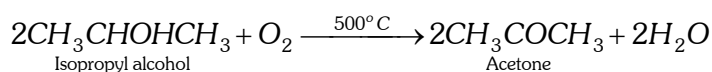


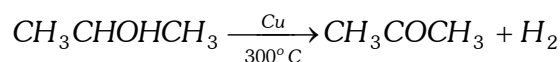
Aldehydes and Ketones Part 3

(2) **Manufacture** : Acetone is manufactured by following methods:

(i) **By air-oxidation of isopropyl alcohol** : The air oxidation occurs at 500°C .

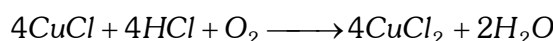
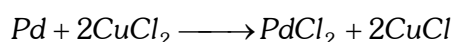
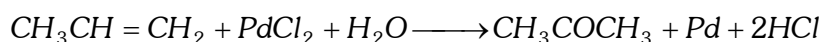


(ii) **By dehydrogenation of isopropyl alcohol** : The vapours of isopropyl alcohol are passed over heated copper at 300°C .

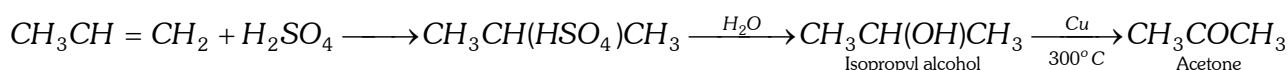


(iii) **From propene**

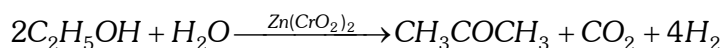
(a) **Wacker's process** : The mixture of propene and air under pressure is passed through palladium chloride and cupric chloride solution when acetone is formed.



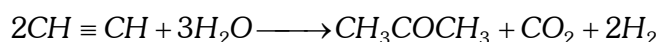
(b) Propene is absorbed in concentrated sulphuric acid and the resulting product is boiled with water when isopropyl alcohol is formed. Isopropyl alcohol on dehydrogenation yields acetone.



(iv) **From ethyl alcohol** : By passing a mixture of ethyl alcohol vapour and steam over a catalyst, zinc chromite at 500°C , acetone is obtained. The yield is about 80%.



(v) **From acetylene** : By passing a mixture of acetylene and steam over a catalyst, magnesium or zinc vanadate at 420°C , acetone is obtained.



(vi) **From pyroligneous acid** : Pyroligneous acid containing acetic acid, acetone and methyl alcohol is distilled in copper vessel and the vapours are passed through hot milk of lime. Acetic acid combines to form nonvolatile calcium acetate. The unabsorbed vapours of methanol and acetone are condensed and fractionally distilled. Acetone distills at 56°C .

The acetone thus obtained is purified with the help of sodium bisulphite as described in laboratory preparation.

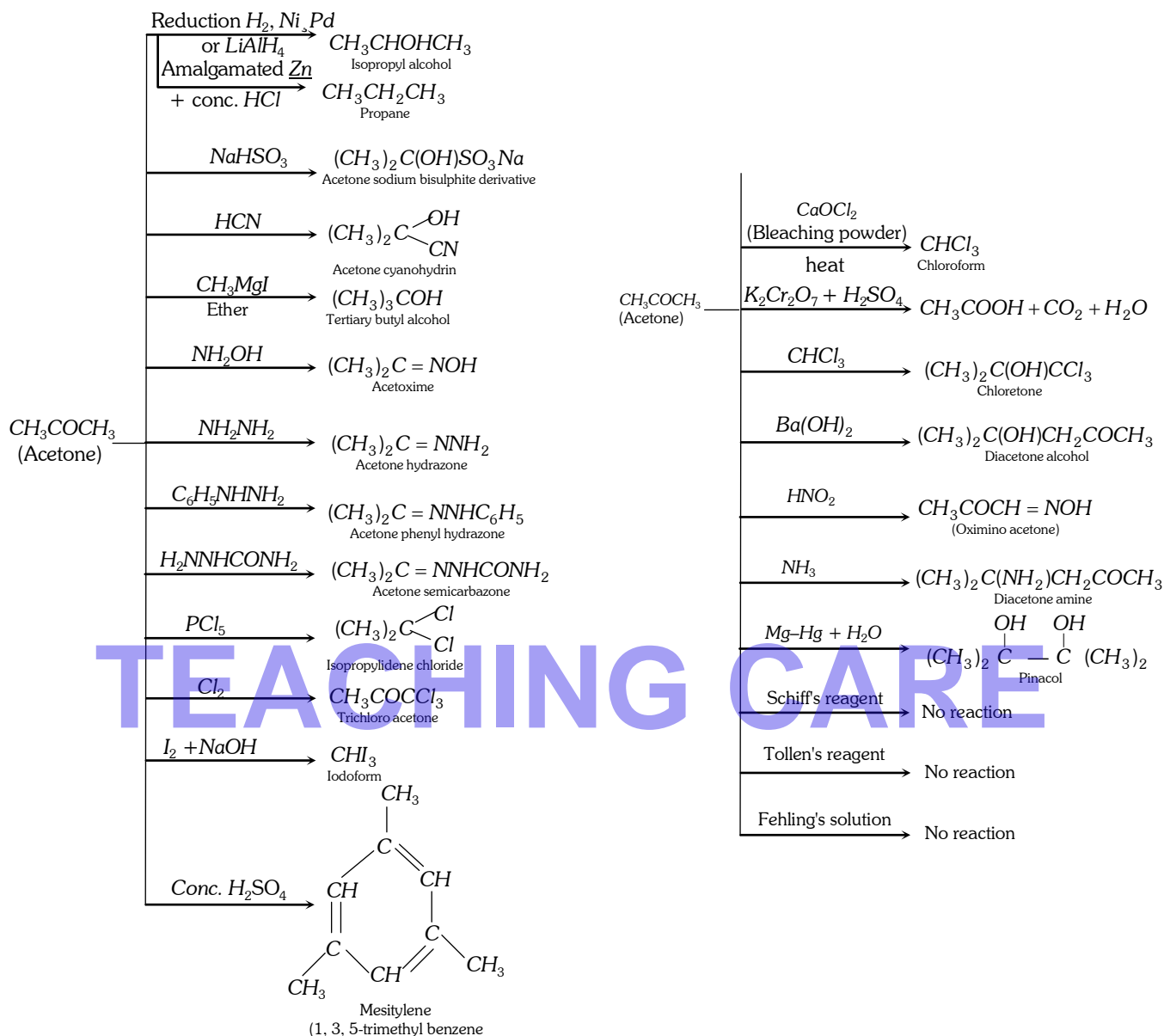
(3) **Physical properties** : (i) It is a colourless liquid with characteristic pleasant odour.

(ii) It is inflammable liquid. It boils at 56°C .

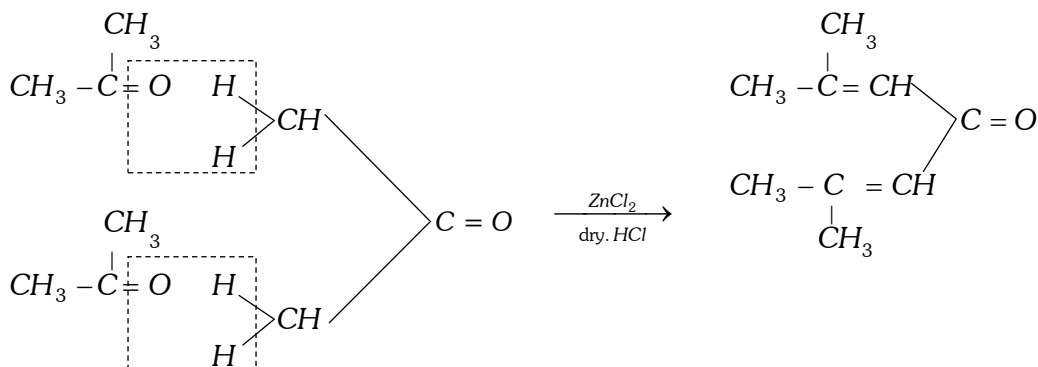
(iii) It is highly miscible with water, alcohol and ether.

Aldehydes and Ketones Part 3

(4) Chemical properties



If acetone would be in excess in ketal condensation or catalyst ($ZnCl_2 / dry HCl$) is used then three moles of acetone undergoes condensation polymerisation and form a compound called '**Phorone**'.

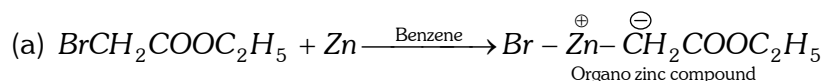


Molecular mass of phorone = 3 mole of acetone - 2 mole of H_2O

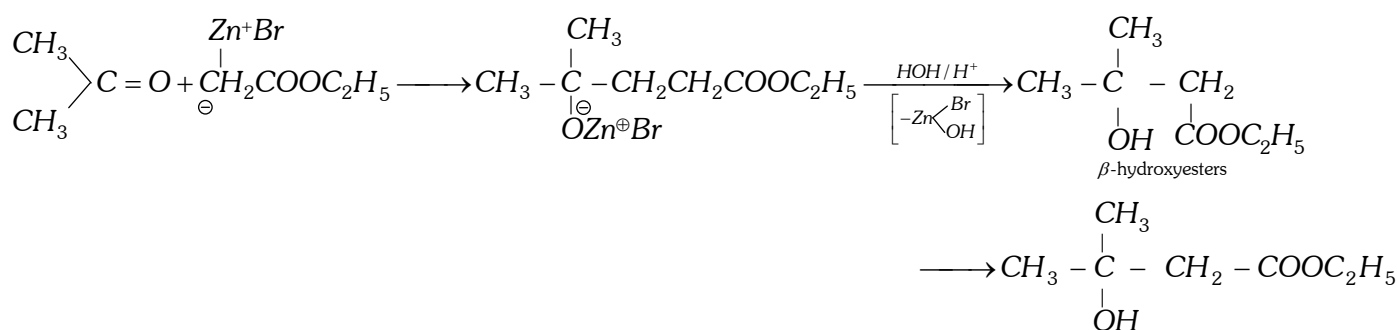
Aldehydes and Ketones Part 3

Note : ✱ If two moles of acetone are used then Mesityl oxide $(CH_3)_2C(OH)CH_2COCH_3$

Reformatsky reaction: This reaction involves the treatment of aldehyde and ketone with a bromo acid ester in presence of metallic zinc to form β -hydroxy ester, which can be easily dehydrated into α, β -unsaturated ester.



(b) Addition to carbonyl group



(5) Uses

- (i) As a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.
- (ii) For storing acetylene.
- (iii) In the manufacture of cordite – a smoke less powder explosive.
- (iv) In the preparation of chloroform, iodoform, sulphonal and chloretone.
- (v) As a nailpolish remover.
- (vi) In the preparation of an artificial scent (ionone), plexiglass (unbreakable glass) and synthetic rubber.

(6) Tests

(i) **Legal's test :** When a few drops of freshly prepared sodium nitroprusside and sodium hydroxide solution are added to an aqueous solution of acetone, a wine colour is obtained which changes to yellow on standing.

(ii) **Indigo test :** A small amount of orthonitrobenzaldehyde is added to about 2 ml. of acetone and it is diluted with KOH solution and stirred. A blue colour of indigotin is produced.

(iii) **Iodoform test :** Acetone gives iodoform test with iodine and sodium hydroxide or iodine and ammonium hydroxide.

Comparison between Acetaldehyde and Acetone

Reaction	Acetaldehyde	Acetone
Similarity		
1. Reduction with H_2 and Ni or LiAlH_4	Forms ethyl alcohol $\text{CH}_3\text{CHO} + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_2\text{OH}$	Forms isopropyl alcohol $\text{CH}_3\text{COCH}_3 + \text{H}_2 \longrightarrow \text{CH}_3\text{CHOHCH}_3$
2. Clemmensen's reduction (Zn/Hg and conc. HCl)	Forms ethane $\text{CH}_3\text{CHO} + 4\text{H} \longrightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{O}$	Forms propane $\text{CH}_3\text{COCH}_3 + 4\text{H} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$
3. Addition of HCN	Forms acetaldehyde cyanohydrin	Forms acetone cyanohydrin

Aldehydes and Ketones Part 3

	$\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3\text{CH} \begin{array}{l} \text{OH} \\ \diagup \\ \text{CN} \end{array}$	$(\text{CH}_3)_2\text{CO} + \text{HCN} \longrightarrow (\text{CH}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{CN} \end{array}$
4. Addition of NaHSO_3	White crystalline derivative $\text{CH}_3\text{CHO} + \text{NaHSO}_3 \longrightarrow \text{CH}_3\text{CH} \begin{array}{l} \text{OH} \\ \diagup \\ \text{SO}_3\text{Na} \end{array}$	White crystalline derivative $(\text{CH}_3)_2\text{CO} + \text{NaHSO}_3 \longrightarrow (\text{CH}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{SO}_3\text{Na} \end{array}$
5. Grignard reagent followed by hydrolysis	Forms isopropyl alcohol $\text{CH}_3\text{CHO} + \text{CH}_3\text{MgI} \longrightarrow (\text{CH}_3)_2\text{CH} - \text{OMgI}$ $\xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHOHCH}_3$	Forms tertiary butyl alcohol $(\text{CH}_3)_2\text{CO} + \text{CH}_3\text{MgI} \longrightarrow (\text{CH}_3)_3\text{COMgI}$ $\xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_3\text{COH}$
6. With hydroxylamine (NH_2OH)	Forms acetaldoxime $\text{CH}_3\text{CHO} + \text{H}_2\text{NOH} \longrightarrow \text{CH}_3\text{CH} = \text{NOH}$	Forms acetoxime $(\text{CH}_3)_2\text{CO} + \text{H}_2\text{NOH} \longrightarrow (\text{CH}_3)_2\text{C} = \text{NOH}$
7. With hydrazine (NH_2NH_2)	Forms acetaldehyde hydrazone $\text{CH}_3\text{CHO} + \text{H}_2\text{NNH}_2 \longrightarrow \text{CH}_3\text{CH} = \text{NNH}_2$	Forms acetone hydrazone $(\text{CH}_3)_2\text{CO} + \text{H}_2\text{NNH}_2 \longrightarrow (\text{CH}_3)_2\text{C} = \text{NNH}_2$
8. With phenyl hydrazine $(\text{C}_6\text{H}_5\text{NHNH}_2)$	Forms acetaldehyde phenylhydrazone $\text{CH}_3\text{CHO} + \text{H}_2\text{NNHC}_6\text{H}_5 \longrightarrow$ $\text{CH}_3\text{CH} = \text{NNHC}_6\text{H}_5$	Forms acetone phenyl hydrazone $(\text{CH}_3)_2\text{CO} + \text{H}_2\text{NNHC}_6\text{H}_5 \longrightarrow$ $(\text{CH}_3)_2\text{C} = \text{NNHC}_6\text{H}_5$
9. With semicarbazide $(\text{H}_2\text{NNHCONH}_2)$	Forms acetaldehyde semicarbazone $\text{CH}_3\text{CHO} + \text{H}_2\text{NNHCONH}_2 \longrightarrow$ $\text{CH}_3\text{CH} = \text{NNHCONH}_2$	Forms acetone semicarbazone $(\text{CH}_3)_2\text{CO} + \text{H}_2\text{NNHCONH}_2 \longrightarrow$ $(\text{CH}_3)_2\text{C} = \text{NNHCONH}_2$
10. With PCl_5	Forms ethylidene chloride $\text{CH}_3\text{CHO} + \text{PCl}_5 \longrightarrow \text{CH}_3\text{CH} \begin{array}{l} \text{Cl} \\ \diagup \\ \text{Cl} \end{array}$	Forms isopropylidene chloride $(\text{CH}_3)_2\text{CO} + \text{PCl}_5 \longrightarrow (\text{CH}_3)_2\text{C} \begin{array}{l} \text{Cl} \\ \diagup \\ \text{Cl} \end{array}$
11. With chlorine	Forms chloral $\text{CH}_3\text{CHO} + \text{Cl}_2 \longrightarrow \text{CCl}_3\text{CHO}$	Forms trichloro acetone $\text{CH}_3\text{COCH}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_3\text{COCH}_3$
12. With alcohols	Forms acetal $\text{CH}_3\text{CHO} + 2\text{C}_2\text{H}_5\text{OH} \longrightarrow \text{CH}_3\text{CH} \begin{array}{l} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{OC}_2\text{H}_5 \end{array}$	Forms ketal $(\text{CH}_3)_2\text{CO} + 2\text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{CH}_3)_2\text{C} \begin{array}{l} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{OC}_2\text{H}_5 \end{array}$
13. With SeO_2	Forms glyoxal $\text{CH}_3\text{CHO} + \text{SeO}_2 \longrightarrow \text{CHOCHO} + \text{Se} + \text{H}_2\text{O}$	Forms methyl glyoxal $(\text{CH}_3)_2\text{CO} + \text{SeO}_2 \longrightarrow \text{CH}_3\text{COCHO} + \text{Se} + \text{H}_2\text{O}$
14. Iodoform reaction $(\text{I}_2 + \text{NaOH})$	Forms iodoform	Forms iodoform
15. Bleaching powder	Forms chloroform	Forms chloroform
16. Aldol condensation with mild alkali	Forms aldol $2\text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CHOHCH}_2\text{CHO}$	Forms diacetone alcohol $2\text{CH}_3\text{COCH}_3 \longrightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3$
17. Polymerisation	Undergoes polymerisation	Does not undergo polymerisation but gives condensation reaction
18. With NH_3	Forms acetaldehyde ammonia	Forms diacetone ammonia

Aldehydes and Ketones Part 3

	$CH_3CHO + NH_3 \longrightarrow CH_3CH \begin{matrix} OH \\ \diagup \\ NH_2 \end{matrix}$	$(CH_3)_2CO + NH_3 + OC(CH_3)_2 \longrightarrow (CH_3)_2C(NH_2)CH_2COCH_3$
19. With conc. $NaOH$	Forms brownish resinous mass	No reaction
20. With HNO_2	No reaction	Forms oximino acetone
		$CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH = NOH$
21. With chloroform	No reaction	Forms chloretone
		$(CH_3)_2CO + CHCl_3 \longrightarrow (CH_3)_2C \begin{matrix} OH \\ \diagup \\ CCl_3 \end{matrix}$
22. With alk. sodium nitroprusside	Deep red colour	Red colour changes to yellow on standing
23. With sodium nitroprusside + Pyridine	Blue colour	No effect
24. Boiling point	$21^\circ C$	$56^\circ C$

Difference

1. With Schiff's reagent	Pink colour	Does not give pink colour
2. With Fehling's solution	Gives red precipitate	No reaction
3. With Tollen's reagent	Gives silver mirror	No reaction
4. Oxidation with acidified $K_2Cr_2O_7$	Easily oxidised to acetic acid	Oxidation occurs with difficulty to form acetic acid
	$CH_3CHO + O \longrightarrow CH_3COOH$	$CH_3COCH_3 + O \longrightarrow CH_3COOH + CO_2 + H_2O$

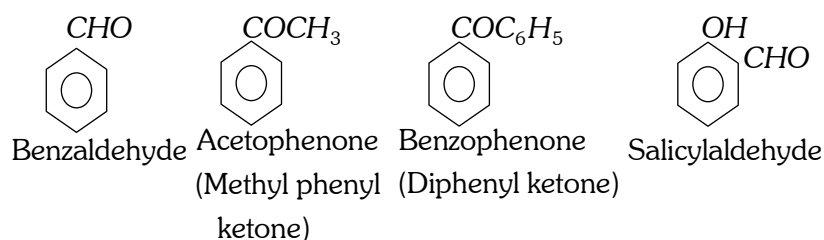
Aromatic Carbonyl Compounds.

Aromatic aldehydes are of two types :

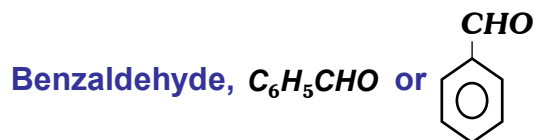
The compounds in which $-CHO$ group is attached directly to an aromatic ring, e.g., benzaldehyde, C_6H_5CHO .

Those in which aldehyde ($-CHO$) group is attached to side chain, e.g., phenyl acetaldehyde, $C_6H_5CH_2CHO$. They closely resemble with aliphatic aldehydes.

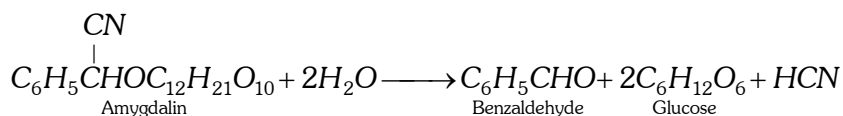
Aromatic ketones are compounds in which a carbonyl group ($>C=O$) is attached to either two aryl groups or one aryl group and one alkyl group. Examples are :



Aldehydes and Ketones Part 3



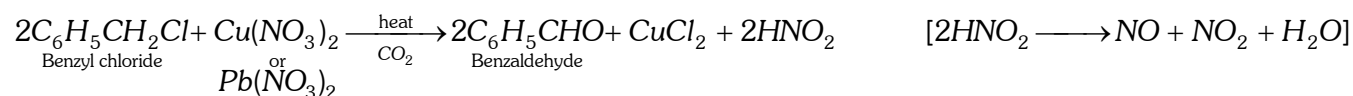
Benzaldehyde is the simplest aromatic aldehyde. It occurs in bitter almonds in the form of its glucoside, **amygdalin** ($C_{20}H_{27}O_{11}N$). When amygdalin is boiled with dilute acids, it hydrolyses into benzaldehyde, glucose and HCN



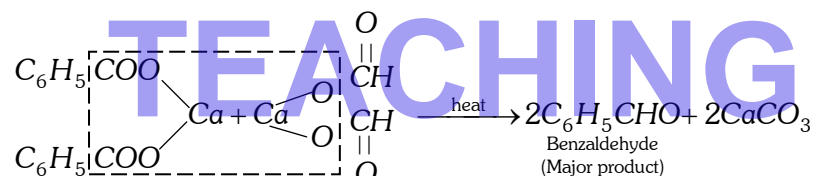
Benzaldehyde is also known as *oil of bitter almonds*.

(1) Method of preparation

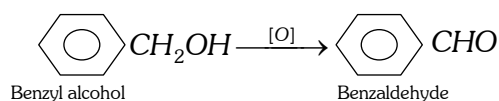
(i) **Laboratory method** : It is conveniently prepared by boiling benzyl chloride with copper nitrate or lead nitrate solution in a current of carbon dioxide.



(iii) By dry distillation of a mixture of calcium benzoate and calcium formate

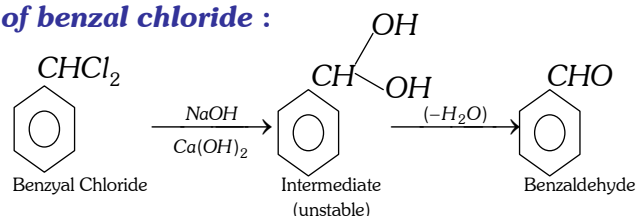


(iv) **By oxidation of benzyl alcohol** : This involves the treatment of benzyl alcohol with dil. HNO_3 or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at $350^\circ C$.



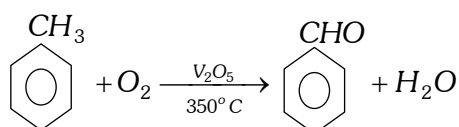
This method is used for commercial production of benzaldehyde.

(v) By hydrolysis of benzal chloride :



This is also an industrial method.

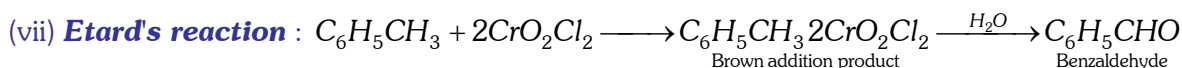
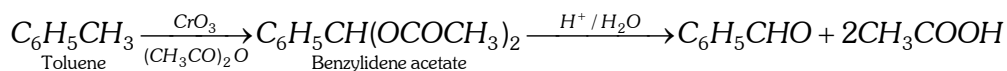
(vi) By oxidation of Toluene



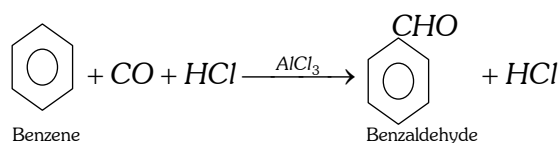
Aldehydes and Ketones Part 3

Commercially the oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at 500°C in the presence of oxides of *Mn*, *Mo* or *Zr* as catalyst.

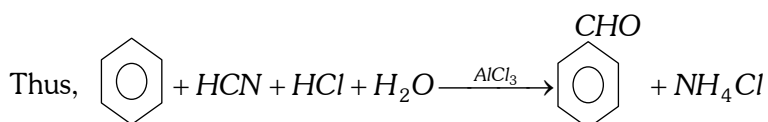
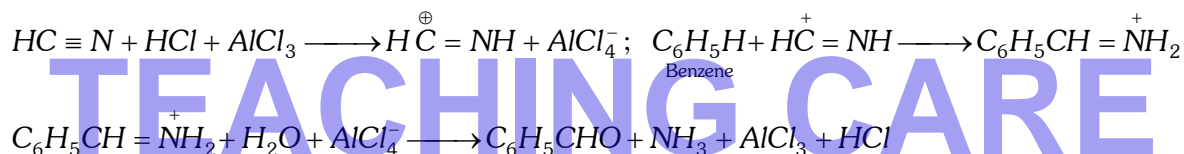
Partial oxidation of toluene with manganese dioxide and dilute sulphuric acid at 35°C, also forms benzaldehyde.



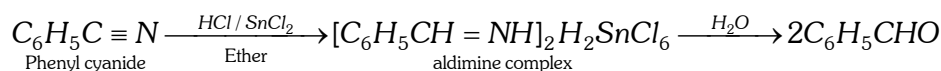
(viii) **Gattermann-koch aldehyde synthesis** : Benzene is converted into benzaldehyde by passing a mixture of carbon monoxide and *HCl* gas under high pressure into the ether solution of benzene in presence of anhydrous aluminium chloride and cuprous chloride.



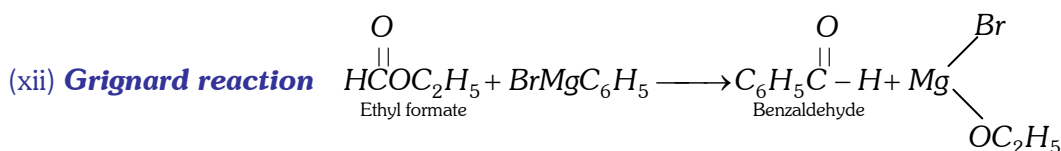
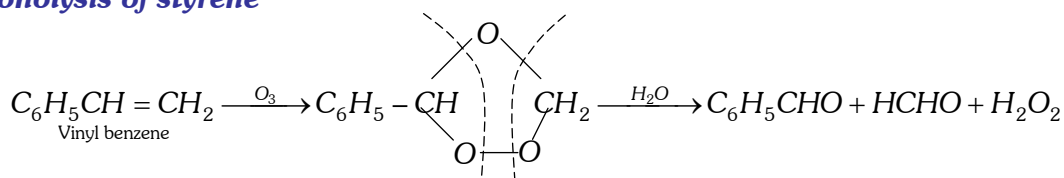
(ix) **Gattermann reaction**



(x) **Stephen's reaction** : Benzaldehyde is obtained by partial reduction of phenyl cyanide with stannous chloride and passing dry *HCl* gas in ether solution followed by hydrolysis of the aldimine stannic chloride with water.



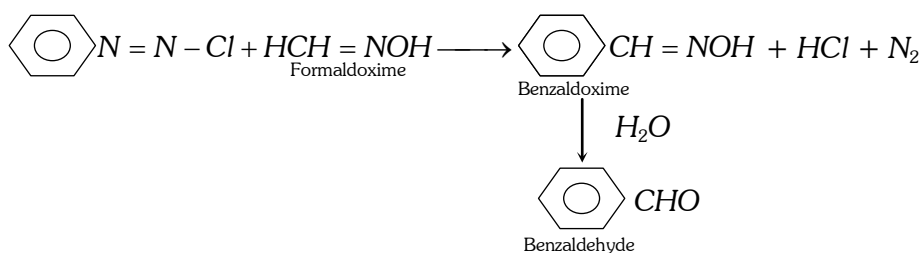
(xi) **By ozonolysis of styrene**



Other reagents like carbon monoxide or *HCN* can also be used.

Aldehydes and Ketones Part 3

(xiii) From Diazonium salt



(2) Physical properties

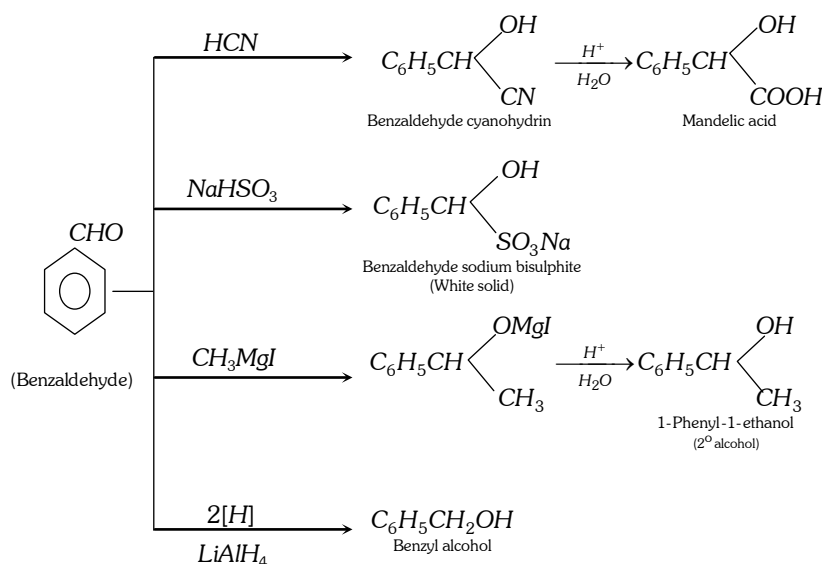
- (i) Benzaldehyde is a colourless oily liquid. Its boiling point is 179°C .
- (ii) It has smell of bitter almonds.
- (iii) It is sparingly soluble in water but highly soluble in organic solvents.
- (iv) It is steam volatile.
- (v) It is heavier than water (sp. gr. 1.0504 at 15°C).
- (vi) It is poisonous in nature.

(3) Chemical properties

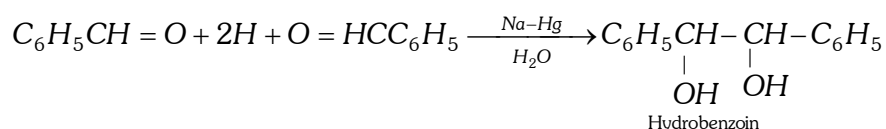
(i) **Addition reaction:** The carbonyl group is polar as oxygen is more electronegative than carbon,

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Thus, The positive part of the polar reagent always goes to the carbonyl oxygen and negative part goes to carbonyl carbon.

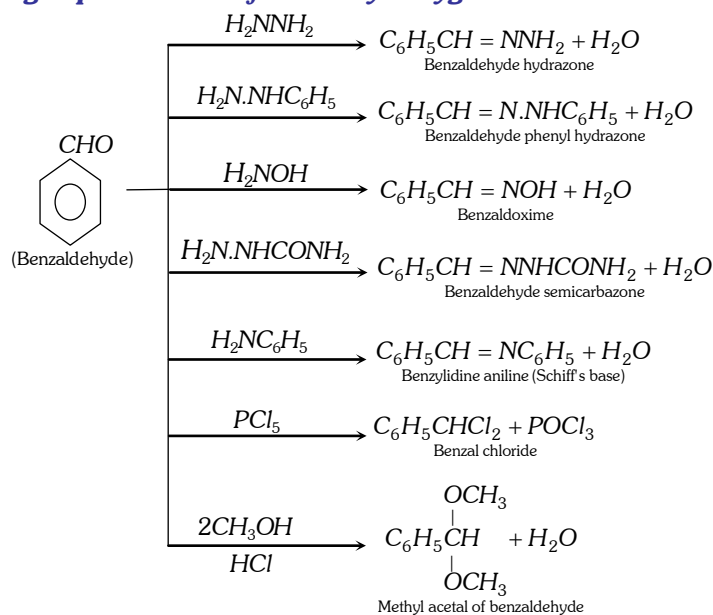


However on reduction with sodium amalgam and water, it gives hydrobenzoin,

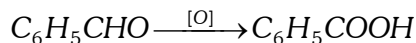


Aldehydes and Ketones Part 3

(ii) Reactions involving replacement of carbonyl oxygen

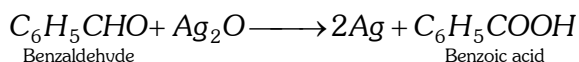


(iii) **Oxidation** : Benzaldehyde is readily oxidised to benzoic acid even on exposure to air.

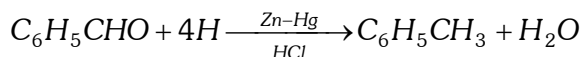


Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$ and dilute HNO_3 can be used as oxidising agents for oxidation.

(iv) **Reducing properties** : Benzaldehyde is a weak reducing agent. It reduces ammoniacal silver nitrate solution (Tollen's reagent) to give silver mirror but does not reduce Fehling's solution.

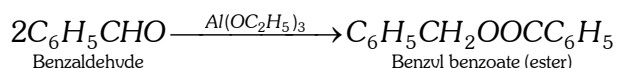


(v) **Clemmensen's reduction** : With amalgamated zinc and conc. HCl , benzaldehyde is reduced to toluene.



(vi) **Schiff's reaction**: It restores pink colour to Schiff's reagent (aqueous solution of *p*-rosaniline hydrochloride decolourised by passing sulphur dioxide).

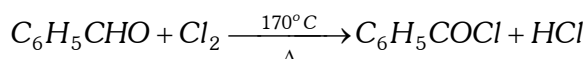
(vii) **Tischenko reaction** : On heating benzaldehyde with aluminium alkoxide (ethoxide) and a little of anhydrous $AlCl_3$ or $ZnCl_2$, it undergoes an intermolecular oxidation and reduction (like aliphatic aldehydes) to form acid and alcohol respectively as such and react to produce benzyl benzoate (an ester).



(viii) Reactions in which benzaldehyde differs from aliphatic aldehydes

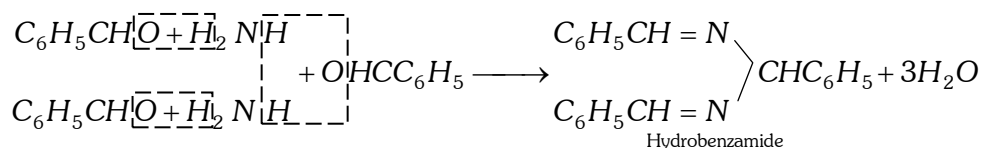
(a) *With fehling's solution* : No reaction

(b) *Action of chlorine* : Benzoyl chloride is formed when chlorine is passed through benzaldehyde at its boiling point in absence of halogen carrier. This is because in benzaldehyde there is no α -hydrogen atom present which could be replaced by chlorine.



Aldehydes and Ketones Part 3

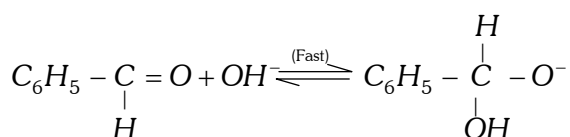
(c) Reaction with ammonia



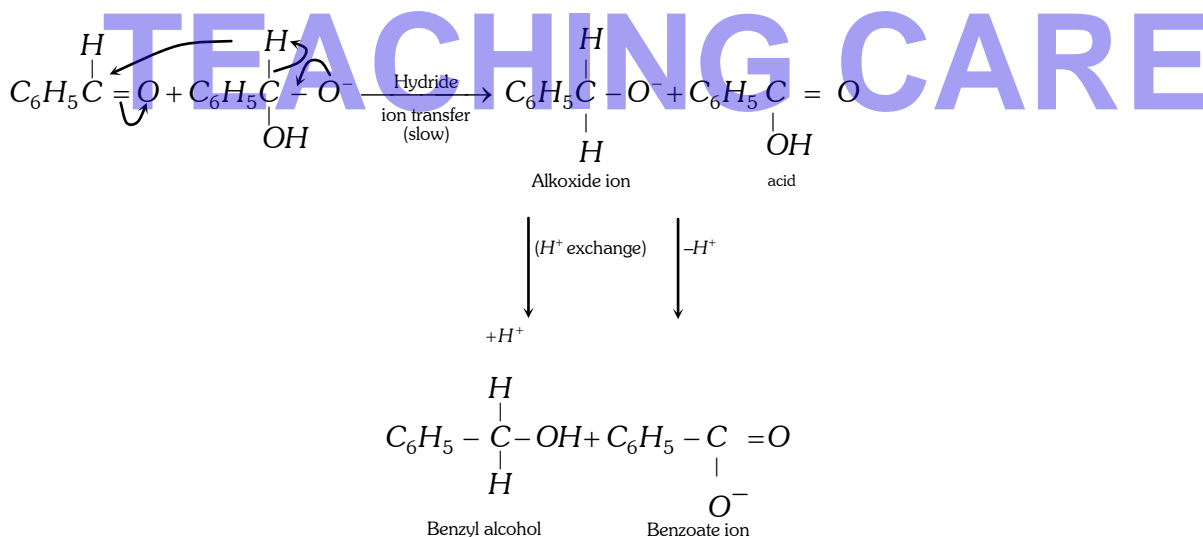
(d) Cannizzaro's reaction : $2\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{KOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COOK}$
Benzaldehyde
Benzyl alcohol
Potassium benzoate

The possible Mechanism is

First step is the reversible addition of hydroxide ion to carbonyl group.



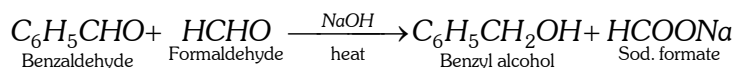
Second step is the transfer of hydride ion directly to the another aldehyde molecule, the latter is thus reduced to alkoxide ion and the former (ion I) is oxidised to an acid.



Third Step is exchange of protons to give most stable pair alcohol and acid anion.

So one molecule of aldehyde acts as hydride donor and the other acts as hydride acceptor. In other words, Cannizzaro's reaction is an example of self reduction and oxidation.

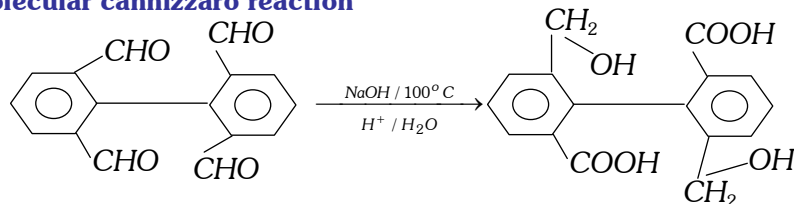
Note : * Two different aldehydes each having no α -hydrogen atom, exhibit crossed Cannizzaro's reaction when heated in alkaline solution.



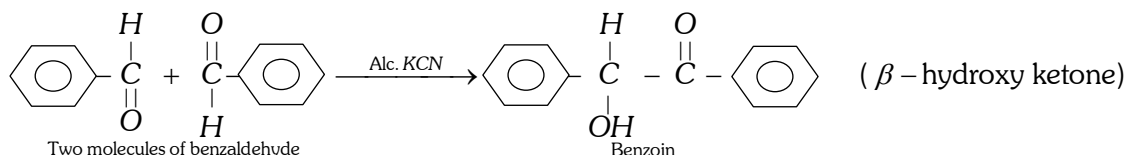
Aldehyde which do not have α -hydrogen ($\text{C}_6\text{H}_5 - \text{CHO}$, CCl_3CHO , $(\text{CH}_3)_3\text{C} - \text{CHO}$, CH_2O etc.) undergoes Cannizzaro's reaction.

Aldehydes and Ketones Part 3

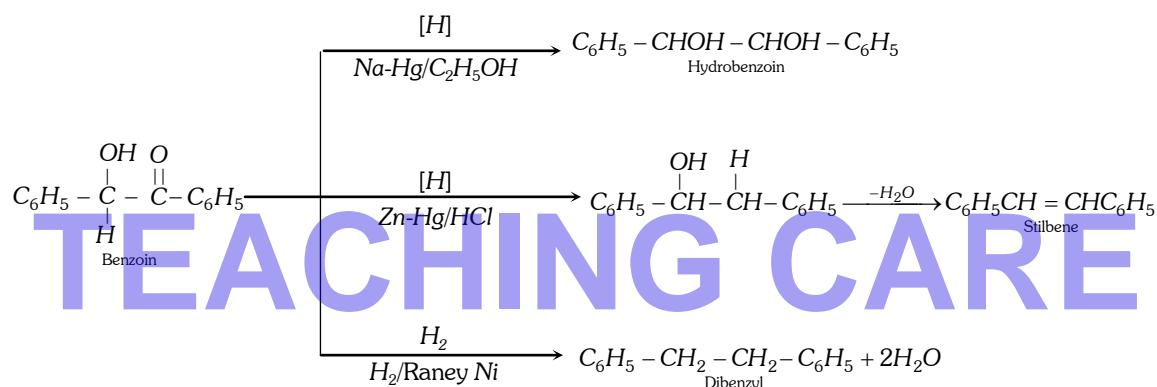
Intramolecular cannizzaro reaction



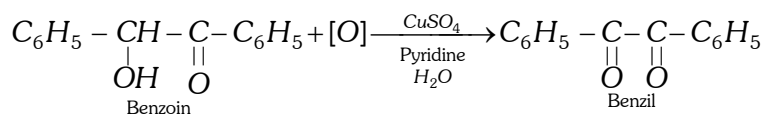
(e) Benzoin Condensation



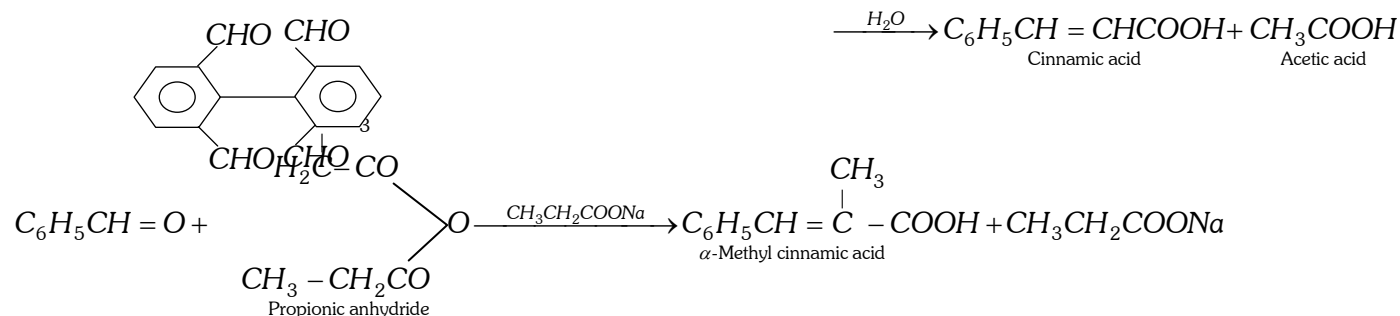
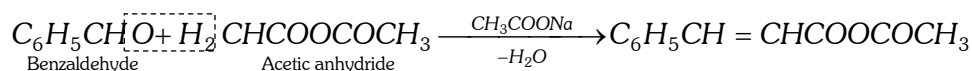
Benzoin can also be reduced to a number of products i.e.,



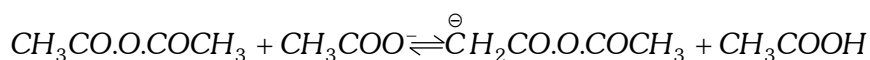
Benzoin can be readily oxidised to a diketone, i.e., benzil.



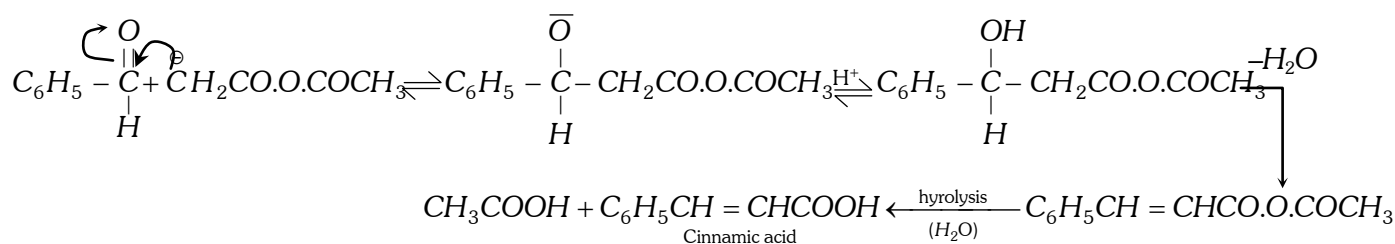
(f) Perkin's reaction



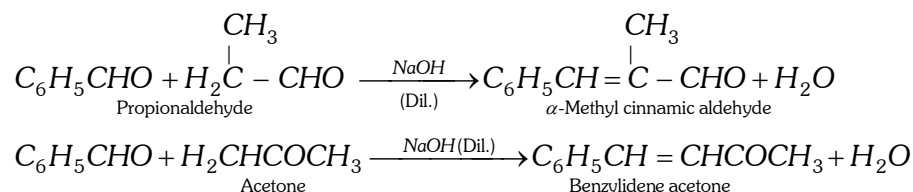
Mechanism



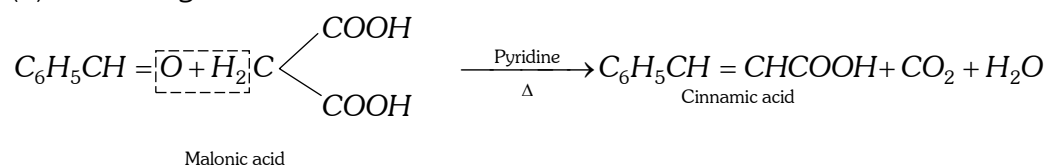
Aldehydes and Ketones Part 3



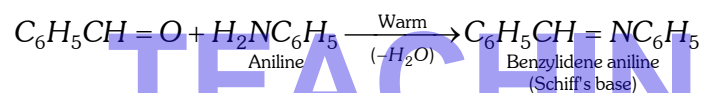
(g) Claisen condensation [Claisen-schmidt reaction]



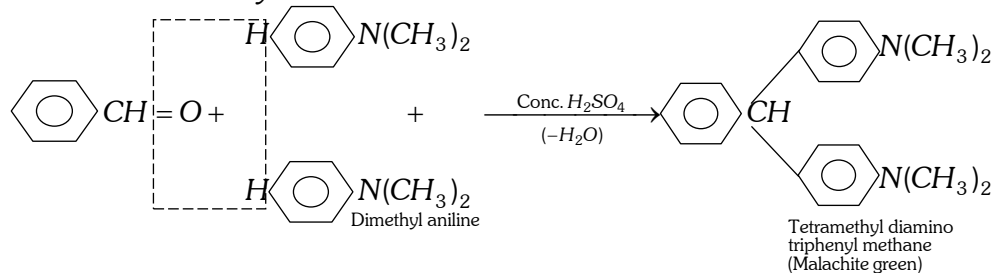
(h) Knoevenagel reaction



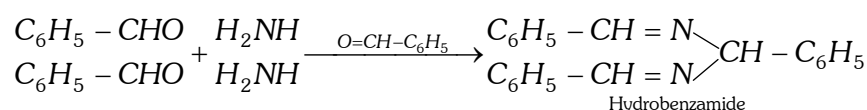
(i) Reaction with aniline : Benzaldehyde reacts with aniline and forms Schiff's base



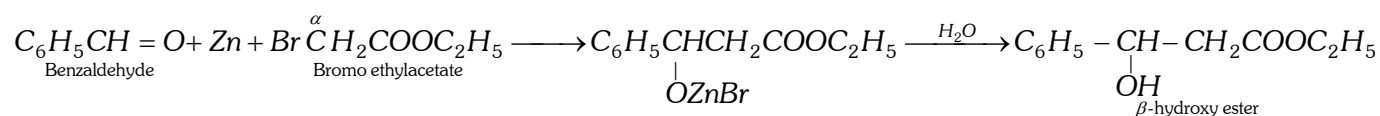
Reaction with Dimethylaniline



(j) Reaction with Ammonia : Benzaldehyde reacts with ammonia to form hydrobenzamide aldehyde other than CH_2O give aldehyde ammonia while CH_2O forms urotropine.

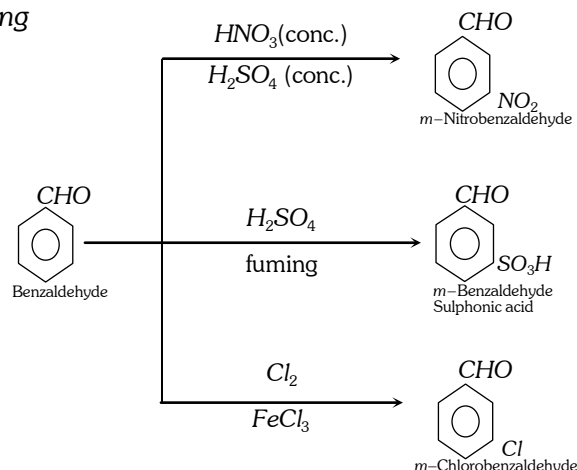


(k) Reformatsky reaction



Aldehydes and Ketones Part 3

(l) Reaction of benzene ring



(4) **Uses** : Benzaldehyde is used,

(i) In perfumery

(ii) In manufacture of dyes

(iii) In manufacture of benzoic acid, cinnamic acid, cinnamaldehyde, Schiff's base, etc.

(5) **Tests** : (i) Benzaldehyde forms a white precipitate with NaHSO_3 solution.

(ii) Benzaldehyde forms a yellow precipitate with 2 : 4 dinitrophenyl hydrazine.

(iii) Benzaldehyde gives pink colour with Schiff's reagent.

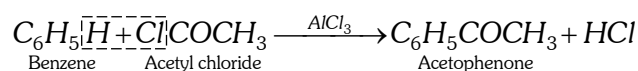
(iv) Benzaldehyde forms black precipitate or silver mirror with Tollen's reagent.

(v) Benzaldehyde on treatment with alkaline KMnO_4 and subsequent acidification gives a white precipitate of benzoic acid on cooling.

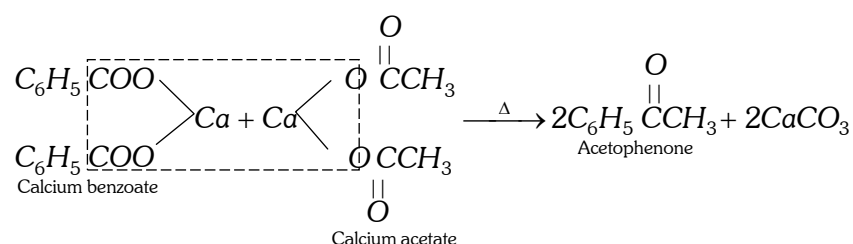
Acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$, Acetyl Benzene

(1) **Method of preparation**

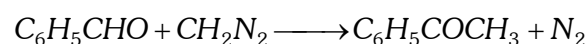
(i) **Friedel-Craft's reaction** : Acetyl chloride reacts with benzene in presence of anhydrous aluminium chloride to form acetophenone.



(ii) By distillation of a mixture of calcium benzoate and calcium acetate.

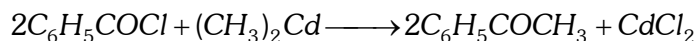


(iii) By methylation of benzaldehyde with diazomethane.

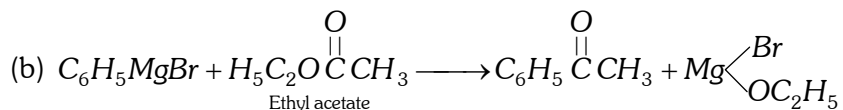
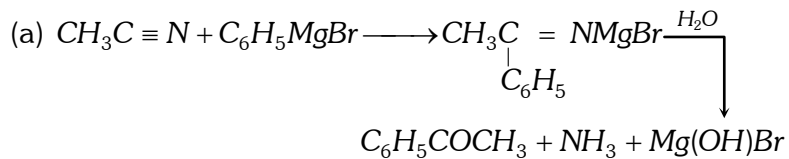


(iv) By treating benzoyl chloride with dimethyl cadmium.

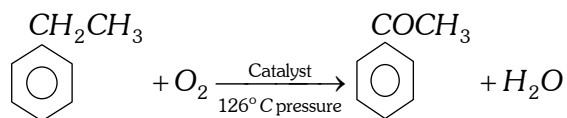
Aldehydes and Ketones Part 3



(v) **By Grignard reagent**



(vi) **Commercial preparation** : Ethylbenzene is oxidised with air at $126^\circ C$ under pressure in presence of a catalyst manganese acetate.

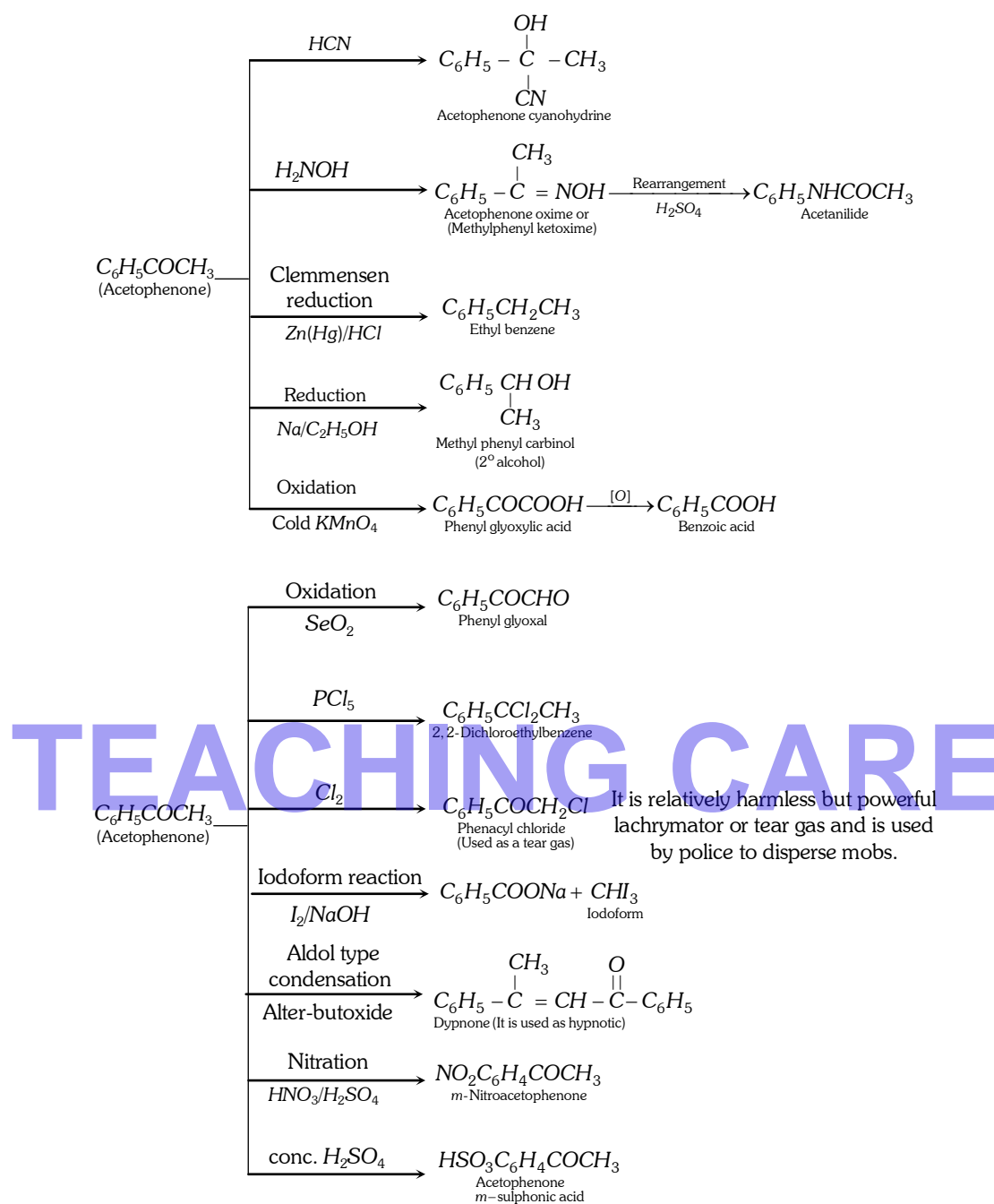


(2) **Physical properties** : It is a colourless crystalline compound with melting point $202^\circ C$ and boiling point $20^\circ C$. It has characteristic pleasant odour. It is slightly soluble in water. Chemically, It is similar to acetone.

(3) **Chemical properties** :

TEACHING CARE

Aldehydes and Ketones Part 3



(4) **Uses** : It is used in perfumery and as a sleep producing drug.

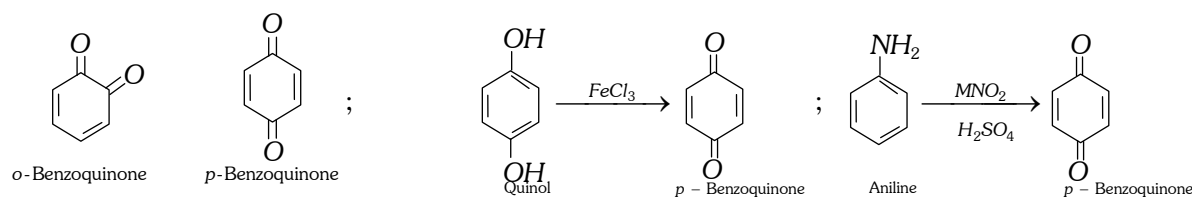
Quinones

Quinones are unsaturated cyclic diketones. Two quinones of benzene are possible (*m*-benzoquinone is not possible as it is not possible to construct such formula by maintaining tetravalency of carbon).

Note that quinones are *non-aromatic conjugated cyclic diketones*. Since they are highly conjugated they are highly **coloured substances**.

p-Benzoquinone, being the most important, is commonly known as quinone. It is prepared by the oxidation of hydroquinone or aniline.

Aldehydes and Ketones Part 3



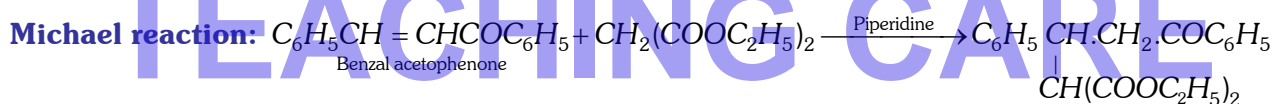
[Laboratory method]

α, β -Unsaturated carbonyl compounds

α, β -Unsaturated carbonyl compounds. As the name represents these compounds contain unsaturation between

α - and β -carbon atoms with respect to carbonyl group, i.e., $-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{C}}{\text{C}}-$. Such molecules are quite stable due to the presence of conjugated system of double bond. Such molecules give properties of the double bond, carbonyl group and some additional properties due to the interaction of the two groups. Due to electron withdrawing nature of the $>C=O$ group, the reactivity of $C=C$ towards electrophilic reagents decreases as compared to an isolated double bond. On the other hand, $C=C$ group undergoes nucleophilic addition reactions which are uncommon for simple alkenes.

Two important addition reactions of α, β -unsaturated carbonyl compounds are Michael reaction and Diels-Alder reaction.



Diels-Alder reaction

