ALDEHYDE AND KETONE

Properties of aldehyde and ketone .

3) Reduction:

a) Reduction to alcohol (partial reduction) :

Aldehydes get reduce to primary alcohol and ketones get reduce to secondary alcohol by suitable reducing agents like catalytic reduction (H_2 / Ni, Pt or Pd) or $Na \mid C_2H_5OH \; or \; LiAlH_4 or \; NaBH_4$.

$$R - \underset{\displaystyle H}{\overset{\displaystyle |}{C}} = O \; + \; [H] \xrightarrow{LiAlH_4} R - CH_2OH$$

aldehyde

1° –alcohol

$$CH_3CHO \; + \; H_2 \xrightarrow{Ni} CH_3CH_2OH$$

$$R-\underset{\displaystyle R}{\underset{|}{C}}=O \;+\; [H] \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R$$

ketone $\qquad\qquad$ $2°-alcohol$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \;+\; [H] \xrightarrow{LiAlH_4} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

acetone $\qquad\qquad$ 2- propanol

b) Reduction to alkane (complete reduction)

i) Clemmensen reduction : Aldehyde and ketone are reduced to corresponding alkane by $Zn\,|Hg$ in presence of conc HCl . This reaction is known as Clemmensen reduction. Here, carbonyl group ($-\underset{|}{\overset{}{C}}=O$) reduces to methylene group ($-CH_2-$).

$$R-\underset{|}{\overset{}{C}}=O \;+\; [H] \xrightarrow{Zn\,Hg|\,HCl} R-CH_3 + H_2O$$

H

aldehyde alkane

$$CH_3-\underset{|}{\overset{}{C}}=O \;+\; [H] \xrightarrow{ZnHg|HCl} CH_3CH_2CH_3 + H_2O$$

CH_3

propane

ii) Wolff- Kishner reduction : Aldehyde and ketone are reduced into respective alkane with a mixture of hydrazine and alkali KOH in ethylene glycol is known as wolff – Kishner reduction.

$$CH_3 - \underset{|}{\overset{H}{C}} = O + NH_2NH_2 \xrightarrow{-H_2O} CH_3\underset{|}{\overset{H}{C}} = NNH_2 \xrightarrow{KOH} CH_3CH_3 + N_2$$

ethane

iii) Reduction by HI (hydrogen iodide)

Aldehyde and ketones are reduced to corresponding alkane by HI in presence of red phosphorus at 150°C

$$CH_3 - \underset{|}{\overset{H}{C}} = O + HI \xrightarrow{red\ P} CH_3CH_3 + I_2 + H_2O$$

4) Oxidation :

Aldehydes are easily oxidized to carboxylic acids containing same number of carbon atoms. The easy oxidation of aldehyde is due to presence of hydrogen atom on the carbonyl group which can be converted to another group without breaking of any bond. Hence they are even oxidized by weak oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution. Therefore, aldehydes are strong reducing agent.

$$RCHO \xrightarrow{[O]} RCOOH$$

aldehyde carboxylic acid

Unlike aldehydes, ketones are not oxidized easily. They undergo oxidation only by strong oxidizing agents under drastic condition. They are oxidized to carboxylic acid containing less number of carbon atoms under these conditions by breaking of carbon- carbon bond.Therfore, ketones are not oxidized by Tollen's reagent, Fehling's solution and Benedict's solution. Hence, ketones are very weak reducing agent.

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = O \; + \; [O] \xrightarrow{strong\ OA} CH_3COOH \; + HCOOH$$

$$HCOOH \xrightarrow{[O]} CO_2 \; + \; H_2O$$

In case of mixed ketones,the carbonyl group remains with the smaller alkyl group during oxidation. This is known as Popoff's rule.

$$CH_3CH_2CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = O \xrightarrow{[O]} CH_3CH_2COOH \; + CH_3COOH$$

2-pentanone

Oxidation of aldehyde by weak oxidizing agents:

i) Oxidation by Tollen's reagent: The ammonical silver nitrate solution which contains diammine silver (I) ion$(Ag\ (NH_3)_2)^+$is called Tollen's reagent.

$$AgNO_3 + NH_4OH \rightarrow AgOH \downarrow + NH_4NO_3$$

$$AgOH + NH_4OH \rightarrow (Ag\ (NH_3)_2)^+ OH^- + H_2O$$

Tollen's reagent

When Tollen's reagent is warmed with an aldehyde ,it gets reduced to metallic silver. This gets deposited on the inner wall of the test tube to form a silver mirror. This reaction therefore, is known as silver mirror test.

$$RCHO + (Ag\ (NH_3)_2)^+ + OH^- \xrightarrow{warm} Ag \downarrow + RCOO^- + NH_3 + H_2O$$

metallic silver

This test is given by both aliphatic and aromatic aldehyde but not given by ketone.

ii) Oxidation by Fehling's solution : The alkaline aq solution of copper sulphate containing some Rochelle salt (sodium potassium tartarate) is called Fehling's solution. The solution is prepared by adding alkaline solution of Rochelle salt (Fehling's solution A) to aqueous solution of copper sulphate (Fehling's solution B) until the ppt of copper hydroxide frist formed dissolves to form a deep blue solution. When Fehling's solution is warmed with aldehyde ,cupric ion of Fehling's solution is reduced to cuprous ion giving red ppt of cuprous oxide and aldehyde itself gets reduced to carboxylic acid. This test is known as Fehling's test.

This test is given by only aliphatic aldehyde therefore can be used to distinguish between aliphatic and aromatic aldehyde.

Fehling's test is not given by ketones.

$$RCHO + Cu^{2+} + OH^- \xrightarrow{warm} Cu_2O + H_2O + RCOO^-$$

Fehling's sol red ppt

iii) Oxidation by Benedict's solution : The alkaline solution of cupric ion complex with sodium citrate in presence of sodium carbonate is known as Benedict's solution.

$$RCHO + Cu^{2+} + OH^- \xrightarrow{warm} RCOO^- + Cu_2O + H_2O$$

Benedict's sol red ppt

Diagnosis of diabetics.

$$C_5H_{11}O_5CHO + Cu^{2+} + OH^- \rightarrow C_5H_{11}O_5COOH + Cu_2O + H_2O$$

glucose gluconic acid red ppt

From urine

5) Iodoform reaction : Aldehydes and ketones having methyl ketonic group ($CH_3 - \underset{|}{C} = O$) on heating with NaOH and I_2 gives iodoform.

Iodoform is a yellow crystalline solid with hospital smell.

$$CH_3 - \underset{|}{\underset{H}{C}} = O + NaOH + I_2 \xrightarrow{warm} \underset{\text{iodoform}}{CHI_3} + NaI + H_2O + HCOONa$$

This reaction can be used to distinguish between formaldehyde and acetaldehyde.

$$CH_3 - \underset{|}{\underset{CH_3}{C}} = O + NaOH + I_2 \xrightarrow{warm} CHI_3 + NaI + H_2O + CH_3COONa$$

6) Polymerization reaction in aldehyde :

Aldehydes like formaldehyde , acetaldehyde undergo polymerization reaction. The nature of products formed depends upon reactions conditions.

$$n(HCHO) \xrightarrow{evaporation} (CH_2O)_n.H_2O$$

aq. Paraformaldehyde(crystalline solid)

where, n= $6\ to\ 50$

$$3HCHO \xrightarrow{on\ long\ standing} (CH_2O)_3$$

gas metaformaldehyde

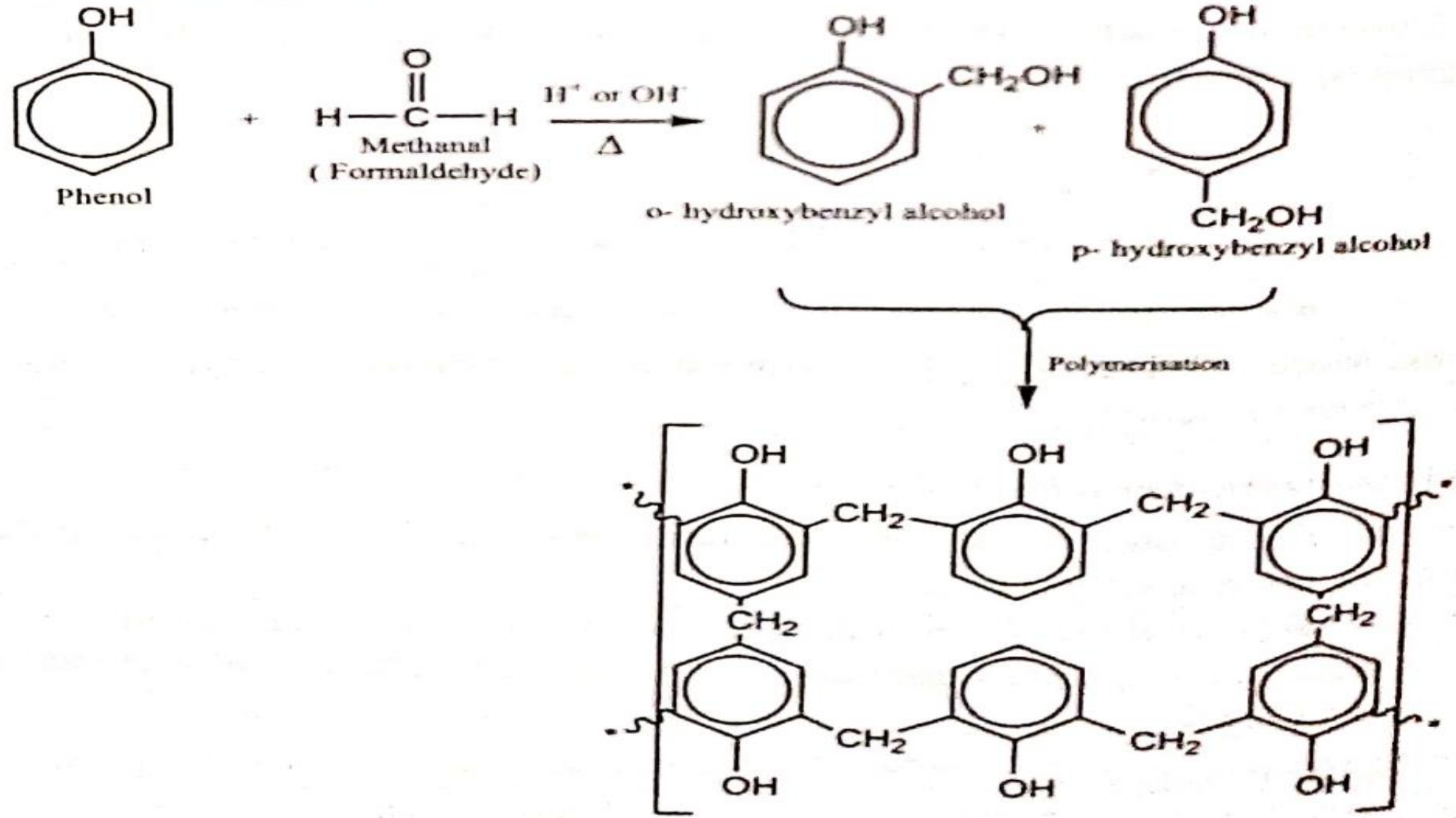
$$6HCHO \xrightarrow{calcium\ hydroxide} CH_2(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2(OH)$$

formose

Reaction of formaldehyde with phenol:

Formaldehyde undergoes condensation reaction with phenol in presence of acid or ba
to give bakelite. Bakelite is thermosetting polymer.

Thermosetting plastic Bakelite is formed.



$$3CH_3CHO \xrightarrow{conc\ H_2SO_4} (CH_3CHO)_3$$

acetaldehyde — paraldehyde

pleasant smelling liquid used as a hypnotic

$$4CH_3CHO \xrightarrow{conc\ H_2SO_4,\ 0℃} (CH_3CHO)_4$$

metaldehyde

Ketones don’t give polymerization reaction.

Some special reactions of aldehyde and ketone:

(reactions involving α −hydrogen atom)

a) Aldol condensation : Aldehydes or ketones having $\alpha -$ hydrogen on treatment with dil alkali like NaOH or KOH , undergoes condensation reaction to give β −hydroxy aldehyde or β −hydroxy ketone. This reaction is known as aldol condensation.

$$CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O \; + \; H - CH_2 - \underset{\displaystyle H}{\underset{|}{C}} = O \xrightarrow{dil\ NaOH} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle H}{\underset{|}{C}} = O$$

two molecules of acetaldehyde β −hydroxyaldehyde

The β −hydroxyaldehyde or ketone loses water molecule on heating giving unsaturated aldehyde or ketone.

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle H}{\underset{|}{C}} = O \xrightarrow{-H_2O} CH_3 - CH = \underset{\displaystyle H}{\underset{|}{CH}} - C = O$$

α, β −unsaturated aldehyde

The condensation of two different carbonyl compounds (one of which must have α −hydrogen) in the presence of alkali is called cross- aldol condensation.

$$CH_3 - \underset{\displaystyle H}{\underset{|}{C}} = O + \; H - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = O \xrightarrow{dil\ NaOH} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH_2}} - C = O$$

acetaldehyde acetone β −hydroxyketone

Formaldehyde ($HCHO$) , $benzaldehyde$ (C_6H_5CHO) don't contain $\alpha -$ $hydrogen$, hence these compounds don’t give aldol condensation. However ,these compounds show cross aldol condensation.

$$H-\underset{\displaystyle H}{\underset{|}{C}}=O \;+\; H-\underset{\displaystyle H}{\underset{|}{CH_2}}-C=O \xrightarrow{dil\ NaOH} H-\underset{\displaystyle H}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}}-C=O$$

formaldehyde acetaldehyde β −hydroxyaldehyde

$$C_6H_5CHO \;+\; H-\underset{\displaystyle H}{\underset{|}{CH_2}}-C=O \xrightarrow{dilNaOH} C_6H_5-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}}-C=O$$

benzaldehyde

b) Cannizzaro reaction : Aldehydes which don't contain any α — hydrogen atom like formaldehyde and benzaldehyde, undergoC self oxidation and reduction (disproportionation) on treatment with concentrated alkali. Thus , one of the molecule of aldehyde gets reduced to alcohol while the other gets oxidized to the acid. As a result, a mixture containing an alcohol and a salt of the carboxylic acid is formed. This reaction is known as cannizzaro reaction.

$$HCHO + HCHO \xrightarrow{conc\ NaOH} CH_3OH + HCOONa$$

two molecules formaldehyde — methanol — sodium formate

$$C_6H_5CHO + C_6H_5CHO \xrightarrow{concNaOH} C_6H_5CH_2OH + C_6H_5COONa$$

two mols of benzaldehyde — benzyl alcohol — sodium benzoate

Canizzaro reaction between molecules of different aldehyde is termed as cross cannizaro reaction.

$$C_6H_5CHO + HCHO \xrightarrow{conc\ NaOH} C_6H_5CH_2OH + HCOONa$$

Note: More reactive aldehyde is oxidized and less reactive is reduced in cross canizzaro reaction.

Some practice questions.

1) An organic compound A (C_4H_8O) $reacts\ with\ phenyl$ hydrazine to give phenyl hydrazine, reduces Fehling's solution but doesn't give iodoform test. Identify the compound A.
2) An alkene on ozonolysis gives aldehyde and ketone. The aldehyde gives positive iodoform test and the ketone on clemmensen reduction gives propane. Write down the structure of alkene.
3) A carbonyl compound (C_3H_6O) decolourise potassium permagnate solution,gives yellow ppt with 2,4-DNP but doesn't give iodoform test. Identify the compound
4) An organic compound X ($C_4H_{10}O$) ,on oxidation gives Y (C_4H_8O). The compound B reacts with sodium hydroxide and iodine gives yellow ppt, gives oxime with hydroxylamine, but gives negative silver mirror test. Identify X and Y with essential reactions.