ATOMIC ENERGY EDUCATION SOCIETY
Anushaktinagar, Mumbai
Class-12th Chemistry
Lesson:12
Aldehydes, Ketones & Carboxylic Acids
MODULE-2/3
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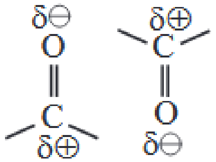
Physical properties

- Nature of intermolecular forces :
- The carbonyl bond (C=O) in aldehydes and ketones is a polar covalent bond. As a result, these compounds contain dipole-dipole forces of attraction. The molecules orient in such a way as to have oppositely polarized atoms facing each other.



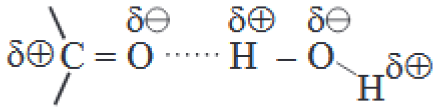
- Carboxyl group of carboxylic acid contains O-H bond which is responsible for formation of hydrogen bonding. Thus, carboxylic acids have the strongest intermolecular forces of attraction

Physical state and boiling points

- Formaldehyde is a gas at room temperature and has irritating odour.
- Acetaldehyde is extremely volatile, colourless liquid.
- Higher aldehydes have pleasant odour.
- Acetone is a liquid at room temperature and has pleasant odour.
- Increasing boiling points in the homologous series of aldehydes and ketones.

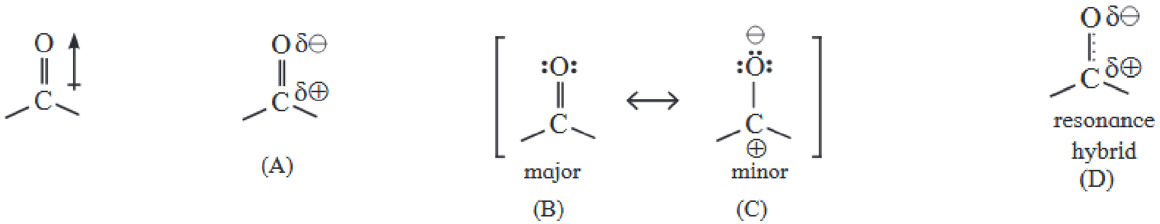
Solubility of aldehydes and ketones

- The oxygen atom of (C=O) can involve in hydrogen bonding with water molecule. As a result of this, the lower aldehydes and ketones are water soluble (For example : acetaldehyde, acetone).
- As the molecular mass increases, the proportion of hydrocarbon part of the molecule increases which cannot form hydrogen bond; and the water solubility decreases.



Polarity of carbonyl group

- The polarity of a carbonyl group originates from higher electronegativity of oxygen relative to carbon as well as resonance effects as shown



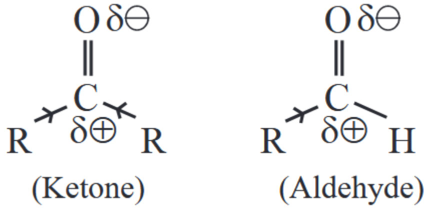
- The carbonyl carbon has positive polarity (see structures (A) and (D). Therefore, it is electron deficient.
- As a result, this carbon atom is electrophilic (electron loving) and is susceptible to attack by a nucleophile (Nu:).

Reactivity of aldehydes and ketones

- Reactivity of aldehydes and ketones is due to the polarity of carbonyl group which results in electrophilicity of carbon.
- Aldehydes are more reactive than ketones toward nucleophilic attack.
- Influence of electronic effects :
- Alkyl groups have +I effect.
- A ketone has two +I groups, decreasing c=o`s elecropositivity.
- In contrast, aldehydes have only one electron donating group, bonded to carbonyl carbon.
- Hence aldehydes more electrophilic than ketones.

2. Steric effects

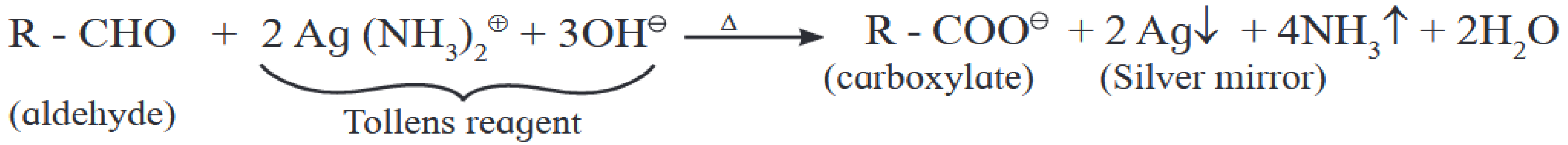
- Two bulky alkyl groups in ketone come in the way of incoming nucleophile. This is called steric hindrance to nucleophilic attack.
- On the other hand, nucleophile can easily attack the carbonyl carbon in aldehyde, because it has one alkyl group and is less crowded or sterically less hindered.
- Hence, aldehyde are more easily attacked by nucleophiles.



Laboratory tests for aldehydes and ketones

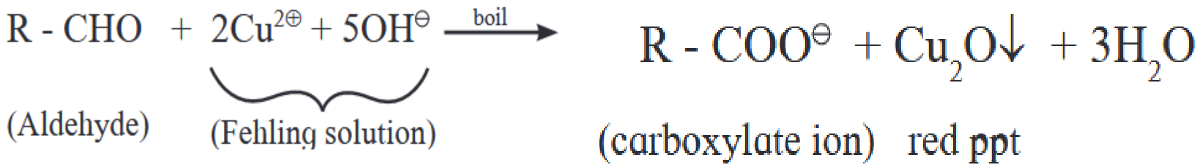
- Aldehydes are easily oxidized to carboxylic acids,
- therefore, act as reducing agents toward mild oxidizing agents.
- Ketones, do not have hydrogen atom directly attached to carbonyl carbon.
- Hence, they are not oxidized by mild oxidizing agents.
- Tests given by only aldehydes :
- 1. **Schiff's test**: When alcoholic solution of aldehyde is treated with few drops of Schiff 's reagent, pink or red or magenta colour appears. This confirms the presence of aldehydic (-CHO) group.

2. **Tollens' test or silver mirror test**: When an aldehyde is boiled with Tollens' reagent (ammonical silver nitrate), silver mirror is formed. The aldehyde is oxidized to carboxylate ion by Tollens' reagent and Ag^+ ion is reduced to Ag.



$$\underset{\text{(aldehyde)}}{R\text{ - }CHO} + \underbrace{2\,Ag(NH_3)_2^{\oplus} + 3OH^{\ominus}}_{\text{Tollens reagent}} \xrightarrow{\Delta} \underset{\text{(carboxylate)}}{R\text{ - }COO^{\ominus}} + \underset{\text{(Silver mirror)}}{2\,Ag\downarrow} + 4NH_3\uparrow + 2H_2O$$

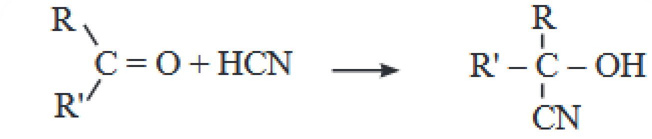
- **Fehling test**: When a mixture of an aldehyde and Fehling solution is boiled in hot water, a <u>red</u> <u>precipitate</u> of cuprous oxide is formed. An aldehyde is oxidized to carboxylate ion by Fehling solution and $Cu_2^{\oplus}$ ion is reduced to $Cu^{\oplus}$ ion. It may be noted that α-hydroxy ketone also gives this test positive.



$$\underset{\text{(Aldehyde)}}{R - CHO} + \underbrace{2Cu^{2\oplus} + 5OH^{\ominus}}_{\text{(Fehling solution)}} \xrightarrow{\text{boil}} \underset{\text{(carboxylate ion)}}{R - COO^{\ominus}} + \underset{\text{red ppt}}{Cu_2O\downarrow} + 3H_2O$$

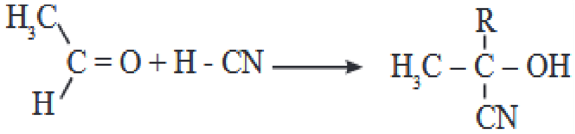
Chemical reactions of ald. and ket. with nucleophile

- all these reactions the nucleophilic reagent attacks on positively polarized electrophilic carbonyl carbon in aldehydes and ketones.
- Addition of hydrogen cyanide (H-CN):
- Hydrogen cyanide (weak acid) adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds called cyanohydrins.
- The negative part of the reagent (CN) attacks the electrophilic carbon of carbonyl group. The reaction requires either acid or base as catalyst.



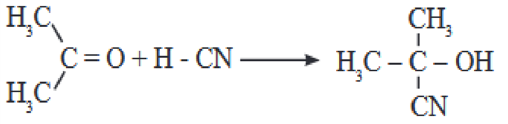
(Aldehyde when R' = H
Ketone : R' = alkyl/aryl group)

(cyanohydrin)



(Acetaldehyde)

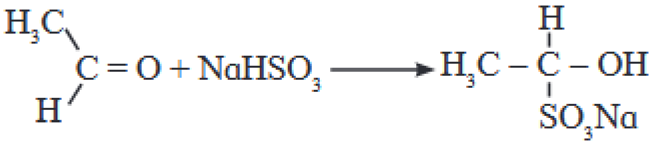
(acetaldehyde cyanohydrin)



(Acetone)

(Acetone cynohydrin)

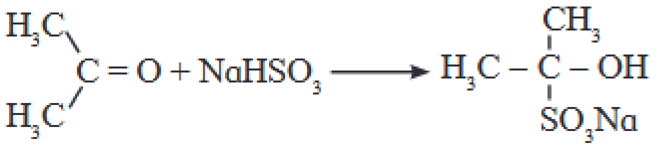
- b. Addition of $NaHSO_3$ (Sodium bisulphite) :
- Aldehydes and ketones react with saturated aqueous solution of sodium bisulfite to give crystalline precipitate of sodium bisulfite adduct (addition compound). For example,



$$CH_3CHO + NaHSO_3 \longrightarrow H_3C-\overset{\displaystyle H}{\underset{\displaystyle SO_3Na}{C}}-OH$$

(Acetaldehyde)

(Acetaldehyde sodium bisulfite adduct)



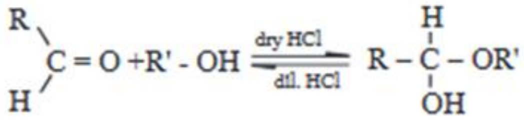
$$(CH_3)_2C{=}O + NaHSO_3 \longrightarrow H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle SO_3Na}{C}}-OH$$

(Acetone)

(Acetonesodium bisulfite adduct)

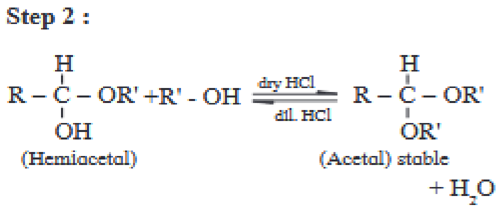
- c. Addition of alcohols :
- Aldehyde reacts with one molecule of anhydrous monohydric alcohol in presence of dry hydrogen chloride to give alkoxyalcohol known as hemiacetal

Step 1 :



$$\underset{H}{\overset{R}{\diagdown\!\!\diagup}}C=O+R'-OH \xrightleftharpoons[\text{dil. HCl}]{\text{dry HCl}} R-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-OR'$$

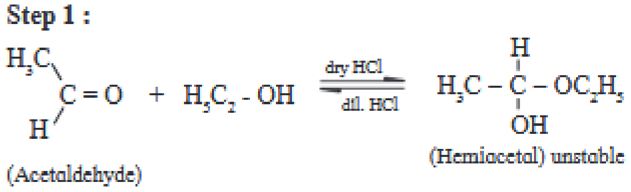
(Aldehyde) (Hemiacetal) unstable

- which further reacts with one more molecule of anhydrous monohydric alcohol to give a geminal-dialkoxy compound known as acetalas shown in the reaction.
- 

Step 2 :

$$R-\underset{OH}{\overset{H}{C}}-OR' + R'-OH \underset{\text{dil. HCl}}{\overset{\text{dry HCl}}{\rightleftharpoons}} R-\underset{OR'}{\overset{H}{C}}-OR' + H_2O$$

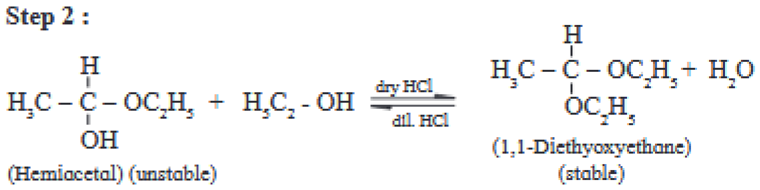
(Hemiacetal) (Acetal) stable



Step 1 :

$$H_3C(H)C=O + H_5C_2-OH \underset{\text{dil. HCl}}{\overset{\text{dry HCl}}{\rightleftharpoons}} H_3C-\underset{OH}{\overset{H}{C}}-OC_2H_5$$

(Acetaldehyde) (Hemiacetal) unstable

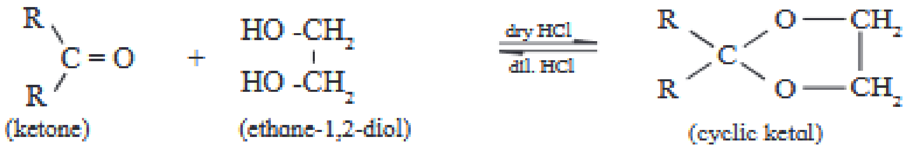


Step 2 :

$$H_3C-\underset{OH}{\overset{H}{C}}-OC_2H_5 + H_5C_2-OH \underset{\text{dil. HCl}}{\overset{\text{dry HCl}}{\rightleftharpoons}} H_3C-\underset{OC_2H_5}{\overset{H}{C}}-OC_2H_5 + H_2O$$

(Hemiacetal) (unstable) (1,1-Diethyoxyethane) (stable)

- Similarly, Ketones react with alcohol in presence of acid catalyst to form hemiketal and ketal.
- Ketones react with 1,2- or 1,3- diols in presence of dry hydrogen chloride to give five- or six -membered cyclic ketals .



- The reaction can be reversed by treating the cyclic ketal with aqueous HCl to regenerate the ketone.
- Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.
- d. Addition of Grignard reagent: Aldehydes and ketones on reaction with alkyl magnesium halide followed by acid hydrolysis give alcohols.(Refer to Chapter 11, sec. 11.4.1 d.)
- By addition of Grignard reagent to aldeheydes and ketones : Grignard reagent reacts with aldehyde or ketone to form an adduct which on hydrolysis with dilute acid gives the corresponding alcohols.

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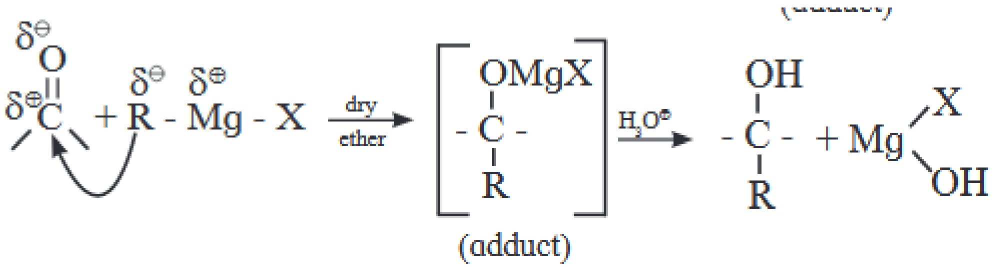
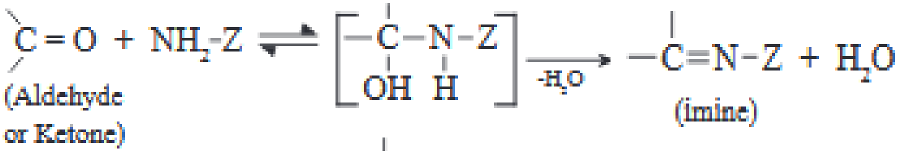
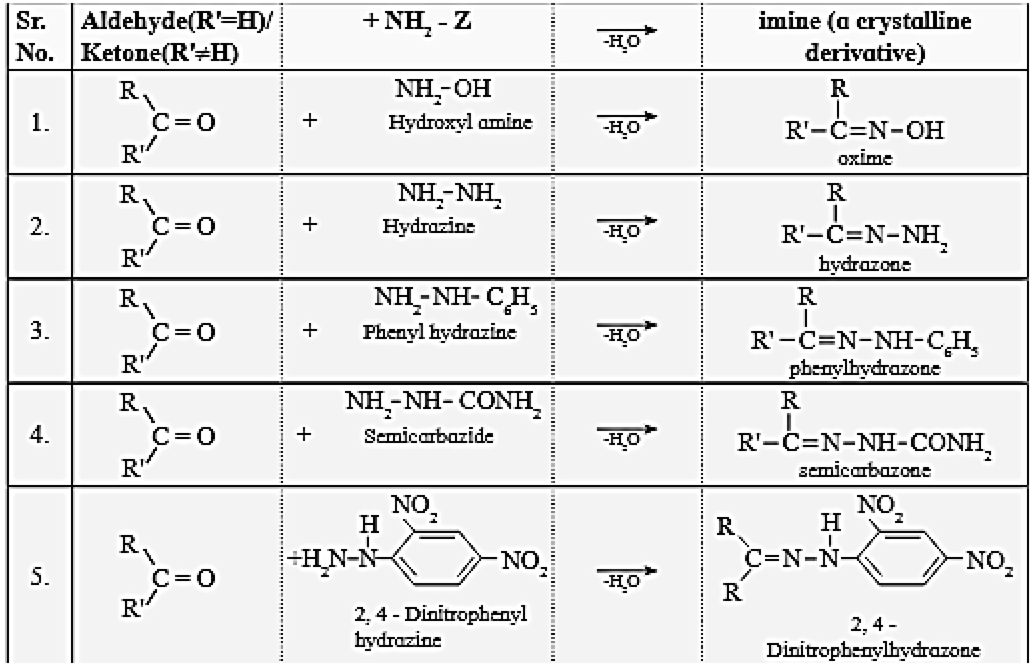


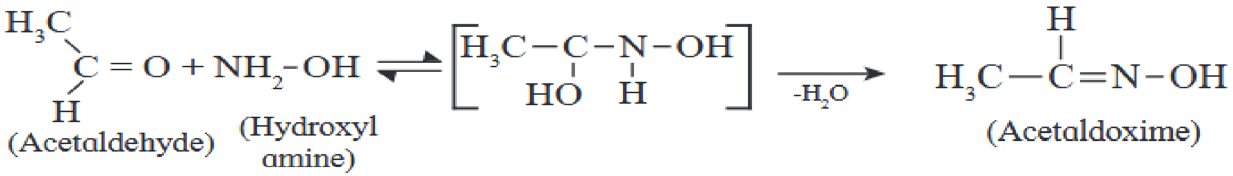
- e. Nucleophilic addition –elimination of aldehydes and ketones with ammonia derivatives: Aldehydes and ketones undergo addition elimination with some ammonia derivatives (NH2-Z) to give product containing C = N bonds (imines). The reaction is reversible and takes place in weakly acidic medium. The substituted imine is called a Schiff 's base



- Where Z = -R, -Ar, $-NH_2$, $-NHC_6H_5$, $-NHCONH_2$, $-NHC_6H_3(NO_2)_2$



Sr. No.	Aldehyde(R'=H)/ Ketone(R'≠H)	$+ NH_2 - Z$	$\xrightarrow{-H_2O}$	imine (a crystalline derivative)
1.	$\underset{R'}{\overset{R}{}}\!\!>C=O$	+ NH_2-OH Hydroxyl amine	$\xrightarrow{-H_2O}$	$R'-\overset{R}{\overset{\vert}{C}}=N-OH$ oxime
2.	$\underset{R'}{\overset{R}{}}\!\!>C=O$	+ NH_2-NH_2 Hydrazine	$\xrightarrow{-H_2O}$	$R'-\overset{R}{\overset{\vert}{C}}=N-NH_2$ hydrazone
3.	$\underset{R'}{\overset{R}{}}\!\!>C=O$	+ $NH_2-NH-C_6H_5$ Phenyl hydrazine	$\xrightarrow{-H_2O}$	$R'-\overset{R}{\overset{\vert}{C}}=N-NH-C_6H_5$ phenylhydrazone
4.	$\underset{R'}{\overset{R}{}}\!\!>C=O$	+ $NH_2-NH-CONH_2$ Semicarbazide	$\xrightarrow{-H_2O}$	$R'-\overset{R}{\overset{\vert}{C}}=N-NH-CONH_2$ semicarbazone
5.	$\underset{R'}{\overset{R}{}}\!\!>C=O$	$+H_2N-\overset{H}{N}-$ (NO_2, NO_2) 2, 4 - Dinitrophenyl hydrazine	$\xrightarrow{-H_2O}$	$\underset{R}{\overset{R}{}}\!\!>C=N-\overset{H}{N}-$ (NO_2, NO_2) 2, 4 - Dinitrophenylhydrazone



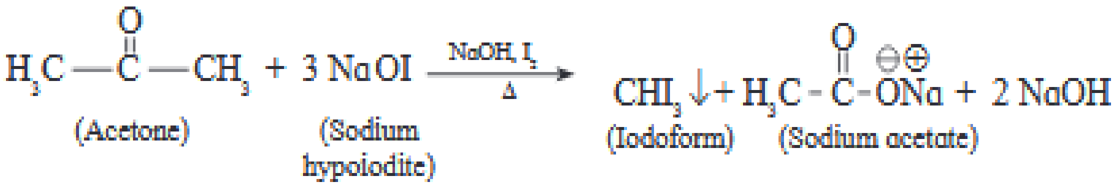
$$\underset{H}{\overset{H_3C}{}}\!\!>C=O + NH_2-OH \rightleftharpoons \left[H_3C-\underset{HO}{C}-\underset{H}{N}-OH\right] \xrightarrow{-H_2O} H_3C-\overset{H}{\overset{\vert}{C}}=N-OH$$

(Acetaldehyde) (Hydroxyl amine) (Acetaldoxime)

- All aldehydes and ketones give similar reactions. The resulting products have high molecular mass and are crystalline solids.
- These reactions are, therefore, useful for characterization of the original aldehydes and ketones

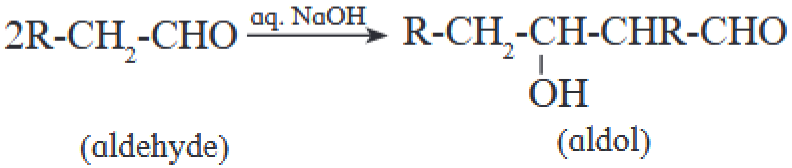
- f. Haloform reaction :
- This reaction is given by acetaldehyde, all methyl ketones (CH$_3$-CO-R) and all alcohols containing CH$_3$-(CHOH)- group.
- When an alcohol or methyl ketone is warmed with sodium hydroxide and iodine, a yellow precipitate is formed.
- Here the reagent sodium hypoiodite is produced in situ.
- During the reaction, sodium salt of carboxylic acid is formed which contains one carbon atom less than the substrate.
- The methyl group is converted in to haloform.
- For example : Acetone is oxidized by sodium hypoiodite to give sodium salt of acetic acid and yellow precipitate of iodoform.

- Haloform reaction:



$$\underset{\text{(Acetone)}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{(Sodium hypoiodite)}}{3\,NaOI} \xrightarrow[\Delta]{NaOH,\ I_2} \underset{\text{(Iodoform)}}{CHI_3\downarrow} + \underset{\text{(Sodium acetate)}}{H_3C-\overset{\overset{O}{\|}}{C}-\overset{\ominus\oplus}{ONa}} + 2\,NaOH$$

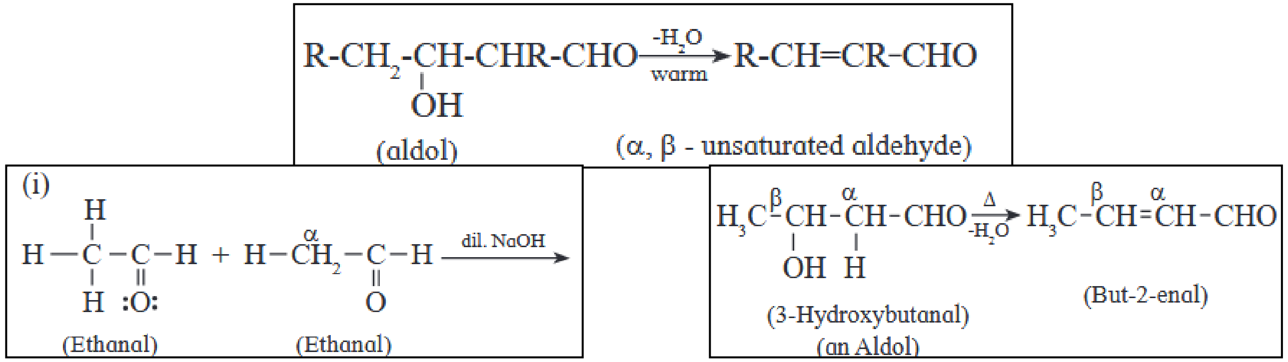
- g. Aldol condensation :
- Aldehydes containing at least one α –hydrogen atom undergo a reaction in presence of dilute alkali (dilute NaOH, KOH or Na_2CO_3) as catalyst to form b-hydroxy aldehydes (aldol). This reaction is known as aldol reaction.



$$2R\text{-}CH_2\text{-}CHO \xrightarrow{aq.\ NaOH} R\text{-}CH_2\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}CHR\text{-}CHO$$

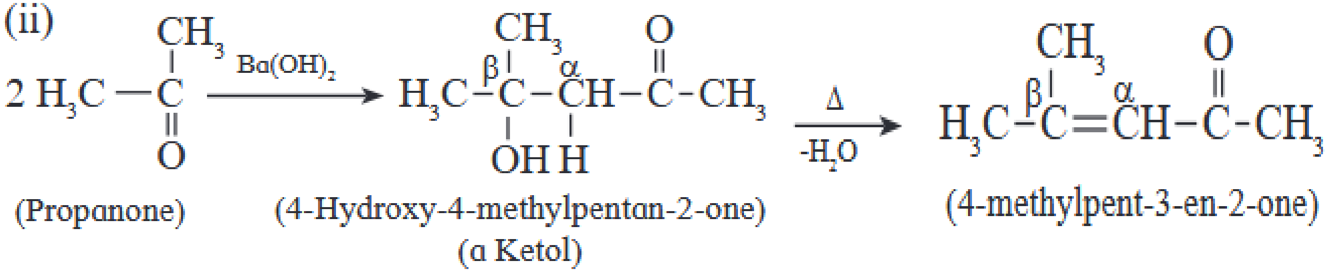
(aldehyde) (aldol)

- Formation of aldol is an addition reaction. Aldol formed from aldehyde having α-hydrogens undergoes subsequent elimination of water molecule on warming, giving rise to α, b - unsaturated aldehyde.



- The overall reaction is called aldol condensation. It is a nuclephilic addition-elimination reaction.
- Ketones containing at least two α- hydrogens, also undergo aldol condensation reaction and give an α, b - unsaturated ketone.
- For example:

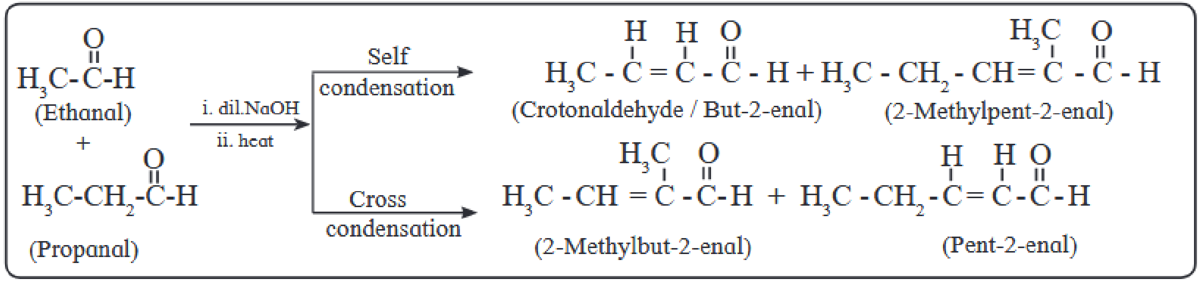
(ii)



$$2\,H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}} \xrightarrow{Ba(OH)_2} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{\overset{\beta}{C}}}-\underset{\underset{\displaystyle H}{|}}{\overset{\alpha}{C}H}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{\Delta} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\overset{\beta}{C}}=\overset{\alpha}{C}H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(Propanone) (4-Hydroxy-4-methylpentan-2-one) (α Ketol) (4-methylpent-3-en-2-one)

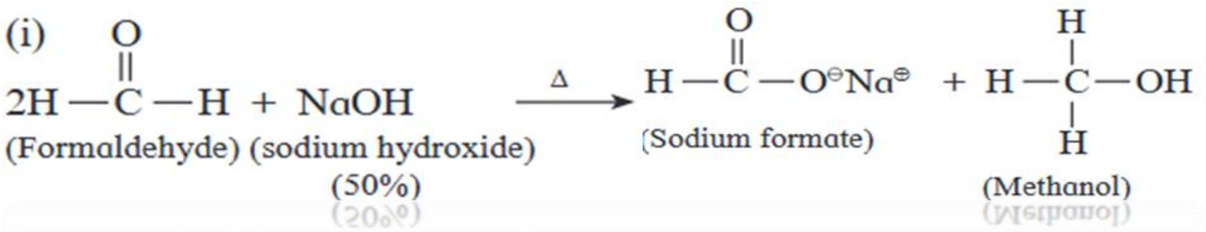
- For example: a mixture of ethanal and propanal on reaction with dilute alkali followed by heating gives a mixture of four products



$$\underset{\text{(Ethanal)}}{H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} + \underset{\text{(Propanal)}}{H_3C\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} \xrightarrow[\text{ii. heat}]{\text{i. dil.NaOH}}$$

$$\xrightarrow[\text{condensation}]{\text{Self}} \underset{\text{(Crotonaldehyde / But-2-enal)}}{H_3C - \overset{H}{C} = \overset{H}{C} - \overset{O}{\overset{\|}{C}} - H} + \underset{\text{(2-Methylpent-2-enal)}}{H_3C - CH_2 - CH = \overset{H_3C}{C} - \overset{O}{\overset{\|}{C}} - H}$$

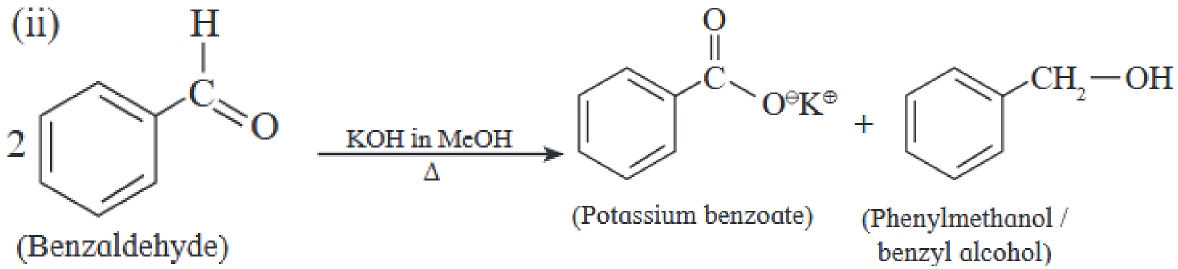
$$\xrightarrow[\text{condensation}]{\text{Cross}} \underset{\text{(2-Methylbut-2-enal)}}{H_3C - CH = \overset{H_3C}{C} - \overset{O}{\overset{\|}{C}} - H} + \underset{\text{(Pent-2-enal)}}{H_3C - CH_2 - \overset{H}{C} = \overset{H}{C} - \overset{O}{\overset{\|}{C}} - H}$$



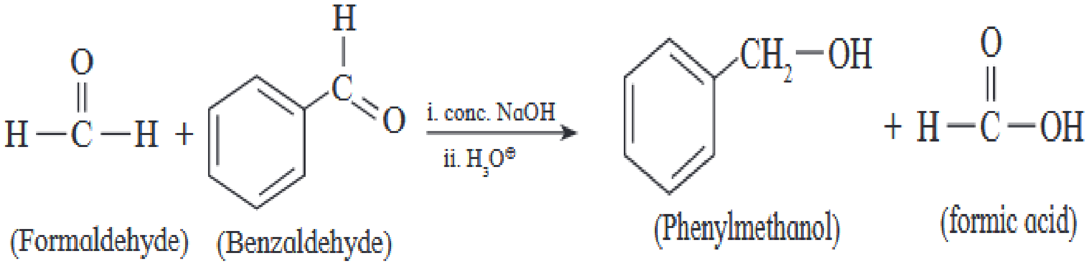
(i)

$$\underset{\text{(Formaldehyde)}}{2H - \overset{O}{\overset{\|}{C}} - H} + \underset{\substack{\text{(sodium hydroxide)} \\ (50\%)}}{NaOH} \xrightarrow{\Delta} \underset{\text{(Sodium formate)}}{H - \overset{O}{\overset{\|}{C}} - O^{\ominus}Na^{\oplus}} + \underset{\text{(Methanol)}}{H - \underset{H}{\overset{H}{C}} - OH}$$

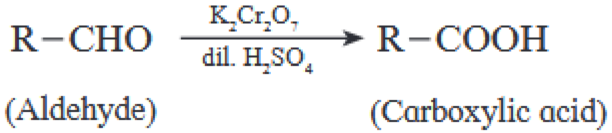
- cannizzaro reaction : one molecule of an aldehyde is reduced to alcohol and at the same time second molecule is oxidized to carboxylic acid salt.
-
- For example, Formaldehyde and benzaldehyde



- h`. Cross Cannizzaro reaction: When a mixture of formaldehyde and non-enolisable aldehyde (aldehyde with no α-hydrogen) is treated with a strong base, formaldehyde is oxidized to formic acid while the other non-enolisable is reduced to alcohol. Formic acid forms sodium formate with NaOH. On acidification sodium formate is converted into formic acid.
- For example :

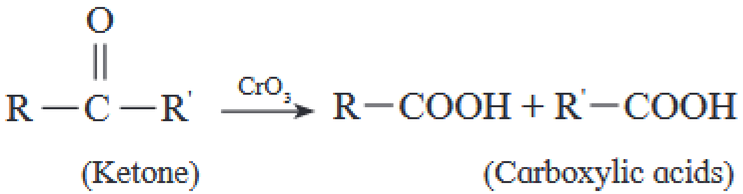


- Oxidation of aldehydes and ketones by dilute HNO3, KMnO4 and K2Cr2O7:
- Aldehydes are oxidized to the corresponding carboxylic acids by oxidant such as dilute nitric acid, potassium permanganate and sodium or potassium dichromate in acidic medium.



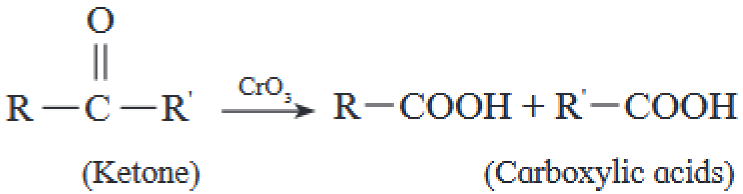
$$\underset{\text{(Aldehyde)}}{R-CHO} \xrightarrow[\text{dil. } H_2SO_4]{K_2Cr_2O_7} \underset{\text{(Carboxylic acid)}}{R-COOH}$$

- Ketones resist oxidation due to strong CO-C bond ,but they are oxidized by strong oxidizing agents such as CrO_3, alkaline KMnO4 or hot concentrated HNO_3 to a mixture of carboxylic acids having less number of carbon atoms than the starting ketone. Thus, Oxidation of ketones is accompanied by breaking C - C bond.



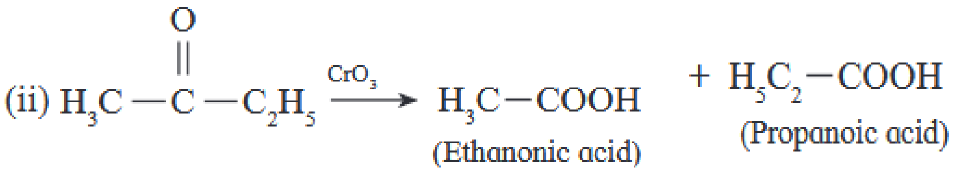
$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{CrO_3} R-COOH + R'-COOH$$

(Ketone) (Carboxylic acids)



$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{CrO_3} R-COOH + R'-COOH$$

(Ketone) (Carboxylic acids)

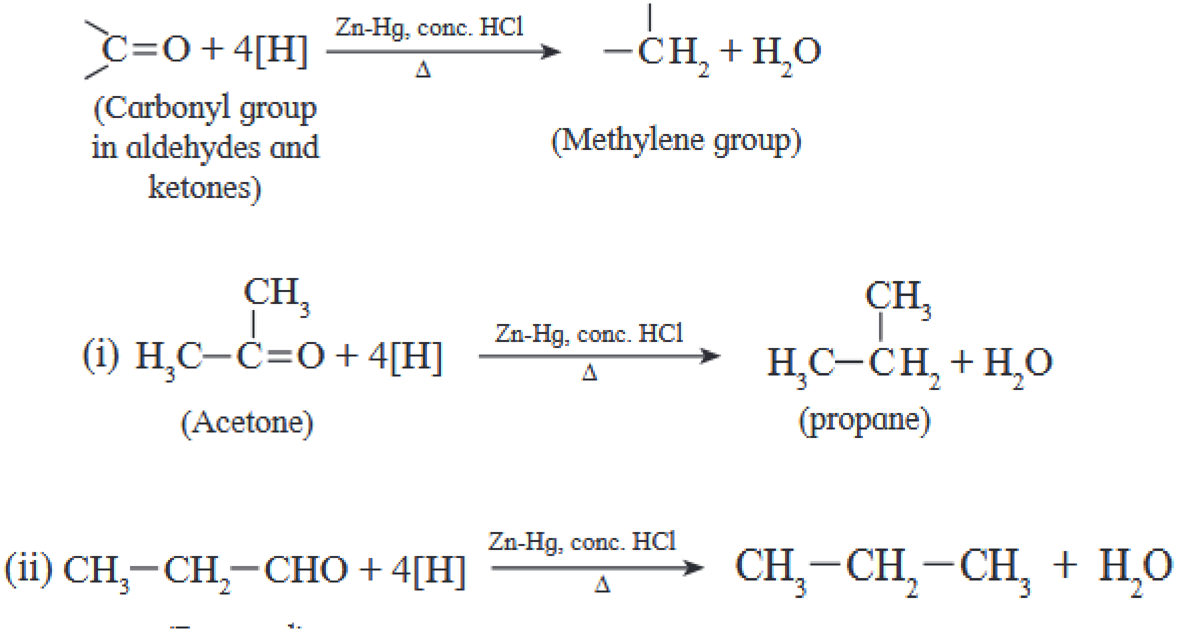


$$\text{(ii) } H_3C-\overset{\overset{O}{\|}}{C}-C_2H_5 \xrightarrow{CrO_3} H_3C-COOH + H_5C_2-COOH$$

(Ethanonic acid) (Propanoic acid)

- b. Clemmensen and Wolf-Kishner reduction:
- The carbonyl group of aldehydes and ketones is reduced to methylene group (-CH2-) on treatment with zinc –amalgam and concentrated hydrochloric acid (Clemmensen reduction) or hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol (Wolf-Kishner reduction).
- In both the reactions, oxygen is replaced by two hydrogen atoms.

- Clemmensen reduction



$$>C=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} -\overset{|}{C}H_2 + H_2O$$

(Carbonyl group in aldehydes and ketones)

(Methylene group)

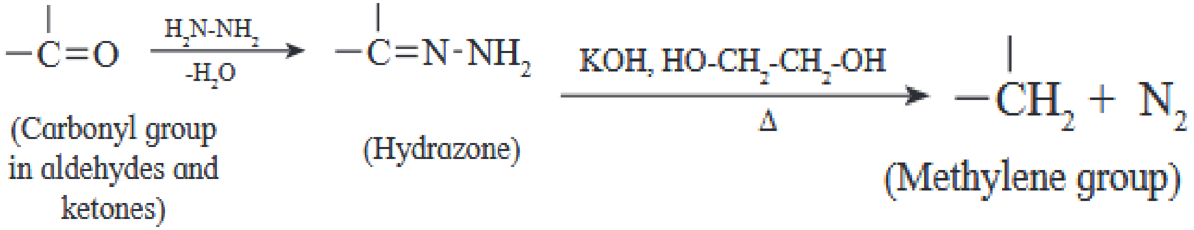
$$\text{(i)}\ H_3C-\overset{\overset{\large CH_3}{|}}{C}=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} H_3C-\overset{\overset{\large CH_3}{|}}{C}H_2 + H_2O$$

(Acetone)

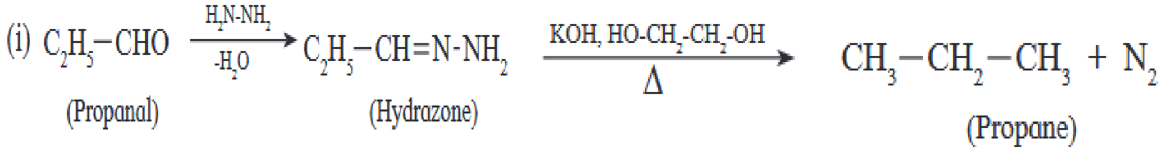
(propane)

$$\text{(ii)}\ CH_3-CH_2-CHO + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} CH_3-CH_2-CH_3 + H_2O$$

- Wolf-Kishner reduction

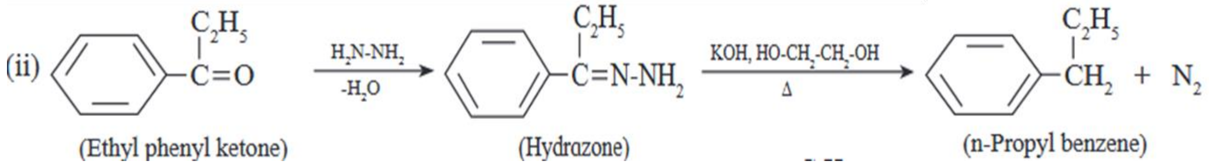


$$\underset{\text{(Carbonyl group in aldehydes and ketones)}}{-\overset{|}{C}=O} \xrightarrow[-H_2O]{H_2N\text{-}NH_2} \underset{\text{(Hydrazone)}}{-\overset{|}{C}=N\text{-}NH_2} \xrightarrow[\Delta]{KOH,\ HO\text{-}CH_2\text{-}CH_2\text{-}OH} \underset{\text{(Methylene group)}}{-\overset{|}{C}H_2 + N_2}$$

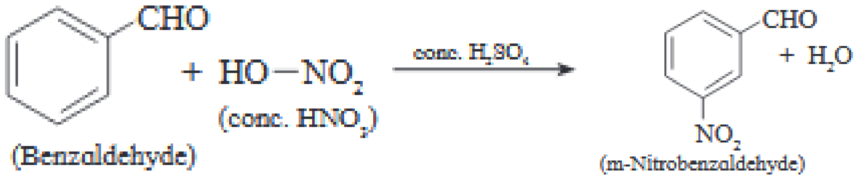


$$\text{(i)}\ \underset{\text{(Propanal)}}{C_2H_5-CHO} \xrightarrow[-H_2O]{H_2N\text{-}NH_2} \underset{\text{(Hydrazone)}}{C_2H_5-CH=N\text{-}NH_2} \xrightarrow[\Delta]{KOH,\ HO\text{-}CH_2\text{-}CH_2\text{-}OH} \underset{\text{(Propane)}}{CH_3-CH_2-CH_3 + N_2}$$

- Wolf-Kishner reduction is used to synthesize straight chain alkyl substituted benzenes which is not possible by Friedel-Crafts alkylation reaction



- **Electrophilic substitution reactions:**
- Aromatic aldehydes and ketones undergo electrophilic substitution reactions such as nitration, Sulfonation and halogenation. The aldehydic (-CHO) and ketonic (>C=O) groups are electron-withdrawing by inductive as well as resonance effects. They deactivate the benzene ring at ortho- and para- positions. This results in the formation of meta-product.
- For example ,



THANK YOU