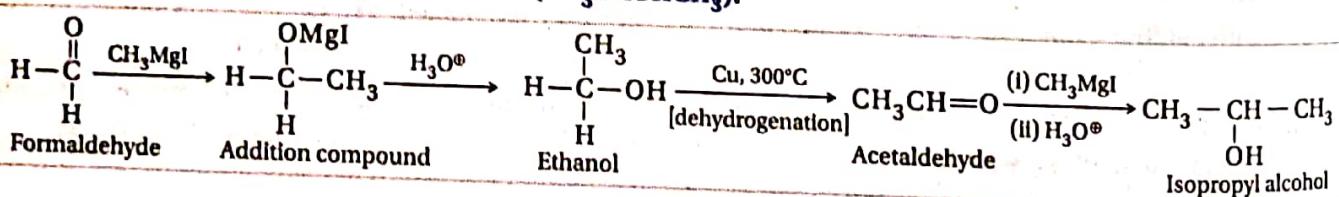
5. Acetone (CH_3COCH_3) \rightarrow *n*-propyl alcohol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$):



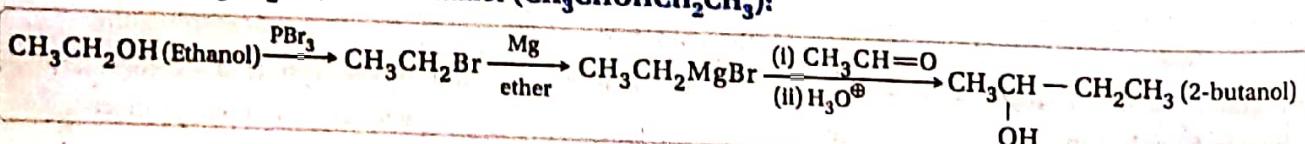
Alternative methods:



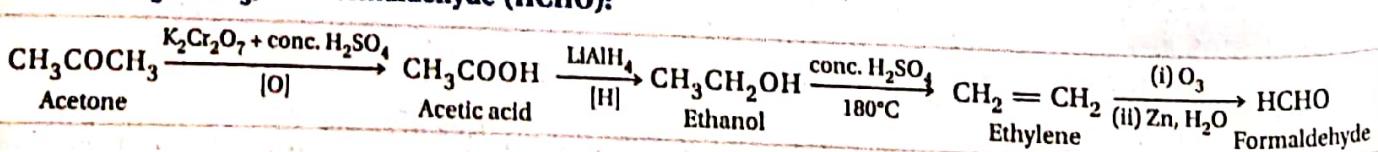
6. Formaldehyde (HCHO) → Isopropyl alcohol ($\text{CH}_3\text{CHOHCH}_3$):



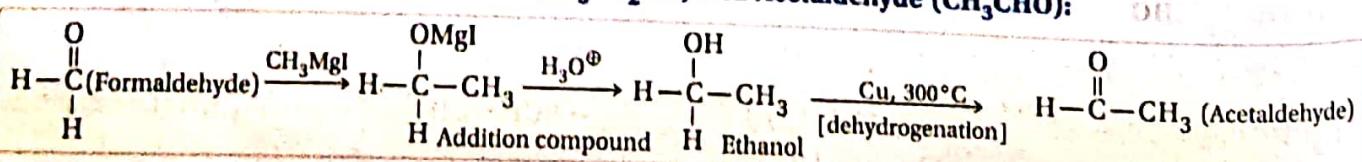
7. Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) → 2-butanol ($\text{CH}_3\text{CHOHCH}_2\text{CH}_3$)



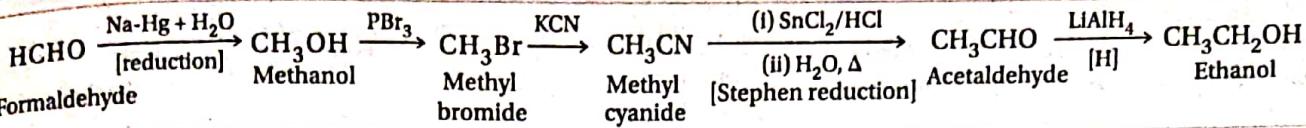
8. Acetone (CH_3COCH_3) → Formaldehyde (HCHO)



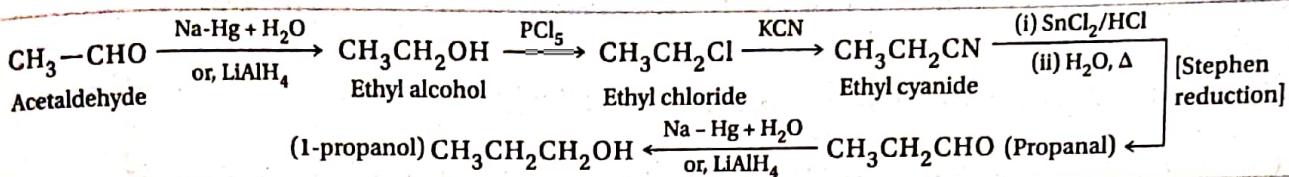
9. Formaldehyde (HCHO) → Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) and Acetaldehyde (CH_3CHO).



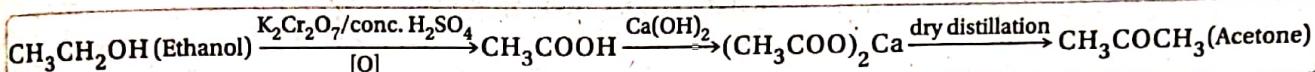
Alternative method:



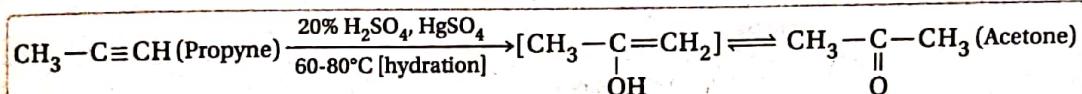
10. Acetaldehyde (CH_3CHO) \rightarrow *n*-propyl alcohol or 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$):



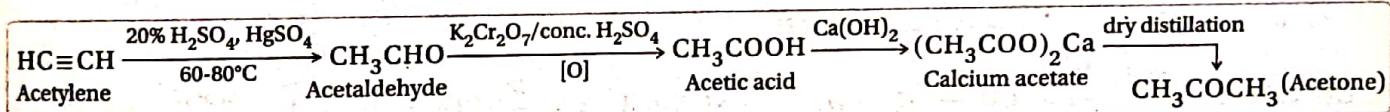
11. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) → Acetone (CH_3COCH_3):



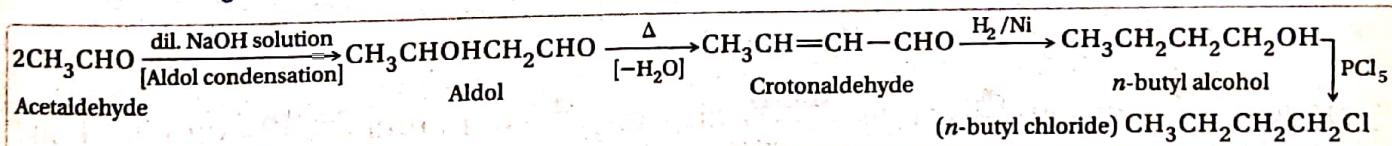
12. Propyne ($\text{CH}_3 - \text{C} \equiv \text{CH}$) \rightarrow Acetone (CH_3COCH_3):



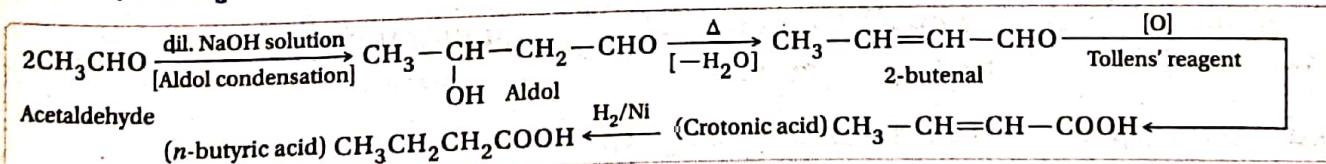
13. Acetylene ($\text{HC}\equiv\text{CH}$) → Acetone (CH_3COCH_3):



14. Acetaldehyde (CH_3CHO) \rightarrow Aldol, Crotonaldehyde, *n*-butyl alcohol and *n*-butyl chloride:



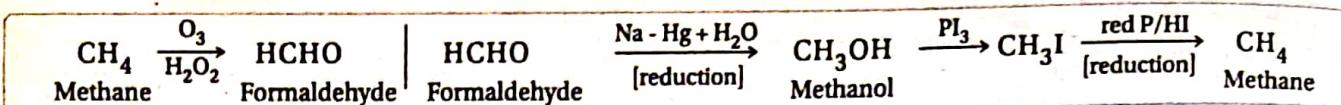
15. Acetaldehyde (CH_3CHO) \rightarrow Crotonic acid ($\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$) and *n*-butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$):



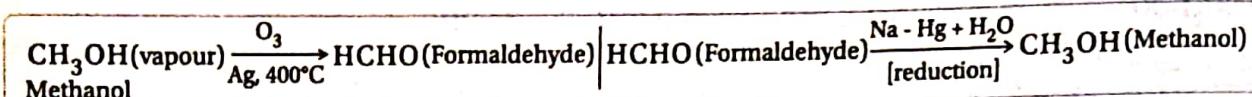
[In the preparation of crotonic acid from 2-butenal, Tollens' reagent is used. Tollens' reagent (ammoniacal silver nitrate solution) being a mild oxidising agent oxidises only the —CHO group to —COOH group; the carbon-carbon double bond remains unaffected. If a strong oxidising agent like $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ is used, both the carbon-carbon double bond and the —CHO group will be attacked.

Again, if the reduction of $\text{CH}_3\text{CH}=\text{CHCHO}$ is carried out first by H_2/Ni , both the carbon-carbon double bond and $-\text{CHO}$ group are reduced. But when the reduction of $\text{CH}_3\text{CH}=\text{CHCOOH}$ is carried out by H_2/Ni , only the carbon-carbon double bond is reduced while the $-\text{COOH}$ group remains unaffected.]

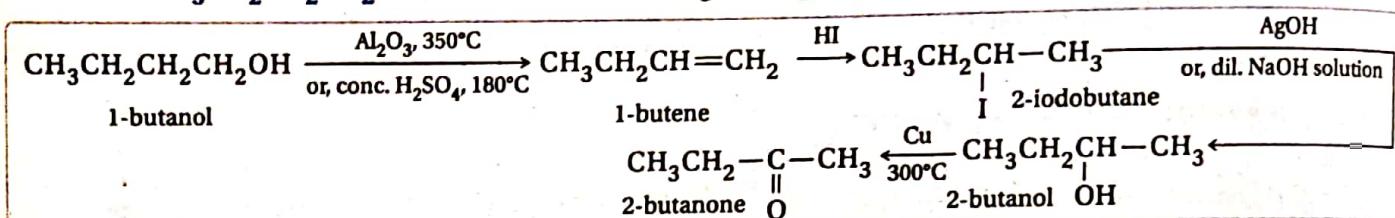
16. Methane (CH_4) → Formaldehyde (HCHO) and vice-versa:



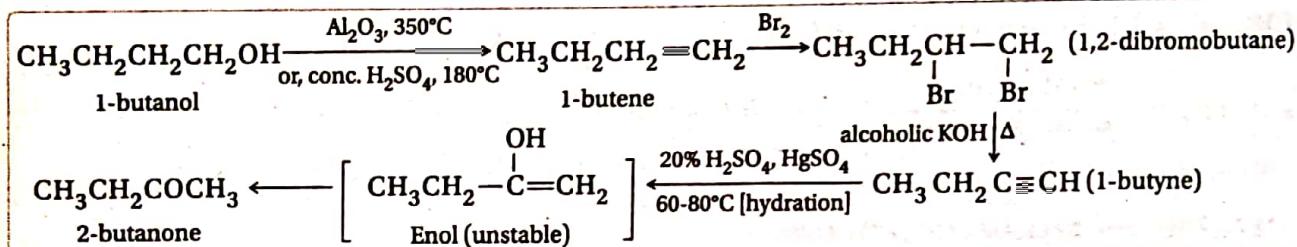
17. Methanol (CH_3OH) → Formaldehyde (HCHO) and vice-versa:



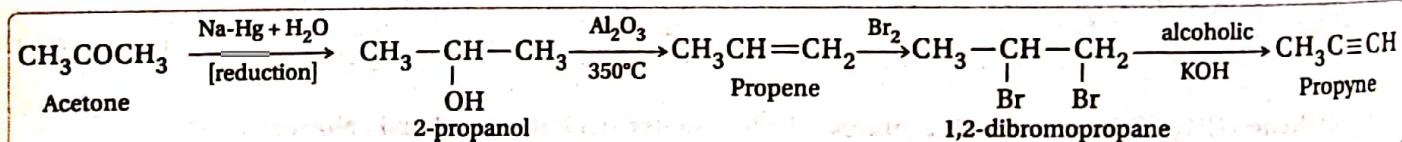
18. 1-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) \rightarrow 2-butanone ($\text{CH}_3\text{COCH}_2\text{CH}_3$):



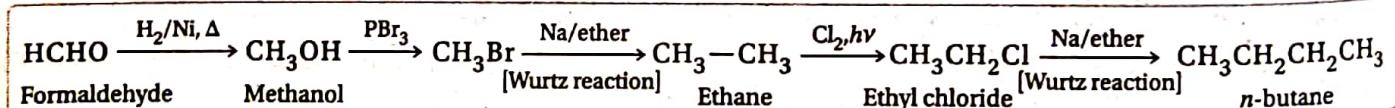
Alternative method:



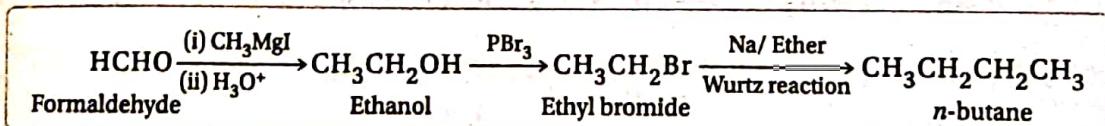
19. Acetone (CH_3COCH_3) → Propyne ($\text{CH}_3\text{C}\equiv\text{CH}$):



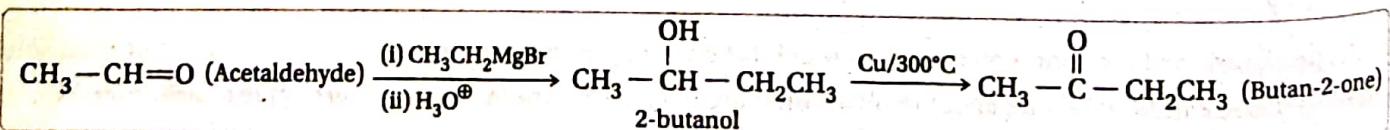
20. Formaldehyde (HCHO) \rightarrow *n*-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$):



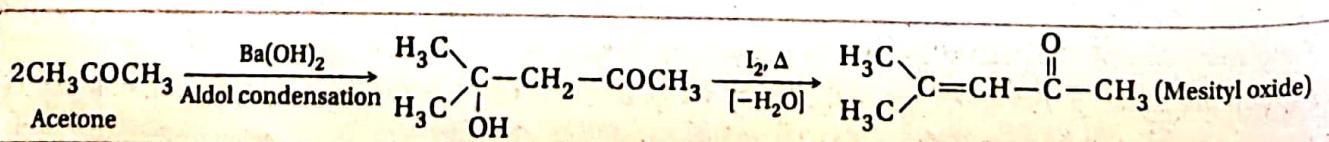
Alternative method:



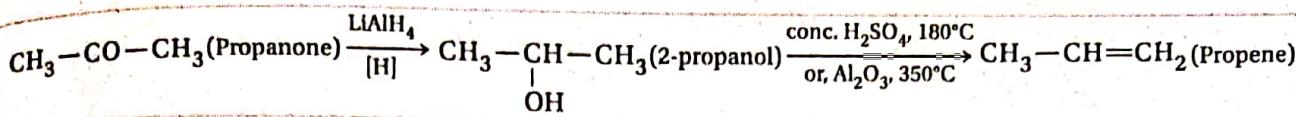
21. Acetaldehyde (CH_3CHO) \rightarrow butan-2-one ($\text{CH}_3\text{COCH}_2\text{CH}_3$):



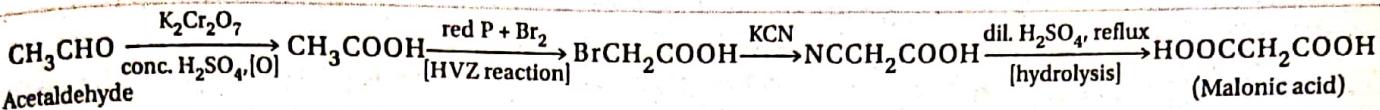
22. Acetone (CH_3COCH_3) → Mesityl oxide [$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$]:



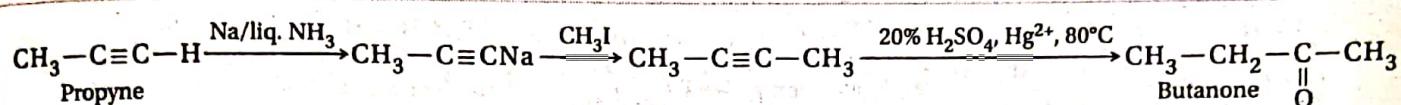
23. Propanone (CH_3COCH_3) \rightarrow Propene ($\text{CH}_3-\text{CH}=\text{CH}_2$):



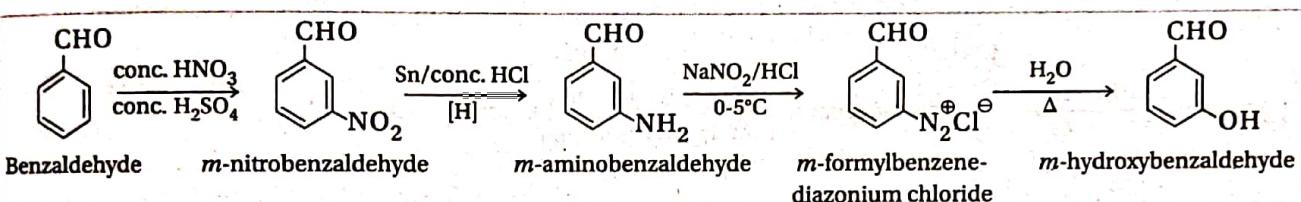
24. Acetaldehyde (CH_3CHO) \rightarrow Malonic acid ($\text{HOOC}-\text{CH}_2-\text{COOH}$):



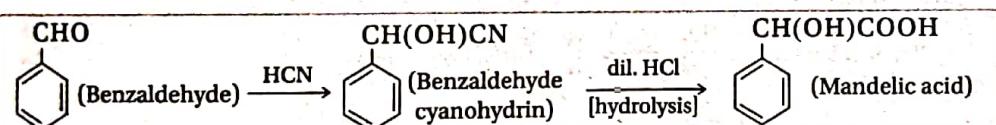
25. Propyne ($\text{CH}_3-\text{C}\equiv\text{CH}$) \rightarrow Butanone ($\text{CH}_3-\text{CH}_2-\text{COCH}_3$):



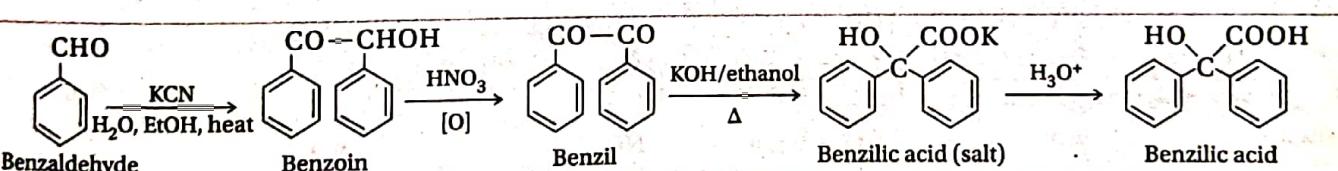
26. Benzaldehyde \rightarrow *m*-hydroxybenzaldehyde:



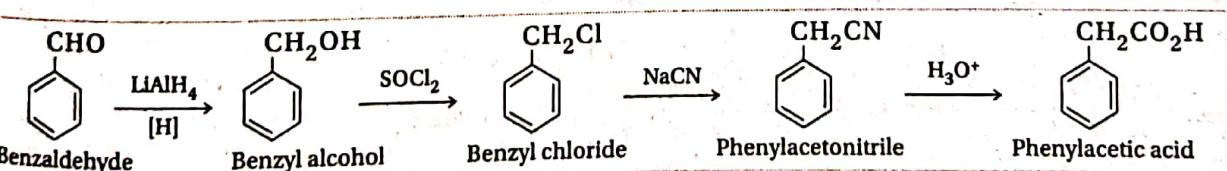
27. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) \rightarrow Mandelic acid ($\text{C}_6\text{H}_5\text{CHOHCOOH}$):



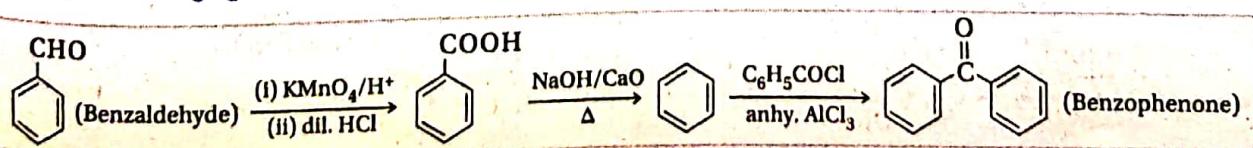
28. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) \rightarrow Benzilic acid [$\text{Ph}_2\text{C}(\text{OH})\text{COOH}$]:

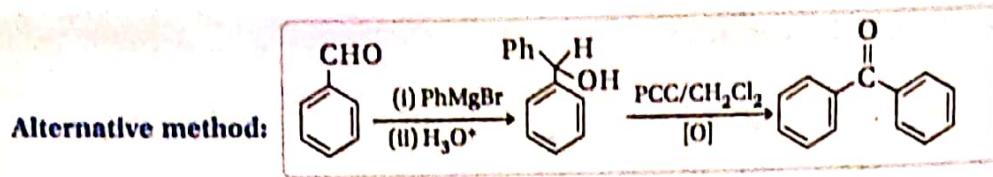


29. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) \rightarrow Phenylacetic acid ($\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$):

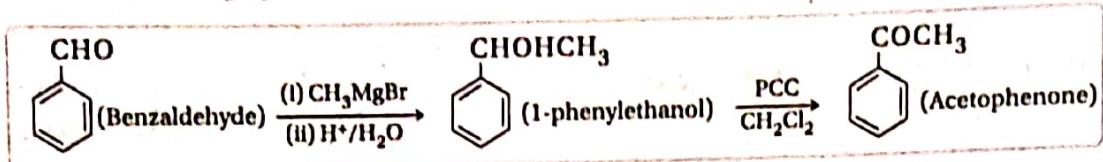


30. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) \rightarrow Benzophenone ($\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$):

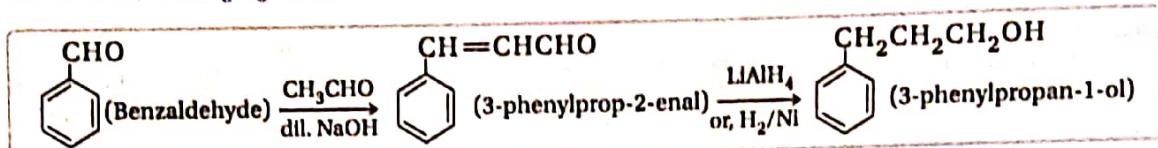




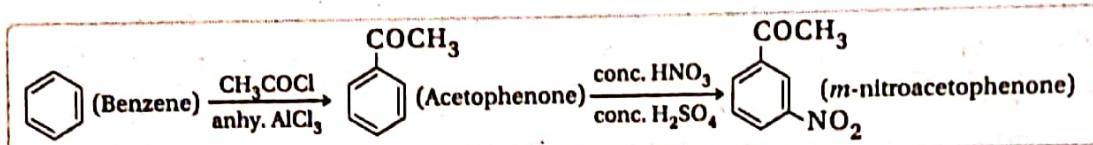
31. Benzaldehyde (C_6H_5CHO) \rightarrow Acetophenone ($C_6H_5COCH_3$):



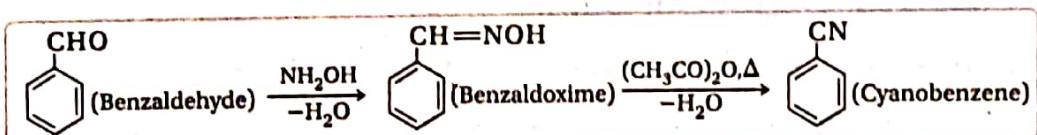
32. Benzaldehyde (C_6H_5CHO) \rightarrow 3-phenylpropan-1-ol ($C_6H_5CH_2CH_2CH_2OH$):



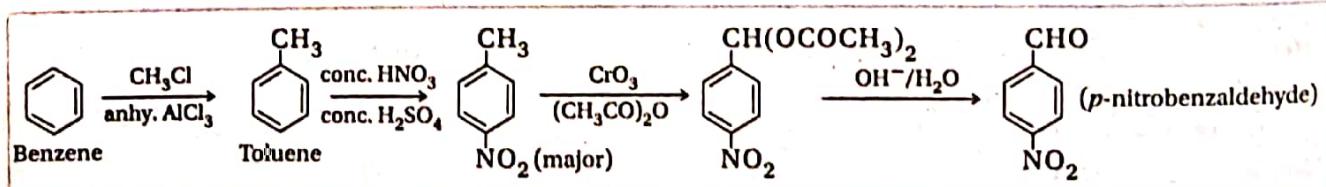
33. Benzene (C_6H_6) \rightarrow m-nitroacetophenone:



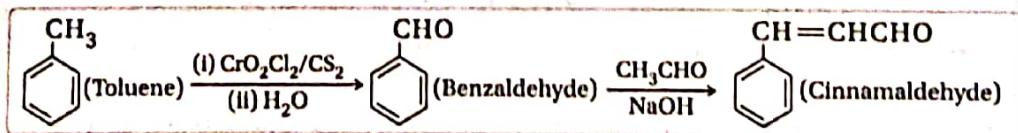
34. Benzaldehyde (C_6H_5CHO) \rightarrow Cyanobenzene (C_6H_5CN):



35. Benzene (C_6H_6) \rightarrow p-nitrobenzaldehyde:



36. Toluene ($C_6H_5CH_3$) \rightarrow Cinnamaldehyde ($C_6H_5CH=CHCHO$):



37. Benzonitrile (C_6H_5CN) \rightarrow Cinnamic acid ($C_6H_5CH=CHCOOH$):

