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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

$$\begin{array}{c} H \\ C = O \\ *H \\ formaldehyde \end{array} \begin{array}{c} C_6H_5CH_2 \\ H \\ phenyl acetaldehyde \end{array} \\ \begin{array}{c} C_6H_5 \\ H \\ C = O \\ H \\ aldehyde \end{array}$$

• 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.

R CH3
$$C_2H_5$$

R CH3 $C = O$

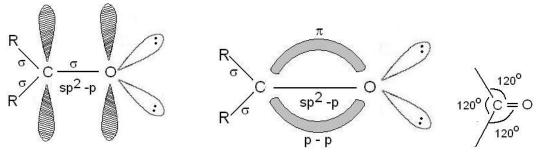
R CH3 $C = O$

CH3 $C = O$

Ketone dimethyl ketone (simple ketone) ethyl methyl ketone (mixed ketone)

STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is sp^2 hybridised, One of the three sp^2 hybridised orbital get involved in σ bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in σ -bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form π -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
 - i) C_4H_8O $CH_3-CH_2-CH_2-CHO$ (butanal)

- (b) Position isomerism: aliphatic aldehydes do not show position isomerism, because –CHO group is always present at the end of carbon chain.

 Aromatic aldehyde show position isomerism. Example
- (c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group $C_5H_{10}O$

(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 C_3H_6O

- (e) Tautomerism: Aldehydes and ketones also show tautomerism
 - (I) C_2H_4O

(II) C_3H_6O

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

- 1. From alcohol
 - (i) Oxidation of alcohol

$$R - CH_2 - OH + [O] \xrightarrow{K_2Cr_2O_7} R - CHO + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

$$R - CH - OH + [O] \xrightarrow{K_2Cr_2O_7} R - C - R + H_2O$$

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

(ii) Catalytic dehydrogenation of alcohols

$$\begin{array}{c}
RCH_2OH \frac{Cu}{300^{\circ}C} > RCHO + H_2 \\
 & \text{Aldehyde}
\end{array}$$

$$\begin{array}{c}
R \\
R
\end{array}
CH - OH \xrightarrow{Cu} \begin{array}{c}
R \\
300^{\circ}C \\
R
\end{array}
C = O + H_{2}$$
ketone

2. From alkenes

(i) Reductive ozonolysis of alkenes.

RCH = CHR +
$$O_3$$

RCH | RCH

(ii) Wacker process.

$$CH_{2} = CH_{2} + \frac{1}{2}O_{2} \frac{PdCl_{2}CuCl_{2}}{air \text{ or } O_{2}} > CH_{3} - CHO$$

$$CH_{3} - CH = CH_{2} + \frac{1}{2}O_{2} \frac{PdCl_{2}CuCl_{2}}{air \text{ or } O_{2}} > CH_{3} - C - CH_{3}$$
propanone

(iii) OXO process [Carbonylation / Hydroformylation]

$$C = \stackrel{\downarrow}{C} + CO + H_2 \xrightarrow{\begin{array}{c} [CoH(CO)_4] \\ 100^{\circ}C \\ pressure \end{array}} - \stackrel{\downarrow}{C} - \stackrel{\downarrow}{C} - CHO$$

3. From alkynes

CH = CH + H₂O
$$\frac{\text{Dil H}_2\text{SO}_4}{\text{HgSO}_4}$$
 CH₂ = CH - OH

CH₃ - CHO $\stackrel{\text{tautomerism}}{\stackrel{\text{acetaldehyde}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}}}{\stackrel{\text{details}}}{\stackrel{\text{details}}{\stackrel{\text{details}$

$$CH_3 - C \equiv CH + H_2O \xrightarrow{Dil H_2SO_4} CH_3 - C - CH_2$$

$$HgSO_4 \rightarrow CH_3 - C - CH_2$$

$$OH$$

$$CH_3 - C - CH_3$$

$$propanone$$

$$tautomerism$$

$$tautomerism$$

- 4. From Grignard reagent
 - (1) By addition to ester

O OMgX
H-C-OC₂H₅ + RMgX
$$\longrightarrow$$
 H-C-OC₂H₅
R
O
H-C-R + Mg
 O
aldehyde

CH₃- C - OC₂H₅ + RMgX
$$\longrightarrow$$
 CH₃ - C - OC₂H₅

CH₃- C - R + Mg

CH₃- C - R + Mg

CH₃- C - R + Mg

X

(iii) By addition to nitriles

$$H - C \equiv N + RMgX \longrightarrow H - C = N - MgX$$

R

O

 $H - C - R + NH_3 + Mg(OH)X \stackrel{H_2O}{\Leftarrow}$

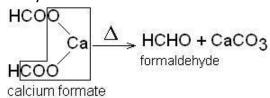
aldehyde

CH₃- C
$$\equiv$$
 N + RMgX \longrightarrow CH₃ - C \equiv N - MgX R
O
CH₃- C \equiv R + NH₃ + Mg(OH)X \rightleftharpoons H₂O

- 5. From carboxylic acids
 - (i) Catalytic decomposition of carboxylic acid.

$$\begin{array}{c} \text{HCOOH} + \text{HCOOH} \\ \hline \text{formic acid} \\ \\ \text{CH_3COOH} + \text{HOOCH_3} \\ \hline \text{acetic acid} \\ \end{array} \xrightarrow{\begin{array}{c} \text{MnO, } 300^{\circ}\text{C} \\ \text{Al}_2\text{O}_3, 400^{\circ}\text{C} \\ \end{array}} \xrightarrow{\begin{array}{c} \text{O} \\ \text{II} \\ \text{Al}_2\text{O}_3, 400^{\circ}\text{C} \\ \end{array}} \xrightarrow{\begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{acetone} \\ \end{array}}$$

(ii) From calcium salt of carboxylic acids



$$\begin{array}{c} \text{CH}_3\text{COO} \\ \text{CH}_3\text{COO} \\ \text{CH}_3\text{COO} \\ \end{array} \rightarrow \begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \text{acetone} \\ + \text{CaCO}_3 \\ \end{array}$$

- 6. From derivatives of carboxylic acids
 - (i) Reduction of acid chlorides (Rosenmund's reaction)

- 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.

2CH₃ - C - CI + (CH₃)₂Cd
$$\longrightarrow$$

CH₃ - C - CH₃ + CdCl₂

acetone

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxy aluminium hydride, LiAlH $[OC(CH_3)_3]$

(iii) Reduction of esters

7. From gem-dihalides by hydrolysis

CI
$$\xrightarrow{-2\text{NaCl}}$$
 OH

R - CH $+ 2\text{NaOH} \longrightarrow \text{R} - \text{CH}$
 $H_2\text{O} + \text{R} - \text{CHO}$

CI OH

R - C - R + 2NaOH $\xrightarrow{-2\text{NaCl}}$ R - C - R

CI OH

 $H_2\text{O} + \text{R} - \text{C} - \text{R}$

- 8. From nitriles by reduction
 - (i) Stephen's reduction.

$$R - C \equiv N \xrightarrow{SnCl_2 + HCl} R - C = NH2Cl$$

$$R - C \equiv N \xrightarrow{Aldimine hydrochloride} O$$

$$R - C - H + 2NH4Cl$$

(ii) Reduction with LiAlH₄

R-C
$$\equiv$$
 N+ LiAlH₄ \longrightarrow (R-CH = N)₃Al

RCHO $\stackrel{2H_2O}{\leftarrow}$

R-C \equiv N+ LiAlH₄ \longrightarrow (R-CH = N)₃Al

RCHO $\stackrel{2H_2O}{\leftarrow}$

RCHO $\stackrel{2H_2O}{\leftarrow}$

9. Preparation of aromatic carbonyl compounds.

(i)

This is known as Etard reaction

(ii) By side chain chlorination followed by hydrolysis

(iii) Gatterman – Koch reaction

(iv) Friedel Craft Acylation

benzophenone

(v) Reimer – Tiemann reaction

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 aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell
 - 2. Boiling point
- Boiling point of aldehyde 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 attributed to reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipoledipole interaction

- 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 C₄) 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

$$H$$
 $C = O$ > CH_3 $C = O$ > CH_3 $C = O$ CH3 formaldehyde acetaldehyde acetone

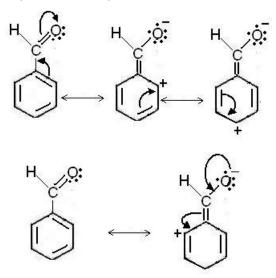
$$C_2H_5$$
 $C = 0$ C_2H_5 $C = 0$ C_2H_5 $C = 0$ C_2H_5 $C = 0$ C_2H_5 Ethyl methyl ketone Diethyl ketone

(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 hinderance, to the attacking group.
 This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is

(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 bezene 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

CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

$$C = O + Nu^{-} \Longrightarrow C = O + Nu^{-} \Longrightarrow C \longrightarrow OH$$

$$C = O + Nu^{-} \Longrightarrow C \longrightarrow OH$$

$$Nu^{-} \Longrightarrow C \longrightarrow OH$$

In this reaction carbon atom of carbonyl group changes from sp² to sp³ hybridised

(i) Addition of hydrogen cyanide (HCN)

$$\begin{array}{c} R \\ C = O + HCN \\ \hline R \\ \hline \\ CN \\ \hline \\ cyanohyrin \\ \end{array}$$

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

$$\begin{array}{c}
\delta^{+} & \delta^{-} \\
C = O & + CN
\end{array}$$

$$\begin{array}{c}
CN \\
C = O$$

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

$$C = O + H + \frac{\text{from H}_{2O}}{\text{or HCN}}$$

$$C = OH$$

$$C = OH$$

$$C = OH$$

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.

$$C = O + SO_2$$

+ NaCl + H₂O
OH
 $C = O + Na_2SO_3 + H_2O$

(iii) Addition of Grignard reagent

$$\begin{array}{c}
\delta^{+} & \delta^{-} \\
C = O + R - MgX \longrightarrow \begin{bmatrix}
C & R \\
O & Mg^{\dagger}X
\end{bmatrix}$$
adduct
$$\begin{array}{c}
Mg & + & C & HOH, H^{+} \\
OH & OH
\end{array}$$

Formaldehyde form a primary alcohol

$$\begin{array}{c} O \\ \parallel \\ H - C - H + RMgI \xrightarrow{ether} R - C - OMgI \xrightarrow{H_2O \atop H^+} RCH_2OH + Mg \\ H \end{array} \begin{array}{c} OH \\ Primary \\ alcohol \end{array}$$

Higher aldehydes give secondary alcohol

$$\begin{array}{c} O \\ \parallel \\ R - C - H + R'MgI \xrightarrow{ether} R - C - OMgI \xrightarrow{H_2O} \\ R' \\ R' \\ \\ RCH_2OR' + Mg \\ \\ Secondary \\ alcohol \\ \end{array}$$

Ketone give tertiary alcohols

(iv) Addition of alcohols

$$R = O + R'OH \longrightarrow R OR' R'OH OR' Hemiacetal ROR' Acetal OR'$$

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

$$\begin{array}{c} R \\ C = O + HC (OC_2H_5)_3 \longrightarrow \\ \begin{array}{c} R \\ \text{ethyl ortho} \\ \text{formate} \end{array} \\ \begin{array}{c} R \\ OC_2H_5 \\ R \\ OC_2H_5 \end{array} + HCOOC_2H_5 \end{array}$$

(v) Addition of ammonia derivative

Z = OH, NH_2 , NHC_6H_5 , $NHCOCH_2$ 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.

$$C = \ddot{O} + H^{\dagger}$$

$$\begin{bmatrix} c = \dot{O} + \dot{O} \\ c = \ddot{O} \end{bmatrix}$$

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

Step III : The unstable intermediate loses a proton, H⁺ and water molecule to form stable product (imines)

(vi) Addition of alkynes

$$H$$
 $C = O + RC \equiv CH \xrightarrow{RO^{-}} H$ $C \equiv CR$

This reaction is also known as ethinylation

2. Reduction reactions

I. Catalytic reduction to alcohol

R
$$C = O + H_2 \xrightarrow{Ni, Pt \text{ or } Pd} R - CH_2 - OH$$
 1° alcohol

R'
$$R = O + H_2 \xrightarrow{Ni, Pt \text{ or Pd}} R'$$

$$R = CH - OH$$

$$R_{2^{O} \text{ alcohol}}$$

II. Clemmensen reduction

$$C = O + 4 [H] \xrightarrow{Zn - Hg, HCI} CH_2 + H_2O$$

$$CH_3CHO + 4 [H] \xrightarrow{Zn - Hg, HCI} CH_3CH_3 + H_2O$$

$$ethane$$

$$CH_3 CH_3 CH_3 + H_2O$$

$$ethane$$

$$CH_3 CH_3 CH_3 + H_2O$$

$$CH_3 CH_3 CH_3 + H_2O$$

$$CH_3 CH_3 CH_3 CH_3 CH_3$$

$$CH_2 + H_2O$$

$$CH_3 CH_3 CH_3$$

$$CH_3 CH_3$$

$$CH_3$$

$$CH_3 CH_3$$

$$CH_3$$

III. Wolf-Kishner reduction

R
$$C = O + NH_2 - NH_2 \longrightarrow C = NNH_2 \xrightarrow{KOH} N2 + R-CH_2 - R$$
 $CH_3CHO + NH_2 - NH_2 \longrightarrow CH_3 - CH = NNH_2$
 $CH_3 - CH_3 - CH_3 \xrightarrow{KOH} CH_3 - CH_3 - CH_3 \xrightarrow{KOH} CH_3 - CH_3 \xrightarrow{KOH} CH_3 - CH_3 \xrightarrow{EH_3 - EH_3 - E$

CH₃COCH₃
$$\frac{\text{NH}_2-\text{NH}_2 + \text{KOH}}{\text{ethylene glycol}} > \text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$$

IV. Reduction with HI + P (red)

CH₃ - CHO + 4HI
$$\xrightarrow{\text{red P}}$$
 CH₃-CH₃ + H₂O + 2I₂
CH₃COCH₃ + 4HI $\xrightarrow{\text{red P}}$ CH₃ - CH₂ - CH₃ + H₂O + 2I₂

V. Reduction to pinacols

3. Oxidation reactions

i. Oxidation with mild oxidizing agents

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen'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.

RCHO + 2 [Ag (NH₃)₂]⁺ + 30H⁻
$$\longrightarrow$$

RCOO⁻ + 2Ag \downarrow + 4NH₃ + 2H₂O
silver mirror

(b) Reduction of Fehling's solution

Fehling's solution is an alkaline solution of CuSO₄ mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduces cupric ion (Cu²⁺) of Fehling's solution to cuprous ions (Cu⁺) to form red precipitate of cuprous oxide

$$RCHO + 2Cu_2^+ + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$$

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

ii. Oxidation with strong oxidizing agent

RCHO + [O]
$$\longrightarrow$$
 RCOOH

aldehyde carboxylic acid

CH3 - C - CH3 + 3 [O] \longrightarrow CH3COOH + HCOOH

iii. Haloform reaction

4. Condensation reactions

(1) Aldol condensation

CH₃ - C - H + H - CH₂ - C - H
$$\stackrel{\text{dil NaOH}}{\longrightarrow}$$
 CH₃ - CH - CH₂ - CHO acetaldehyde 3 - hydroxy butanal $\begin{vmatrix} -H_2O \\ \Delta \end{vmatrix}$

CH₃ - CH = CH - CHO But - 2 - enal OH O CH₃ - C - CH₃ + H - CH₂ - C - CH₃ $\stackrel{\text{Ba(OH)}_2}{\longrightarrow}$ CH₃ - C - CH₂ - C - CH₃

CH₃ O - CH₃ - C - CH₃ $\stackrel{\text{CH}_3}{\longrightarrow}$ CH₃ O - H₂O CH₃ - C = CH - C - CH₃

Mechanism

HO + H - CH₂ - C - H
$$\rightleftharpoons$$
 CH₂ = C - H \rightleftharpoons CH₂ = C - H \rightleftharpoons carbanion Enolate ion + H₂O

CH₃ - C + :CH₂ - C - H
$$\rightleftharpoons$$
 CH₃ - C - CH₂ - C - H

H

OH

CH₃ - C - CH₂ - C - H

H

H

OH

CH₃ - C - CH₂ - CHO + OH

Aldehyde or ketones which do not contain α -hydrogen atom like formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation.

(2) Cross aldol condensation CH3 -CHO + CH3 - CH2- CHO (A) (B) dil. NaOH CH3 - CH = CH - CHO + CH3 - CH2 - CH = C - CHO But-2-en-1-al CH3 2-methylpent-2en-1-al + CH3 - CH = C - CHO CH3 2-methyl but - 2-en-1-al + CH3 - CH2- CH3 - CH = CH - CHO

A- A Condensation

O
$$\alpha$$
 dil. NaOH α CH3 - CH - CH2 - CHO \rightarrow CH3 - CH - CH2 - CHO \rightarrow CH3 - CH - CH2 - CHO \rightarrow CH3 - CH = CH - CHO \rightarrow But-2-en-1-al

pent-2-en-1-al

B-B Condensation

CH₃ - CH₂ - CH = O + CH₃ - CH₂ - CH = O
$$\xrightarrow{\text{dil. NaOH}}$$
 OH

CH₃ - CH₂ - CH - CH - CHO

CH₃

$$\downarrow - \text{H}_2\text{O}$$
CH₃ - CH₂ - CH= C - CHO

CH₃

$$2\text{-methylpent-2-en-1-al}$$

A-B Condensation

CH₃ - C - H + CH₂ - CHO
$$\xrightarrow{\text{dil NaOH}}$$
 CH₃ - CH - CH - CHO $\xrightarrow{\text{CH}_3}$ CH₃ - CH₂O

CH₃ - CH = C - CHO $\xrightarrow{\text{CH}_3}$ CH₃

2-methyl but - 2-en-1-al

B-A Condensation

$$\begin{array}{c} \text{O} \\ \text{H} \\ \text{CH}_3\text{-CH}_2\text{-C-H} + \text{H-CH}_2\text{-CHO} \xrightarrow{\text{dil NaOH}} \\ \text{OH} \\ \text{CH}_3\text{-CH}_2\text{-CH-CH}_2\text{-CHO} \\ \Delta \downarrow^{-\text{H}_2\text{O}} \\ \text{CH}_3\text{-CH}_2\text{-CH} = \text{CH}\text{-CHO} \\ \text{pent-2-en-1-al} \end{array}$$

(3) Claisen – Schmidt condensation

$$C_{6}H_{5} - C - CH_{3} - C - CH_{3} \xrightarrow{\text{dil NaOH}}$$

$$C_{6}H_{5} - CH - CH_{2} - C - CH_{3}$$

$$C_{6}H_{5} - CH - CH_{2} - C - CH_{3}$$

$$C_{6}H_{5} - CH - C - CH_{3} + H_{2}O$$

$$C_{6}H_{5} - CH - C - CH_{3} + H_{2}O$$

$$C_{6}H_{5} - CH - C - CH_{3} + CH_{4}O$$

$$C_{6}H_{5} - CH_{5} - CH_{5}O$$
Dibenzal acetone

5. Cannizzaro reaction

Mechanism

Step I: The OH⁻ ion attacks the carbonyl carbon to form hydroxyl alkoxide

$$C_6H_5 - C + OH \xrightarrow{fast} C_6H_5 - C - OH H$$

Step II: Anion (I) acts as hybride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer H⁺ to acquire stability.

C6H5 - C - OH + C - C6H5
$$\xrightarrow{\text{hydride}}$$
 C6H5 - C - OH + C - C6H5 $\xrightarrow{\text{transfer}}$ C6H5 - C - OH + H - C - C6H5 $\xrightarrow{\text{H}}$ C6H5 - C - O $\xrightarrow{\text{salt of benzoic acid}}$ C6H5 - C - O $\xrightarrow{\text{benzyl alcohol}}$

6. Reaction with chloroform

$$CH_3$$
 CH_3 CCI_3
 CH_3 CCI_3
 CH_3 CH_3 CH_3
 CH_3 CH_3 CH_3 CH_3 CH_3

Chloretone is used as hypnotic.

7. Reaction with primary amine

$$RCHO + H_2 NR' \xrightarrow{H^{\dagger}} RCH = NR' + H_2O$$
schiff's base

8. Electrophilic substitution reaction of aromatic carbonyl compounds

CH= O

$$+ Br_2 \xrightarrow{anhyd. AlCl_3}$$

Benzaldehyde

CH= O

 $+ HNO_3 \xrightarrow{conc. H_2SO_4}$

CH= O

 $+ HNO_3 \xrightarrow{conc. H_2SO_4}$
 $+ H_2SO_4(conc.)$

CH= O

 $+ H_2SO_4(conc.)$

Benzaldehyde

USES OF ALDEHYDES AND KETONES

- (a) Uses of formaldehyde
 - The 40% solution of formaldehyde in water (formaline) 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