ALDEHYDES AND KETONES

- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogen atom and one carbon containing group such as alkyl, aryl or aralkyl group. Examples:
  - Formaldehyde: \( H\text{CHO} \)
  - Phenyl acetaldehyde: \( \text{C}_6\text{H}_5\text{CH}_2\text{CHO} \)
  - Benzaldehyde: \( \text{C}_6\text{H}_5\text{CHO} \)
  - Acetaldehyde: \( \text{CH}_3\text{CHO} \)

- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two \( R \) and \( R' \) groups are same, the ketone is called simple or symmetrical ketone and if \( R \) and \( R' \) are different, then ketone is known as mixed or an unsymmetrical ketone.

**STRUCTURE**

- Carbonyl carbon of both aldehyde and ketones is \( sp^2 \)– hybridised, One of the three \( sp^2 \) hybridised orbital get involved in \( \sigma \)-bond formation with half–filled p-orbital of oxygen atom whereas rest of the two are consumed in \( \sigma \)-bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form \( \pi \)-bond with another half-filled p-orbital of oxygen atom by sideways overlapping.

**ISOMERISM IN ALDEHYDES AND KETONES**

(a) Chain isomerism: Aldehydes (with 4 or more carbon atoms) and ketone (with 5 or more carbon atoms) show chain isomerism. Example
  - \( \text{C}_4\text{H}_8\text{O} \)
  - \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \) (butanal)
ii) Position isomerism: Aliphatic aldehydes do not show position isomerism, because –CHO group is always present at the end of carbon chain. Aromatic aldehydes show position isomerism. Example

(c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group

(d) Functional isomerism: Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. Example
ALDEHYDES AND KETONE

CH₃CH₂CHO  propanal
CH₃ - C - CH₃  propanone
CH₂=CH - CH₂ - OH  Prop-2-en-1-ol
CH₂ = CH - OCH₃  methoxy ethene

(e) Tautomerism: Aldehydes and ketones also show tautomerism

(I)  C₂H₄O

CH₃ - C - H  {Acetaldehyde}
\( \text{and} \)  \( \text{CH₂ = CH} \)  {Vinyl alcohol}

(II)  C₃H₆O

CH₃ - C - CH₃  {Keto form}
\( \text{and} \)  \( \text{CH₂ = C - CH₃} \)  {Enol form}

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohol
   (i)  Oxidation of alcohol

   \[
   \begin{align*}
   \text{R - CH₂ - OH} + [\text{O}] & \xrightarrow{\text{K₂Cr₂O₇} \cdot \text{H₂SO₄}} \text{R-CHO} + \text{H₂O} \\
   \text{R - CH - OH} + [\text{O}] & \xrightarrow{\text{K₂Cr₂O₇} \cdot \text{H₂SO₄}} \text{R - C - R} + \text{H₂O}
   \end{align*}
   \]

   • Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketones further to carboxylic acids.
   • To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc), CrO₃C₅H₅N·HCl or CrO₃NH⁺CrO₃Cl⁻ are used. Collin’s reagent \([\text{(C₅H₅N)₂·CrO₃}]\) can also be used.

   \[
   \begin{align*}
   \text{R - CH₂OH} & \xrightarrow{\text{pcc, collin's reagent}} \text{RCHO} \\
   \text{R - CH₂OH} & \xrightarrow{\text{Cu, 300°C}} \text{RCHO} + \text{H₂}
   \end{align*}
   \]

   (ii)  Catalytic dehydrogenation of alcohols
2. From alkenes
   (i) Reductive ozonolysis of alkenes.
   \[
   \text{RCH} = \text{CHR} + \text{O}_3 + \text{CuCl}_4 \rightarrow \text{RCH}_1 \text{RCH}_2 \rightarrow 2\text{R} - \text{CHO} + \text{ZnO} \]

   (ii) Wacker process.
   \[
   \text{CH}_2 = \text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{PdCl}_2 \text{CuCl}_2, \text{air or O}_2} \text{CH}_3 - \text{CHO}
   \]
   \[
   \text{CH}_3 - \text{CH} = \text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{PdCl}_2 \text{CuCl}_2, \text{air or O}_2} \text{CH}_3 - \text{C} - \text{CH}_3
   \]

   (iii) OXO process [Carbonylation / Hydroformylation]
   \[
   \text{C} = \text{C} + \text{CO} + \text{H}_2 \xrightarrow{\text{[CoH(CO)_4]}} \text{C} - \text{C} - \text{CHO}
   \]

3. From alkynes
   \[
   \text{CH} \equiv \text{CH} + \text{H}_2 \xrightarrow{\text{Dil H}_2\text{SO}_4, \text{HgSO}_4} \text{CH}_2 = \text{CH} - \text{OH}
   \]
   \[
   \text{CH}_3 - \text{CHO} \xrightarrow{\text{tautomerism}} \text{acetaldehyde}
   \]

   \[
   \text{CH}_3 - \text{C} \equiv \text{CH} + \text{H}_2 \text{O} \xrightarrow{\text{Dil H}_2\text{SO}_4, \text{HgSO}_4} \text{CH}_3 - \text{C} - \text{CH}_2 \text{OH}
   \]
   \[
   \text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{tautomerism}} \text{propanone}
   \]

4. From Grignard reagent
   (1) By addition to ester
ALDEHYDES AND KETONE

(iii) By addition to nitriles

\[
\begin{align*}
H - C \equiv N + RMgX &\rightarrow H - C = N - MgX \\
\text{aldehyde} + \text{Mg(OH)}_2 &\rightarrow H - C = N - MgX \\
\text{ketone} + \text{Mg(OH)}_2 &\rightarrow H - C = N - MgX
\end{align*}
\]

5. From carboxylic acids

(i) Catalytic decomposition of carboxylic acid.

\[
\begin{align*}
\text{HCOOH} + \text{HCOOH} &\xrightarrow{\text{MnO}_2, 300^\circ C} \text{HCHO} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{CH}_3\text{COOH} + \text{HOOCH}_3 &\xrightarrow{\text{MnO}_2, 300^\circ C} \text{CH}_3\text{C} - \text{CH}_3 \\
\text{acetic acid} &\xrightarrow{\text{Al}_2\text{O}_3, 400^\circ C} \text{acetic acid}
\end{align*}
\]
(ii) From calcium salt of carboxylic acids

\[
\begin{align*}
\text{HCOO} & \quad \text{Ca} \\
\rightarrow & \\
\text{HCHO} + \text{CaCO}_3 \\
\end{align*}
\]

Formaldehyde

\[
\begin{align*}
\text{CH}_3\text{COO} & \quad \text{Ca} \\
\rightarrow & \\
\text{CH}_3\text{C} = \text{CH}_3 + \text{CaCO}_3 \\
\end{align*}
\]

Acetone

6. From derivatives of carboxylic acids

(i) Reduction of acid chlorides (Rosenmund’s reaction)

\[
\text{R} - \text{C} - \text{Cl} + \text{H}_2 \xrightarrow{\text{Pd, BaSO}_4, 5} \text{RCHO} + \text{HCl}
\]

- Above reaction is known as Rosenmund’s reduction and is applicable for preparation of aldehydes
- BaSO₄, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH₂OH

(ii) Reduction of acid chloride with dialkyl cadmium.

\[
\begin{align*}
2\text{CH}_3\text{C} = \text{Cl} + (\text{CH}_3)_2\text{Cd} & \rightarrow \\
2\text{CH}_3\text{C} = \text{CH}_3 + \text{CdCl}_2
\end{align*}
\]

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxide aluminium hydride, LiAlH[OC(CH₃)₃]

\[
\begin{align*}
\text{R} - \text{C} - \text{Cl} + \text{LiAlH [OC(CH₃)₃]} & \rightarrow \\
\text{R} - \text{CHO} + \text{Al [OC(CH₃)₃]} + \text{LiCl}
\end{align*}
\]

(iii) Reduction of esters

\[
\begin{align*}
\text{R} - \text{C} - \text{OR} \xrightarrow{\text{NaAlH}_4} \text{RCHO} + \text{R' - OH}
\end{align*}
\]
7. From gem-dihalides by hydrolysis

\[ R-\text{CHCl}_2 + 2\text{NaOH} \rightarrow R-\text{CHO} \]

8. From nitriles by reduction
   (i) Stephen's reduction.
   \[ R-C\equiv N \xrightarrow{\text{SnCl}_2 + \text{HCl}} R-C=\text{NH}_2\text{Cl} \]
   Aldimine hydrochloride
   \[ R-C-H + 2\text{NH}_4\text{Cl} \rightarrow \text{H}_2\text{O} \]
   (ii) Reduction with LiAlH₄
   \[ R-C\equiv N + \text{LiAlH}_4 \rightarrow (R-\text{CH} = \text{N})_3\text{Al} \]
   \[ \text{RCHO} \xrightarrow{2\text{H}_2\text{O}} \text{aldehyde} \]

9. Preparation of aromatic carbonyl compounds.
   (i)

   This is known as Etard reaction
(ii) By side chain chlorination followed by hydrolysis

\[
\text{CH}_3\text{C}_6\text{H}_4\text{Cl}_2, \text{hy} \rightarrow \text{CHCl}_2\text{C}_6\text{H}_4\text{H}_2\text{O} \rightarrow \text{CHCl}_2\text{C}_6\text{H}_4\text{H}_2\text{O} + 2\text{HCl}
\]

Benzal Chloride

Benzaldehyde

(iii) Gatterman – Koch reaction

\[
\text{CO}, \text{HCl} \rightarrow \text{CHO}
\]

Anhyd. AlCl₃/CuCl

Benzaldehyde

(iv) Friedel Craft Acylation

\[
\text{O} \rightarrow \text{Cl} \rightarrow \text{Anhyd. AlCl}_3 \rightarrow \text{O} - \text{C} - \text{R}
\]

aromatic ketone

(v) Reimer – Tiemann reaction

\[
\text{OH} + \text{CHCl}_3 \text{NaOH} \rightarrow \text{OH} + \text{CHCl}_2 \text{Na}^+ \rightarrow \text{OH} + \text{CHO} \rightarrow \text{OH} + \text{CHO} + \text{H}^+
\]

Benzophenone
ALDEHYDES AND KETONE

PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

1. Physical state
   - Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
   - Higher members of aldehydes and ketones are solids with fruity odour
   - Lower aldehydes have unpleasant odour but ketones possess pleasant smell

2. Boiling point
   - Boiling point of aldehydes and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However, their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may be attributed to the reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipole-dipole interaction:

     \[ \overset{\delta^+}{\overset{\delta^-}{C}} = O \quad \overset{\delta^+}{\overset{\delta^-}{C}} = O \quad \overset{\delta^+}{\overset{\delta^-}{C}} = O \]

   - Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

3. Solubility
   - Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
   - However, solubility decreases with increase in molecular weight
   - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However, all carbonyl compounds are fairly soluble in organic solvents.

RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

(a) Aliphatic aldehydes and ketones
   (i) Inductive effect:
       The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl
group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed

\[
\text{formaldehyde} \quad > \quad \text{acetaldehyde} \quad > \quad \text{acetone}
\]

(ii) Steric effect
- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hindrance, to the attacking group. This factor is called steric hindrance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is

\[
\text{formaldehyde} \quad > \quad \text{acetaldehyde} \quad > \quad \text{acetone}
\]

(b) Aromatic aldehydes and ketones
- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of benzene ring
Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude of positive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.

The order of reactivity of aromatic aldehydes and ketones is

\[
\text{C}_6\text{H}_5\text{CH}_2\text{CHO} > \text{C}_6\text{H}_5\text{CHO} > \text{C}_6\text{H}_5\text{COCH}_3 > \text{C}_6\text{H}_5\text{CO} \text{C}_6\text{H}_5
\]

CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

In this reaction carbon atom of carbonyl group changes from sp\(^2\) to sp\(^3\) hybridised

(i) Addition of hydrogen cyanide (HCN)

Mechanism
Step I : The hydrogen cyanide interacts with the base to form nucleophile
Step II: The nucleophile attacks the carbonyl carbon to form an anion

\[ C = O + CN^- \rightarrow C = O^- \]

Step III: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pethenone and pinacolone form cyanohydrins.

(ii) Addition of sodium bisulphate (NaHSO₄)

- All ketones do not undergo this reaction only methyl ketone form addition product with sodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.

(iii) Addition of Grignard reagent
ALDEHYDES AND KETONE

Formaldehyde form a primary alcohol

\[
\text{H - C - H + RMgl} \xrightarrow{\text{ether}} \text{R} - \text{C} - \text{OMgl} \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{RCH}_2\text{OH} + \text{Mg} \]

- Higher aldehydes give secondary alcohol

\[
\text{R - C - H + R'Mgl} \xrightarrow{\text{ether}} \text{R} - \text{C} - \text{OMgl} \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{RCH}_2\text{OR'} + \text{Mg} \]

- Ketone give tertiary alcohols

\[
\text{R'} \quad \text{OH} \quad \text{MgI} \quad + \quad \text{R} - \text{C} - \text{OMgl} \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{RCH}_2\text{OR'} \]

(iv) Addition of alcohols

Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol
molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate

$$\text{R} = \text{O} + \text{HC (OC}_2\text{H}_5\text{)}_3 \rightarrow \text{R} = \text{O} \text{C}_2\text{H}_5 + \text{HCOOC}_2\text{H}_5$$

(v) Addition of ammonia derivative

$$\begin{align*}
\delta^+ \quad \delta^- & \quad \text{C} = \text{O} + \text{NH}_2 - \text{Z} \\
& \quad \text{R} \quad \text{R} \quad \text{C} = \text{O}^- \\
& \quad \text{R} \quad \text{R} \quad \text{NH}_2 - \text{Z} \\
\text{H}_2\text{O} + & \quad \text{C} = \text{N} - \text{Z} \\
\quad & \quad \text{H}^+ \\
\end{align*}$$

$Z = \text{OH, NH}_2, \text{NHC}_6\text{H}_5, \text{NHCOCH}_2$ etc.

The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

Step I: In acidic medium, the carbonyl oxygen gets protonated.

$$\begin{align*}
\text{C} = & \quad \text{O} \quad + \text{H}^+ \\
& \quad \text{form} \\
\text{acid} & \quad \text{C} = \quad \text{O} \quad \text{H}^- \\
& \quad \text{C} = \quad \text{O} \quad \text{H}^- \\
\end{align*}$$

Step II: In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack the positively charged carbonyl carbon and results in positive charge on nitrogen atom

$$\begin{align*}
\text{C} = & \quad \text{O} \quad - \text{H} + \text{N} - \text{Z} \\
& \quad \text{H} \\
\text{N} - \text{Z} & \quad \text{OH} \\
\text{H} & \quad \text{N} - \text{Z} \\
\end{align*}$$

Step III: The unstable intermediate loses a proton, $\text{H}^+$ and water molecule to form stable product (imines)
(vi) Addition of alkynes

\[ \text{C} = \text{O} + \text{RC} \equiv \text{CH} \rightarrow \text{C} = \text{N} - \text{Z} \]

This reaction is also known as ethinylation

2. Reduction reactions

I. Catalytic reduction to alcohol

\[ \text{C} = \text{O} + \text{H}_2 \xrightarrow{\text{Ni, Pt or Pd}} \text{R} - \text{CH}_2 - \text{OH} \quad \text{1° alcohol} \]

\[ \text{C} = \text{O} + \text{H}_2 \xrightarrow{\text{Ni, Pt or Pd}} \text{R'} - \text{CH} - \text{OH} \quad \text{2° alcohol} \]

II. Clemmensen reduction

\[ \text{C} = \text{O} + 4 [\text{H}] \xrightarrow{\text{Zn, Hg, HCl}} \text{CH}_2 + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{CHO} + 4 [\text{H}] \xrightarrow{\text{Zn, Hg, HCl}} \text{CH}_3\text{CH}_2\text{H}_2\text{O} \quad \text{ethane} \]

\[ \text{C} = \text{O} + 4 [\text{H}] \xrightarrow{\text{Zn, Hg, HCl}} \text{CH}_3\text{H}_2 + \text{H}_2\text{O} \quad \text{propane} \]

III. Wolf-Kishner reduction

\[ \text{C} = \text{O} + \text{NH}_2 - \text{NH}_2 \rightarrow \text{C} = \text{NNH}_2 \xrightarrow{\text{KOH, ethyleneglycol}} \text{N}_2 + \text{R-CH}_2 - \text{R} \quad \text{alkane} \]

\[ \text{CH}_3\text{CHO} + \text{NH}_2 - \text{NH}_2 \rightarrow \text{CH}_3 - \text{CH} = \text{NNH}_2 \]

\[ \text{N}_2 + \text{CH}_3 - \text{CH}_3 \xrightarrow{\text{KOH, ethyleneglycol}} \]
IV. Reduction with HI + P (red)

\[ \text{CH}_3\cdot\text{CHO} + 4\text{HI} \xrightarrow{150^\circ\text{C}} \text{CH}_3\cdot\text{CH}_3 + \text{H}_2\text{O} + 2\text{I}_2 \]

\[ \text{CH}_3\text{COCH}_3 + 4\text{HI} \xrightarrow{150^\circ\text{C}} \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3 + \text{H}_2\text{O} + 2\text{I}_2 \]

V. Reduction to pinacols

\[ \text{CH}_3\cdot\text{C} + \overset{\text{Mg-Hg, H}_2\text{O}}{\text{C} \cdot \text{CH}_3 + 2[H]} \overset{\text{pinacol}}{\text{CH}_3\cdot\text{C} \cdot \text{C} \cdot \text{CH}_3} \]

3. Oxidation reactions

i. Oxidation with mild oxidizing agents

\[ \text{R - C - H} + [\text{O}] \rightarrow \text{R - C - OH} \]

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduce Tollens’s reagent to metallic silver which appears as a silver mirror on wall of test tube. Thus the reaction is also known as silver mirror test.

\[ \text{RCCHO} + 2 [\text{Ag(NH}_3)_2]^+ + 3\text{OH}^- \rightarrow \]

\[ \text{RCOO}^- + 2\text{Ag} \downarrow + 4\text{NH}_3 + 2\text{H}_2\text{O} \]

(b) Reduction of Fehling’s solution

Fehling’s solution is an alkaline solution of CuSO\(_4\) mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduce cupric ion (Cu\(^{2+}\)) of Fehling’s solution to cuprous ions (Cu\(^+\)) to form red precipitate of cuprous oxide

\[ \text{RCOO}^- + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O} \]

Fehling’s solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketones so not give this reaction.

ii. Oxidation with strong oxidizing agent

\[ \text{RCHO} + [\text{O}] \xrightarrow{\text{HCl}_3\text{(conc.)}} \text{RCOOH} \]

\[ \text{CH}_3\cdot\text{C} \cdot \text{CH}_3 + 3[\text{O}] \rightarrow \text{CH}_3\text{COOH} + \text{HCOOH} \]

iii. Haloform reaction
4. Condensation reactions

(1) Aldol condensation

Mechanism
Aldehyde or ketones which do not contain α-hydrogen atom like formaldehyde (HCHO), benzaldehyde (C₆H₅CHO) and benzophenone (C₆H₅COC₆H₅) do not undergo aldol condensation.

(2) Cross aldol condensation
\[
\begin{align*}
&\text{CH}_3 - \text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CHO} \\
&\text{(A)} \quad \text{(B)} \\
&\text{dil. NaOH} \\
\end{align*}
\]
\[
\begin{align*}
\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO} + \text{CH}_3 - \text{CH} - \text{CH} = \text{C} - \text{CHO} \\
\text{But-2-en-1-al} \quad \text{2-methylpent-2-en-1-al} \\
\text{CH}_3 \\
\text{2-methyl but - 2-en-1-al} \\
\text{CH}_3 - \text{CH} = \text{C} - \text{CHO} \\
\text{pent-2-en-1-al}
\end{align*}
\]

# A- A Condensation
\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{H} + \text{H}-\text{CH}_2 - \text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CHO} \\
\text{But-2-en-1-al} \\
\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO} \\
\text{H}_2\text{O}
\end{align*}
\]

# B-B Condensation
\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{O} + \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{O} \xrightarrow{\text{dil. NaOH}} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH} - \text{CHO} \\
\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{C} - \text{CHO} \\
\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{C} - \text{CHO} \\
\text{2-methylpent-2-en-1-al}
\end{align*}
\]
ALDEHYDES AND KETONE

# A-B Condensation

\[
\begin{align*}
\text{CH}_3\cdot\text{C} &= \text{H} + \text{CH}_2\cdot\text{CHO} \xrightarrow{\text{dil NaOH}} \text{CH}_3\cdot\text{CH} &= \text{CH} &= \text{CHO} \\
\text{CH}_3\cdot\text{CH} &= \text{C} &= \text{CHO} \\
\text{CH}_3\cdot\text{CH} &= \text{H} &= \text{CHO}
\end{align*}
\]

2-methyl but-2-en-1-ol

# B-A Condensation

\[
\begin{align*}
\text{CH}_3\cdot\text{CH}_2\cdot\text{C} &= \text{H} + \text{H}\cdot\text{CH}_2\cdot\text{CHO} \xrightarrow{\text{dil NaOH}} \\
\text{OH} \\
\text{CH}_3\cdot\text{CH}_2\cdot\text{CH} &= \text{CH} &= \text{CHO} \\
\text{pent-2-en-1-ol}
\end{align*}
\]

(3) Claisen – Schmidt condensation

\[
\begin{align*}
\text{C}_6\text{H}_5\cdot\text{C} &= \text{H} + \text{CH}_3\cdot\text{C} &= \text{CH}_3 \xrightarrow{\text{dil NaOH}} \\
\text{[C}_6\text{H}_5\cdot\text{CH} &= \text{CH}_2\cdot\text{C} &= \text{CH}_3] \\
\text{C}_6\text{H}_5\cdot\text{CH} &= \text{H} &= \text{C} &= \text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{dil NaOH}} \\
\text{C}_6\text{H}_5\cdot\text{CH} &= \text{C} &= \text{H} &= \text{C} &= \text{CH}_3 + \text{C}_6\text{H}_5 \\
\text{Dibenzoalacetone}
\end{align*}
\]

5. Cannizaro reaction

\[
\begin{align*}
\text{H} &= \text{C} &= \text{O} + \text{H} &= \text{C} &= \text{O} \xrightarrow{\text{conc KOH}} \text{H} &= \text{C} &= \text{OH} + \text{H} &= \text{C} &= \text{O} \quad \text{K}
\end{align*}
\]
Mechanism

Step I: The $\text{OH}^-$ ion attacks the carbonyl carbon to form hydroxyl alkoxide

$$C_6H_5 - C - OH \xrightarrow{\text{fast}} C_6H_5 - C - OH$$

Step II: Anion (I) acts as hydride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer $\text{H}^+$ to acquire stability.

6. Reaction with chloroform

$$\text{CH}_3\text{C} = \text{O} + \text{CHCl}_3 \xrightarrow{\text{NaOH}} \text{CH}_3\text{C} = \text{C} - \text{Cl}_3$$

Chloretone is used as hypnotic.

7. Reaction with primary amine

$$\text{RCH} = \text{O} + \text{H}_2\text{NR'} \xrightarrow{\Delta, \text{H}^+} \text{RCH} = \text{NR'} + \text{H}_2\text{O}$$

 Schiff's base.
8. Electrophilic substitution reaction of aromatic carbonyl compounds

USES OF ALDEHYDES AND KETONES

(a) Uses of formaldehyde
i. The 40% solution of formaldehyde in water (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
ii. It is used for silvering of mirrors
iii. It is used for making synthetic plastics, like Bakelite, urea-formaldehyde resin etc

(b) Uses of acetaldehyde
i. It is used in preparation of acetic acid, dyes, drugs, etc
ii. As an antiseptic inhalant in nose troubles

(c) Uses of benzaldehyde
i. As flavouring agent in perfume industry
ii. In manufacture of dyes.

(d) Uses of acetone
i. As a solvent for cellulose acetate, resin etc.
ii. As a nailpolish remover
iii. In the preparation of an artificial scent and synthetic rubber