Aldehydes, Ketones & Carboxylic Acids

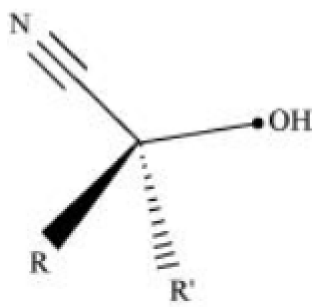
Q. 1. What is meant by the following terms? Give an example of the reaction in each case.

(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone (iv) Aldol
(v) Hemiacetal (vi) Oxime (vii) Ketal (viii) Imine
(ix) 2, 4-DNP-derivative (x) Schiff's base

ANSWER:-

(i) Cyanohydrin:

Cyanohydrins are a class of organic compounds with the general formula RR′C(OH)CN, where R and R′ can be either alkyl or aryl groups.

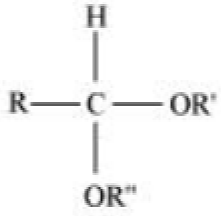


Aldehydes and ketones react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide (NaCN) acting as a catalyst to form cyanohydrins. These reactions are referred to as cyanohydrin reactions. Cyanohydrins are useful synthetic intermediates

$$RR'C = O + HCN \xrightarrow{NaCN} RR'C(OH)CN$$

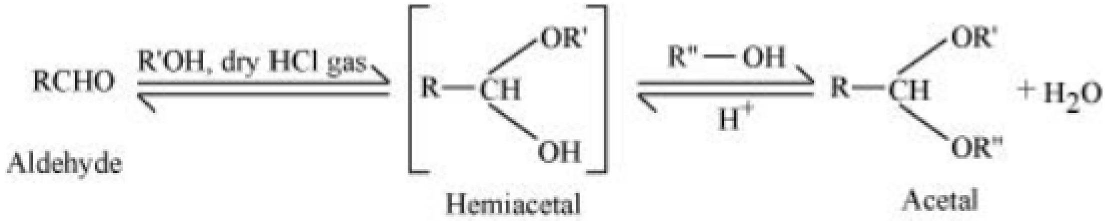
Ketone Cyanohydrin

(ii) Acetal: Acetals are geminal dialkoxy alkanes where two alkoxy groups are attached to the same carbon atom. One of these bonds is linked to an alkyl group, while the other is connected to a hydrogen atom.



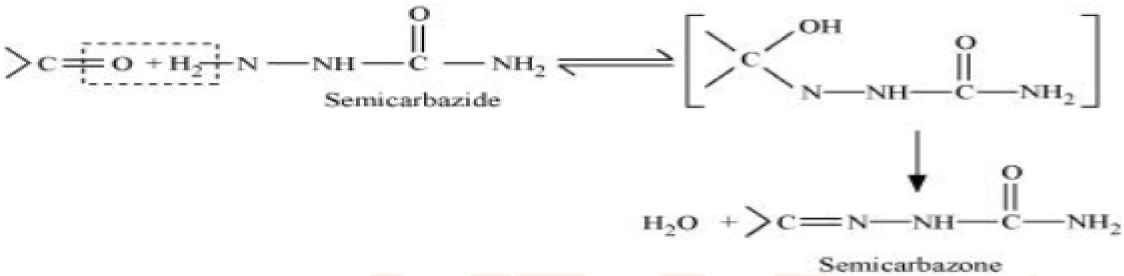
General structure of an acetal

When aldehydes react with two equivalents of a monohydric alcohol in the presence of dry HCl gas, they first form hemiacetals. These hemiacetals then react with an additional molecule of alcohol to produce an acetal.



(iii) Semicarbazone

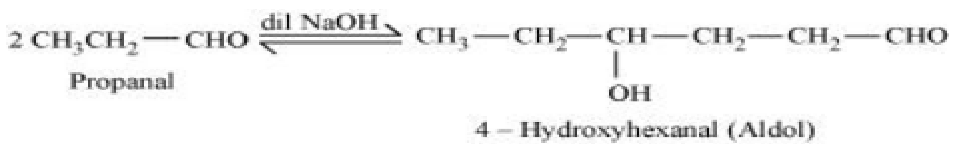
Semicarbazones are compounds derived from aldehydes and ketones, formed through a condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazones are valuable for the identification and characterization of aldehydes and ketones.

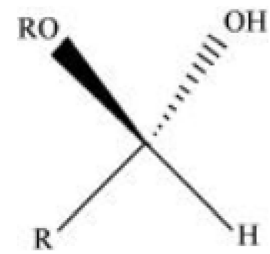
(iv) Aldol

A β-hydroxy aldehyde or ketone is referred to as an aldol. It is formed through a condensation reaction between two molecules of the same aldehyde or ketone, or one molecule of each of two different aldehydes or ketones, in the presence of a base.

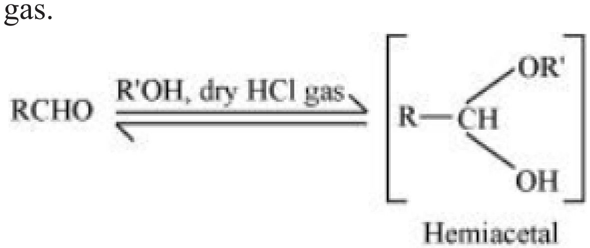


(v) Hemiacetal

Hemiacetals are α-alkoxy alcohols.

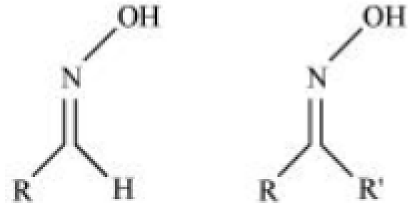


A hemiacetal forms when an aldehyde reacts with one molecule of a monohydric alcohol in the presence of dry HCl gas.



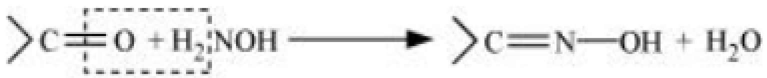
(vi) Oxime

Oximes are a group of organic compounds with the general formula RR′CNOH, where R is an organic side chain and R′ can be either hydrogen or an organic side chain. When R′ is hydrogen, the compound is called an aldoxime, and when R′ is an organic side chain, it is referred to as a ketoxime.



Aldoxime Ketoxime

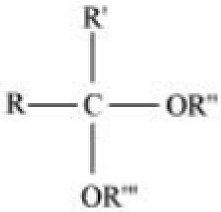
Aldehydes or ketones form oximes when treated with hydroxylamine in a weakly acidic medium.



Hydroxylamine

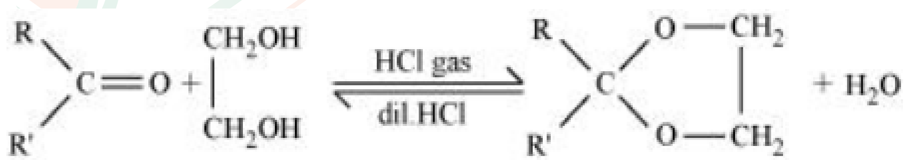
(vii) Ketal

Ketals are gem-dialkoxyalkanes where two alkoxy groups are attached to the same carbon atom in the chain, with the other two bonds of the carbon connected to two alkyl groups.



General structure of a ketal

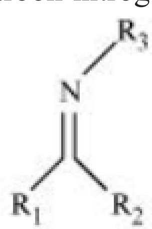
Ketones react with ethylene glycol in the presence of dry HCl gas to form a cyclic compound called ethylene glycol ketal.



Ketane Ethylene glycol Ethylene glycol ketal

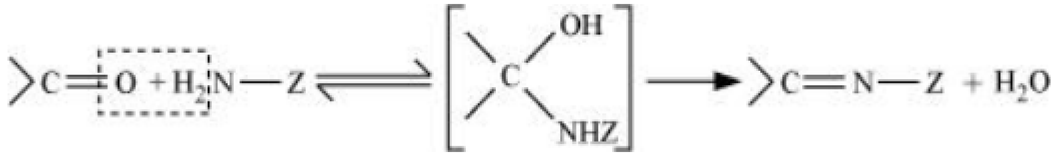
(viii) Imine

Imines are compounds that contain a carbon-nitrogen double bond.



General structure of an imine

Imines are formed when aldehydes and ketones react with ammonia or its derivatives.



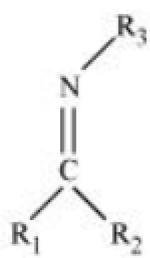
(ix) 2, 4−DNP−derivative

2, 4-Dinitrophenylhydrazones are 2, 4-DNP derivatives formed when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in a mildly acidic medium.

2, 4-DNP derivatives are used to identify and characterize aldehydes and ketones.

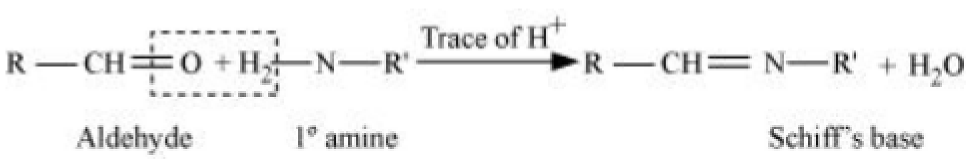
(x) Schiff's base

Schiff's base (or azomethine) is a compound featuring a carbon-nitrogen double bond, where the nitrogen atom is bonded to an aryl or alkyl group, but not hydrogen. They have the general formula $R_1R_2C = NR_3$.



General structure of schiff's base

Aldehydes and ketones react with primary aliphatic or aromatic amines in the presence of a small amount of acid to form a Schiff's base.



Q. 2. Name the following compounds according to IUPAC system of nomenclature:

(i) $CH_3CH(CH_3)CH_2CH_2CHO$

(ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$

(iii) $CH_3CH = CHCHO$

(iv) $CH_3COCH_2COCH_3$

(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$

(vi) $(CH_3)_3CCH_2COOH$

(vii) $OHCC_6H_4CHO$-p

ANSWER:-

(i) 4-methylpentanal

(ii) 6-Chloro-4-ethylhexan-3-one

(iii) But-2-en-1-al

(iv) Pentane-2,4-dione

(v) 3,3,5-Trimethylhexan-2-one

(vi) 3,3-Dimethylbutanoic acid

(vii) Benzene-1,4-dicarbaldehyde

Q. 3. **Draw the structures of the following compounds.**

(i) 3-Methylbutanal

(ii) p-Nitropropiophenone

(iii) p-Methylbenzaldehyde

(iv) 4-Methylpent-3-en-2-one

(v) 4-Chloropentan-2-one

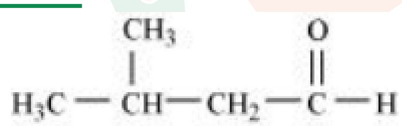
(vi) 3-Bromo-4-phenylpentanoic acid

(vii) p,p'-Dihydroxybenzophenone

(viii) Hex-2-en-4-ynoic acid.

ANSWER:-

(i)



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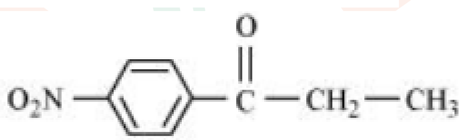

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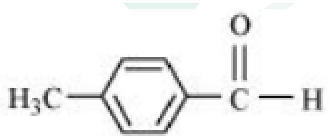

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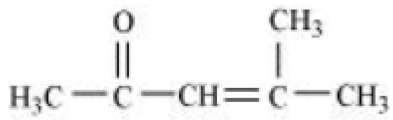

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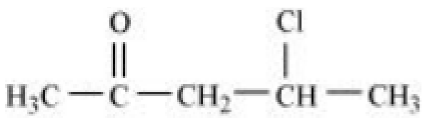

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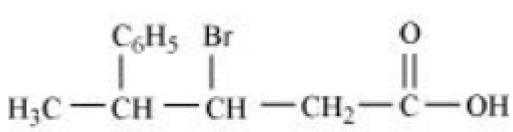

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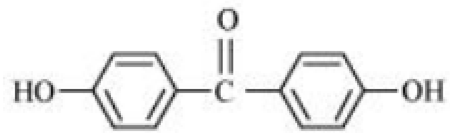

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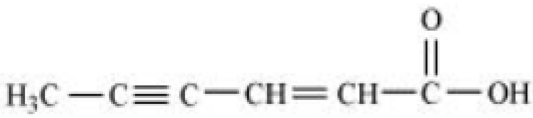
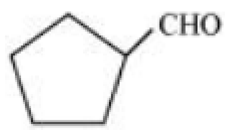


Q. 4. **Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.**

(i) $CH_3CO(CH_2)_4CH_3$
(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$
(iii) $CH_3(CH_2)_5CHO$
(iv) Ph-CH = CH-CHO
(v)



(vi) PhCOPh

ANSWER:-

Here is the information arranged in tabular form:

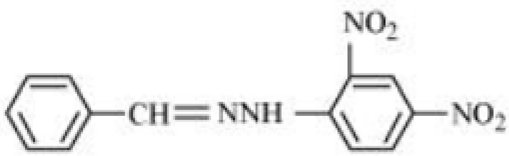
Compound	IUPAC Name	Common Name
(i) $CH_3CO(CH_2)4CH_3$	Heptan-2-one	Methyl n-propyl ketone
(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$	4-Bromo-2-methylhexanal	γ-Bromo-α-methyl-caproaldehyde
(iii) $CH_3(CH_2)_5CHO$	Heptanal	-
(iv) Ph-CH=CH-CHO	3-Phenylprop-2-enal	β-Phenylacrolein
(v) 	Cyclopentanecarbaldehyde	-
(vi) PhCOPh	Diphenylmethanone	Benzophenone

Q. 5. **Draw structures of the following derivatives.**

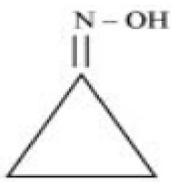
(i) The 2, 4-dinitrophenylhydrazone of benzaldehyde
(i) Cyclopropanone oxime
(i) Acetaldehydedimethylacetal
(i) The semicarbazone of cyclobutanone
(i) The ethylene ketal of hexan-3-one
(i) The methyl hemiacetal of formaldehyde

ANSWER:-

(i)



(ii)



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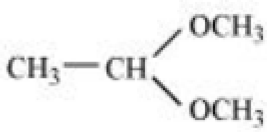

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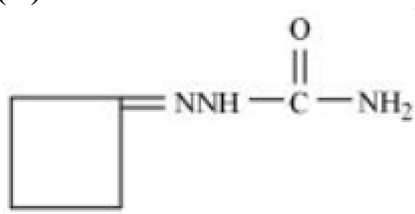

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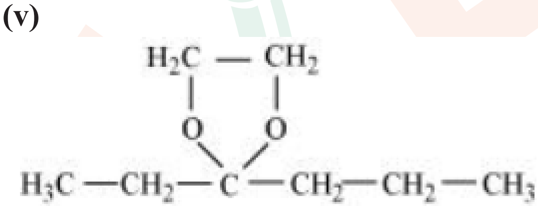

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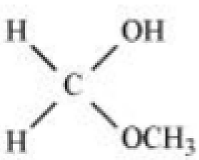


Q. 6. **Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.**

(i) **PhMgBr and then H_3O^+**

(ii) **Tollens' reagent**

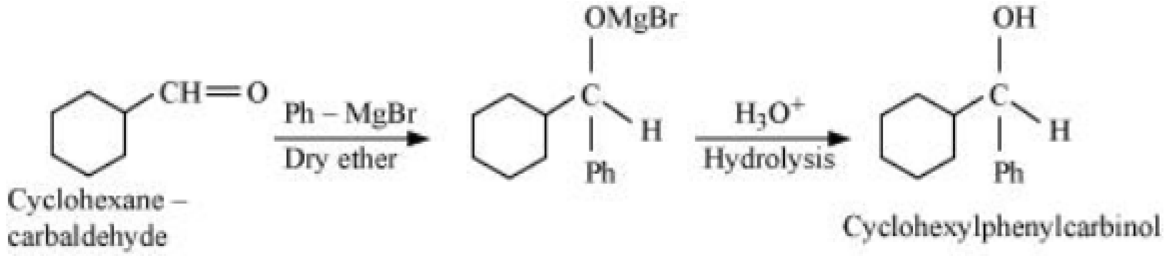
(iii) **Semicarbazide and weak acid**

(iv) **Excess ethanol and acid**

(v) **Zinc amalgam and dilute hydrochloric acid**

ANSWER:-

(i)



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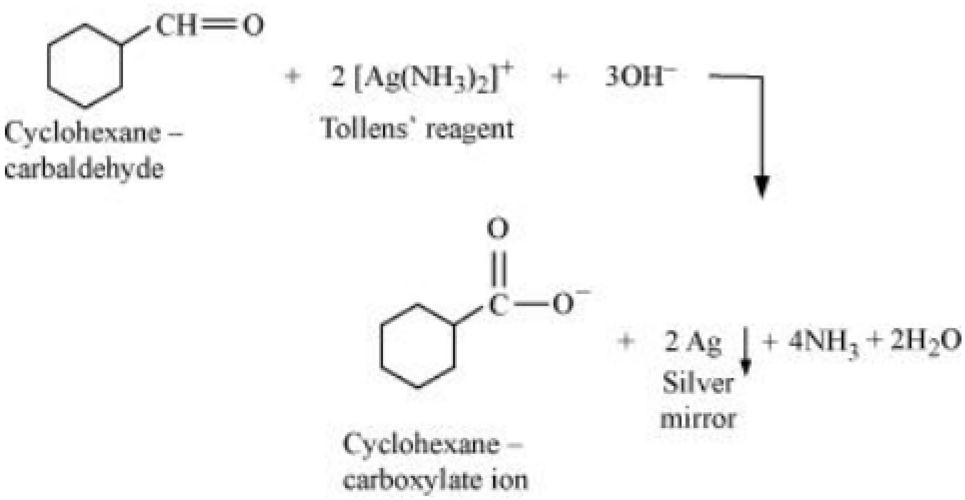

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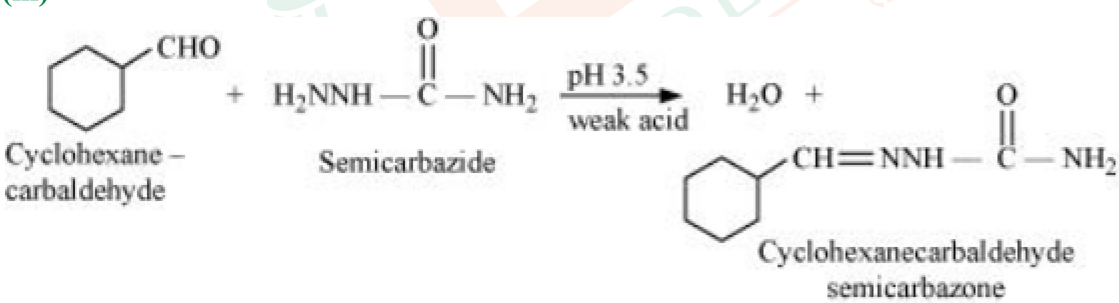

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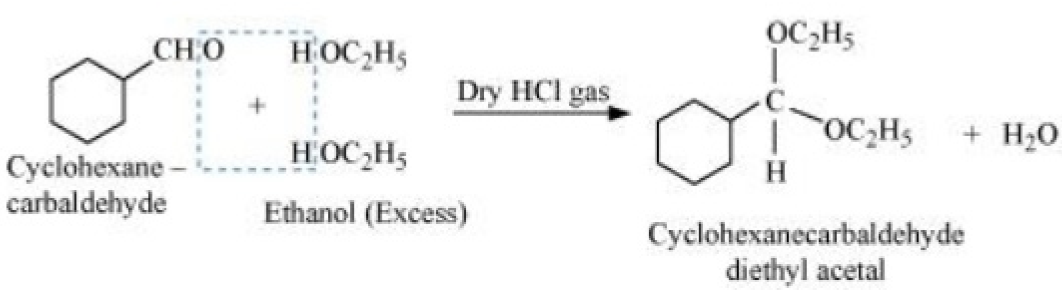

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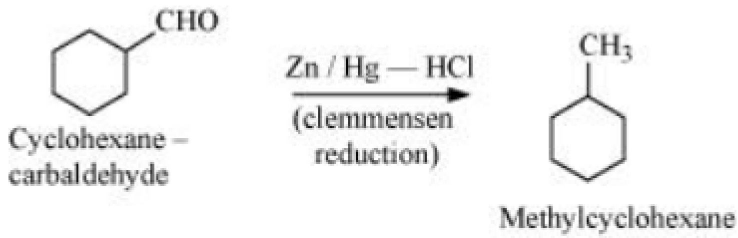


Q. 7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal
(ii) 2-Methylpentanal
(iii) Benzaldehyde
(iv) Benzophenone
(v) Cyclohexanone
(vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde
(viii) Butan-1-ol
(ix) 2, 2-Dimethylbutanal.

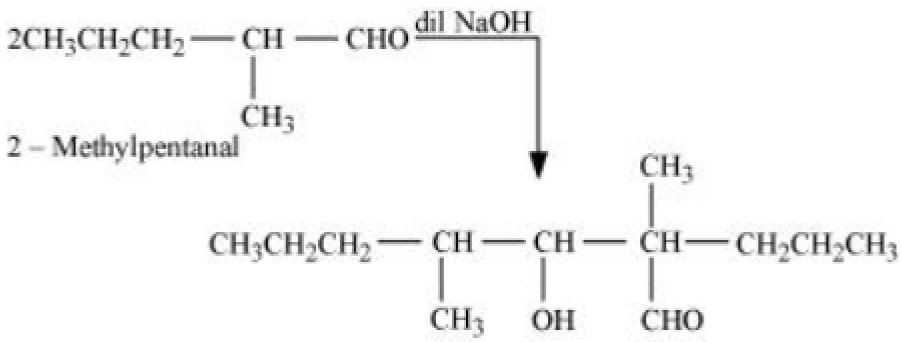
ANSWER:-

Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation
Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions.

Compound	Type of Reaction	Reason
(i) Methanal	Cannizzaro Reaction	No α-hydrogen present
(ii) 2-methylpentanal	Aldol Condensation	Contains α-hydrogen
(iii) Benzaldehyde	Cannizzaro Reaction	No α-hydrogen present
(iv) Benzophenone	Neither Aldol nor Cannizzaro	No α-hydrogen present, ketone
(v) Cyclohexanone	Aldol Condensation	Contains α-hydrogen
(vi) 1-phenylpropanone	Aldol Condensation	Contains α-hydrogen
(vii) Phenylacetaldehyde	Aldol Condensation	Contains α-hydrogen
(viii) Butan-1-ol	Neither Aldol nor Cannizzaro	Alcohol, does not undergo these reactions
(ix) 2, 2-dimethylbutanal	Cannizzaro Reaction	No α-hydrogen present

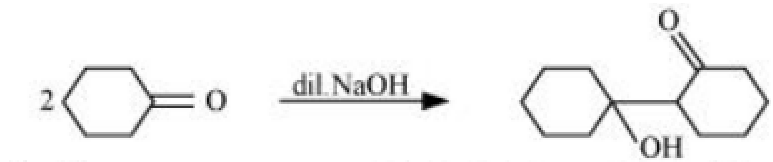
Aldol Condensation

(ii)



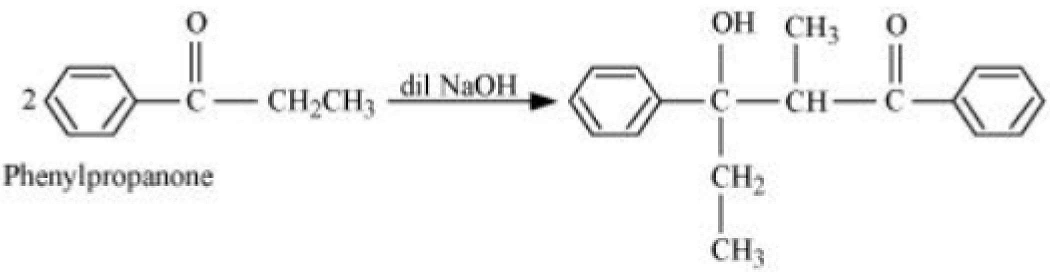
3 – Hydroxy –2, 4 – dimethyl – 2 – propylheptanal

(v)



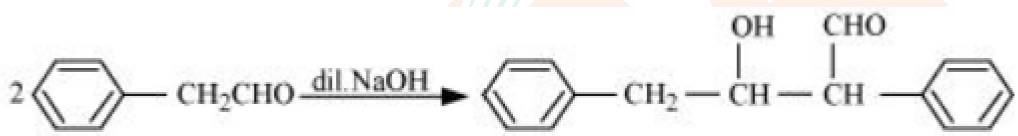
Cyclohexanone — 2 – (1 – Hydroxy – 1 – cyclohexyl) – cyclohexan –1– one

(vi)



1 – Phenylpropanone — 3 – Hydroxy – 2 – methyl – 1, 3 – diphenylpentan – 1 – one

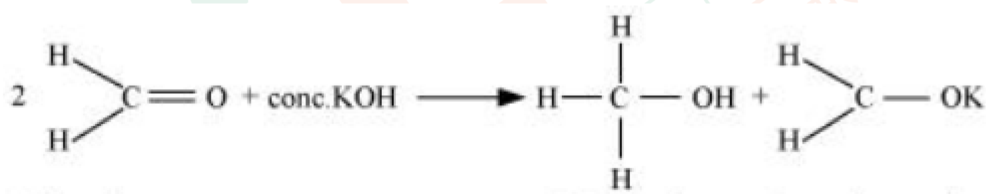
(vii)



Phenylacetaldehyde — 3 – hydroxy – 2, 4 – diphenylbutanal

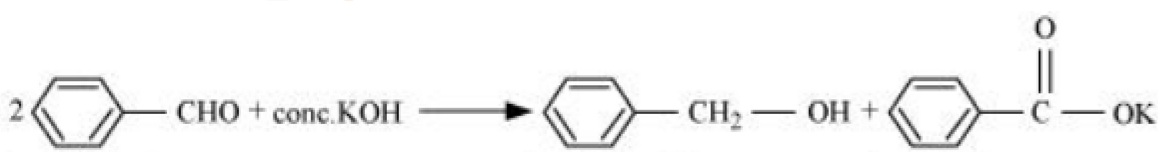
Cannizzaro reaction

(i)



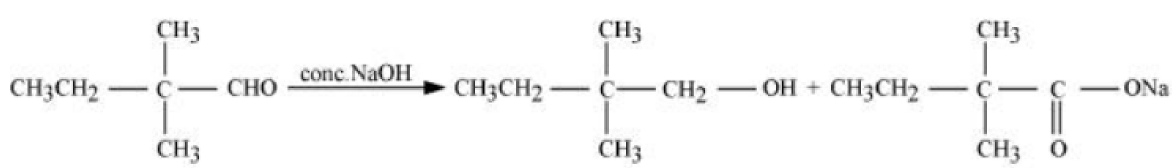
Methanal — Methanol — Potassium methanoate

(iii)



Benzaldehyde — Benzyl alcohol — Potassium benzoate

(ix)



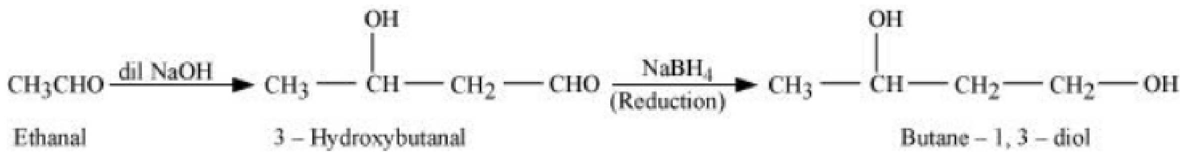
2, 2 – Dimethylbutanal — 2, 2 – Dimethylbutan – 1 – ol — Sodium 2, 2 – dimethylbutanoate

Q. 8. **How will you convert ethanal into the following compounds?**

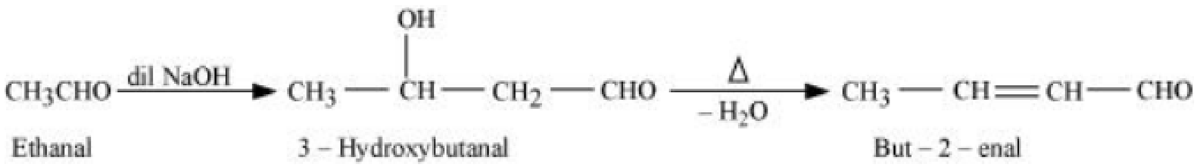
(i) **Butane-1, 3-diol** **(ii)** **But-2-enal** **(iii)** **But-2-enoic acid**

ANSWER:-

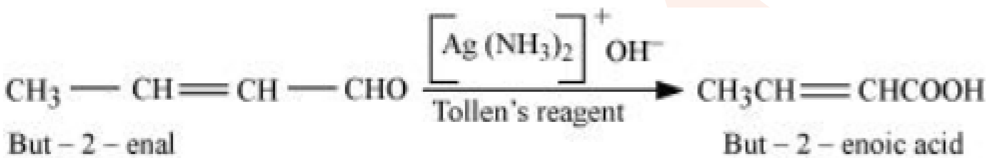
(i)



(ii)



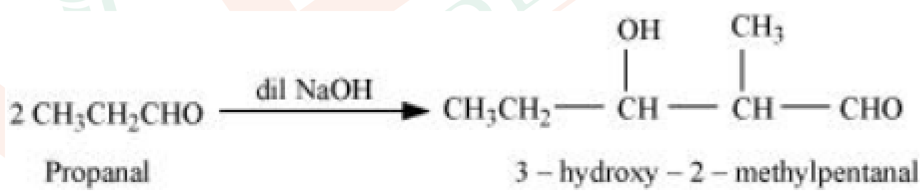
(iii)



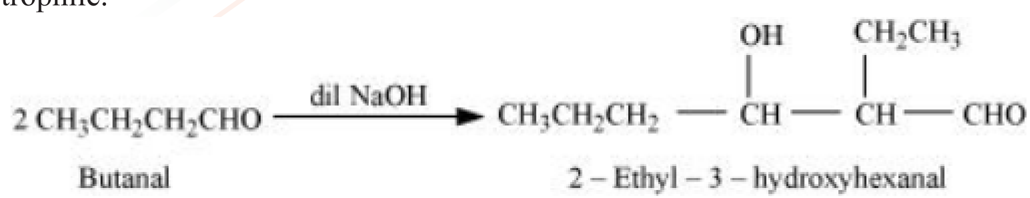
Q. 9. **Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.**

ANSWER:-

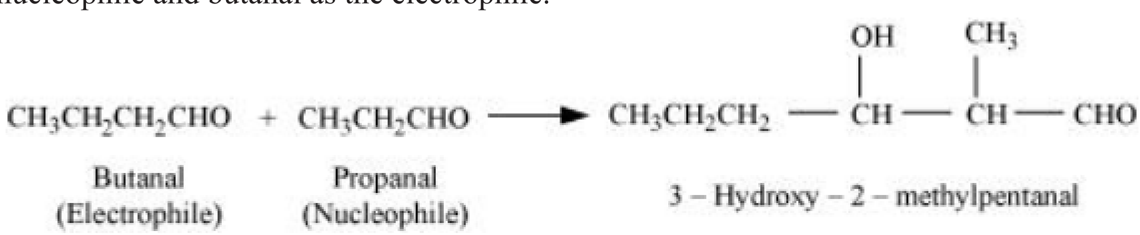
(i) Two molecules of propanal are used, with one acting as a nucleophile and the other as an electrophile.



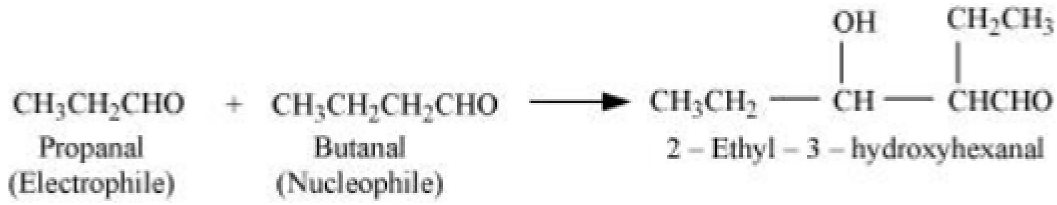
(ii) Two molecules of butanal are used, with one functioning as a nucleophile and the other as an electrophile.



(iii) One molecule of propanal and one molecule of butanal are used, with propanal acting as the nucleophile and butanal as the electrophile.



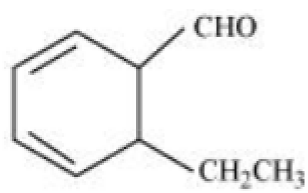
(iv) One molecule of propanal and one molecule of butanal are used, with propanal acting as the electrophile and butanal as the nucleophile.



Q. 10. **An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.**

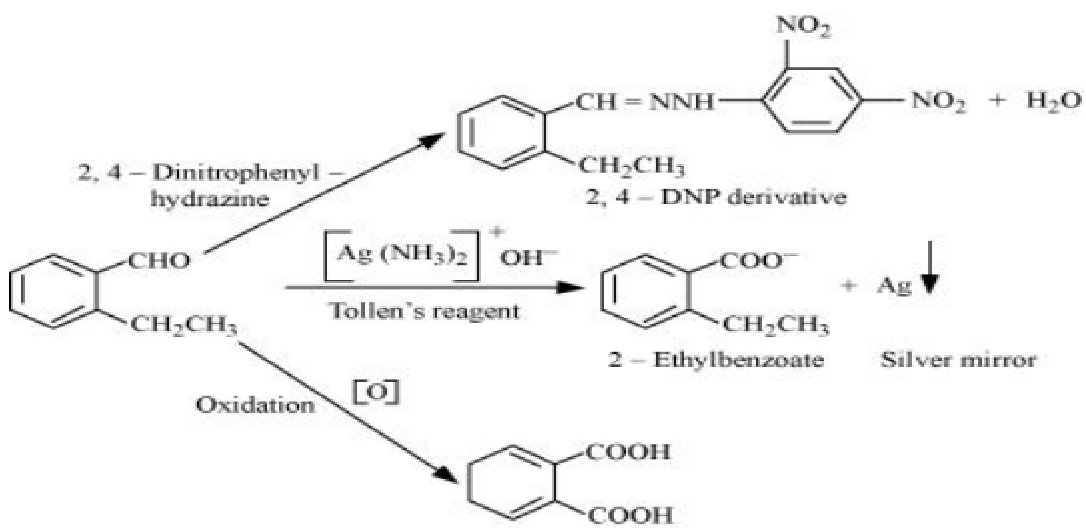
ANSWER:-

The compound, with the molecular formula $C_9H_{10}O$, forms a 2, 4-DNP derivative and reduces Tollen's reagent, indicating that it is an aldehyde. Additionally, the compound undergoes a Cannizzaro reaction and, upon oxidation, yields 1, 2-benzenedicarboxylic acid. This suggests that the −CHO group is directly attached to a benzene ring, and the benzaldehyde is ortho-substituted. Therefore, the compound is 2-ethylbenzaldehyde.



2 – Ethylbenzaldehyde

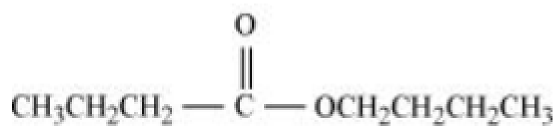
The following equations can explain the given reactions.



Q.11. **An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene.Write equations for the reactions involved.**

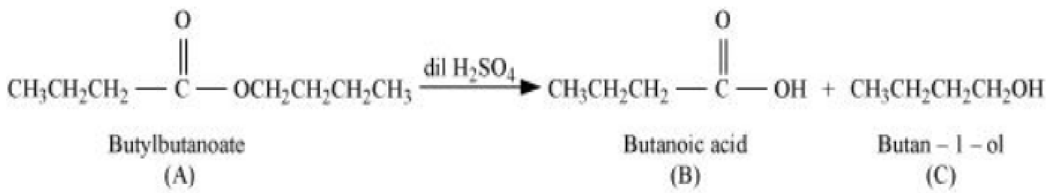
ANSWER:-

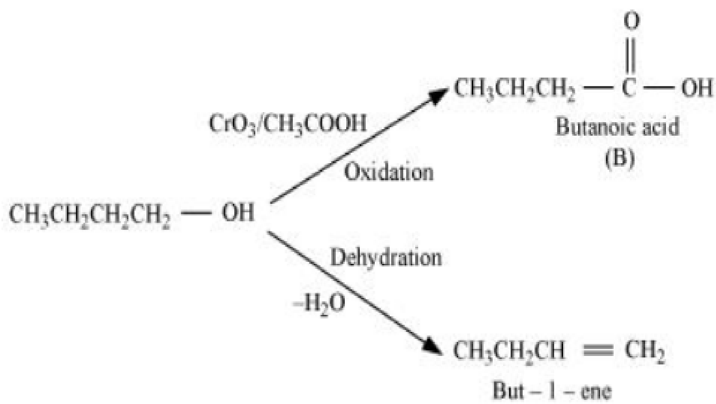
An organic compound A with molecular formula $C_8H_{16}O_2$ gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms. Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms. Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is of straight chain and hence, it is butan-1-ol. On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid. Hence, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.



Butylbutanoate

All the given reactions can be explained by the following equations.





Q. 12. **Arrange the following compounds in increasing order of their property as indicated:**

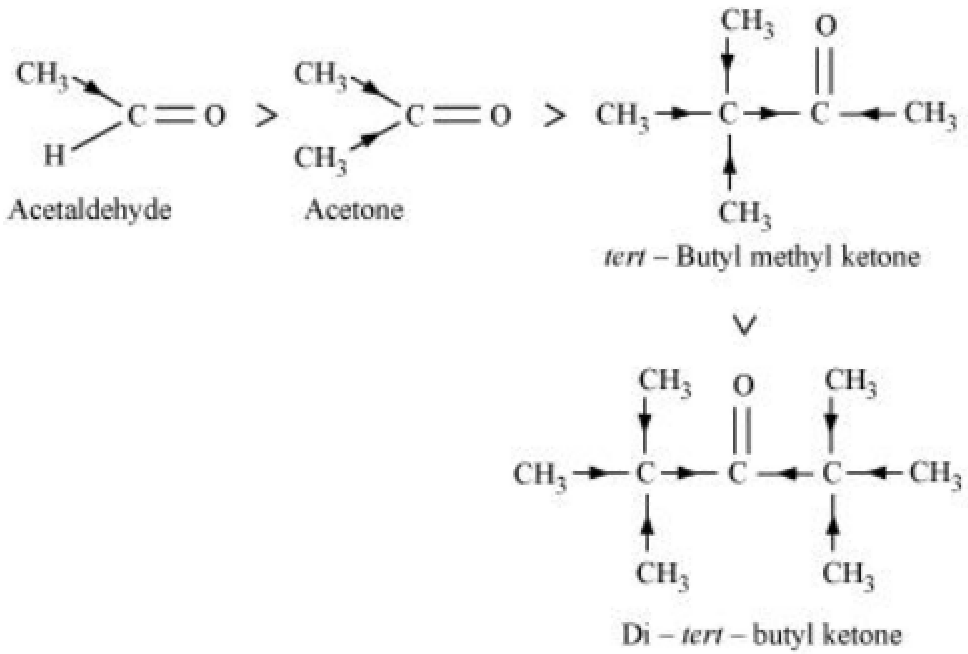
(i) **Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)**

(ii) **$CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)**

(iii) **Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)**

ANSWER:-

(i) When HCN reacts with a compound, the attacking species is the nucleophile, CN^-. As the negative charge on the compound increases, its reactivity with HCN decreases. In the given compounds, the +I effect increases, as shown below, and it can also be observed that steric hindrance increases correspondingly.



Therefore, the given compounds can be arranged in order of increasing reactivity toward HCN as follows: Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde.

(ii) When carboxylic acids lose a proton, they acquire a negative charge, as shown:

$$R-COOH \longrightarrow R-COO^- + H^+$$

Any group that helps stabilize the negative charge will enhance the stability of the carboxyl ion, thereby increasing the acid's strength. As a result, groups with a +I effect will reduce acid strength, while groups with a −I effect will increase it. In the given compounds, the $-CH_3$ group exerts a +I effect, while the Br^- group exerts a −I effect. Therefore, acids containing Br^- are stronger. Additionally, the +I effect of the isopropyl group is greater than that of the n-propyl group, making $(CH_3)_2CHCOOH$ a weaker acid than $CH_3CH_2CH_2COOH$. Furthermore, the −I effect weakens with increasing distance. Thus, $CH_3CH(Br)CH_2COOH$ is a weaker acid than $CH_3CH_2CH(Br)COOH$. The strengths of the given acids increase in the following order: $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$.

(iii) Electron-donating groups reduce the strength of acids, while electron-withdrawing groups enhance the strength of acids. Since the methoxy group is electron-donating, 4-methoxybenzoic acid is a weaker acid than benzoic acid. The nitro group, being electron-withdrawing, increases acid strength. Given that 3,4-dinitrobenzoic acid contains two nitro groups, it is slightly stronger than 4-nitrobenzoic acid. Therefore, the strengths of the given acids increase in the following order: 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

Q. 13. Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone
(ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid
(iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one
(vi) Benzaldehyde and Acetophenone
(vii) Ethanal and Propanal

ANSWER:-

(i) Propanal and propanone can be distinguished by the following tests.

(a) Tollen's test: Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But, propanone being a ketone does not reduce Tollen's reagent.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2\underset{\text{Tollen's reagent}}{\left[Ag(NH_3)_2\right]^+} + 3OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Fehling's test: Aldehydes respond to Fehling's test, but ketones do not. Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu_2O, but propanone being a ketone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2Cu^{2+} + 5OH^- \longrightarrow \underset{\text{Propanoateion}}{CH_3CH_2COO^-} + \underset{\text{Cuprous oxide (Red-brown ppt)}}{Cu_2O\downarrow} + 3H_2O$$

(c) Iodoform test: Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom respond to iodoform test. They are oxidized by sodium hypoiodite (NaOI) to give iodoforms. Propanone being a methyl ketone responds to this test, but propanal does not.

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Iodoform (yellow ppt)}}{CHI_3} + 2NaOH$$

(ii) Acetophenone and Benzophenone can be differentiated using the iodoform test. In the iodoform test, methyl ketones are oxidized by sodium hypoiodite to form a yellow precipitate of iodoform. Since acetophenone is a methyl ketone, it gives a positive result for this test, whereas benzophenone does not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\text{Sodium hypoiodite}}{3NaOI} \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Iodoform (yellowppt)}}{CHI_3} + 2NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

(iii) Phenol and benzoic acid can be distinguished by ferric chloride test. Ferric chloride test: Phenol reacts with neutral $FeCl_3$ to form an iron-phenol complex giving violet colouration.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Iron-phenol complex (Violet colour)}}{\left[Fe(OC_6H_5)_6\right]^{3-}} + 3H^+ + 3Cl^-$$

However, benzoic acid reacts with neutral $FeCl_3$ to form a buff-colored precipitate of ferric benzoate.

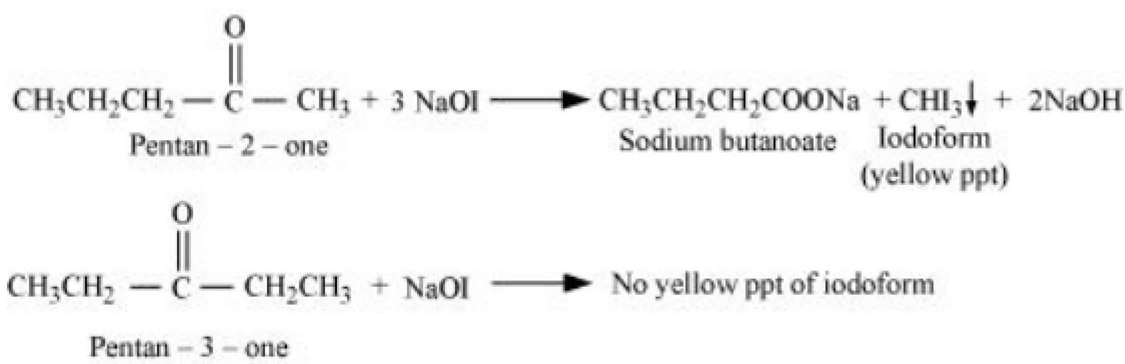
$$\underset{\text{Benzoic acid}}{3C_6H_5OH} + FeCl_3 \rightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt)}}}{(C_6H_5COO)_3\,Fe} + 3HCl$$

(iv) Benzoic acid and ethyl benzoate can be differentiated using the sodium bicarbonate test. In this test, acids react with $NaHCO_3$ to produce brisk effervescence due to the release of CO_2 gas. Benzoic acid, being an acid, gives a positive response, while ethyl benzoate does not.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \rightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + CO_2\uparrow + H_2O$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \rightarrow \text{ No effervescence due to evolution of } CO_2 \text{ gas}$$

(v) Pentan-2-one and pentan-3-one can be distinguished using the iodoform test. In this test, pentan-2-one, being a methyl ketone, gives a positive response. However, pentan-3-one, not being a methyl ketone, does not respond to the test.



(vi) Benzaldehyde and acetophenone can be distinguished using the following tests:

(a) Tollen's Test: Aldehydes react with Tollen's reagent. Benzaldehyde, being an aldehyde, reduces Tollen's reagent to form a red-brown precipitate of Cu_2O, whereas acetophenone, a ketone, does not react.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Tollen's reagent}}{2\left[Ag(NH_3)_2\right]^+} + 3OH^- \rightarrow \underset{\text{Benzoate ion}}{C_6H_5COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Iodoform test Acetophenone being a methyl ketone undergoes oxidation by sodium hypoiodite (NaOI) to give a yellow ppt. of iodoform. But benzaldehyde does not respond to this test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \rightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellowppt)}}}{CHI_3} + 2NaOH$$

(vii) Ethanal and propanal can be distinguished using the iodoform test. In this test, aldehydes and ketones with at least one methyl group attached to the carbonyl carbon respond positively. Ethanal, having a methyl group attached to the carbonyl carbon, gives a positive result. However, propanal lacks a methyl group attached to the carbonyl carbon, so it does not respond to the test.

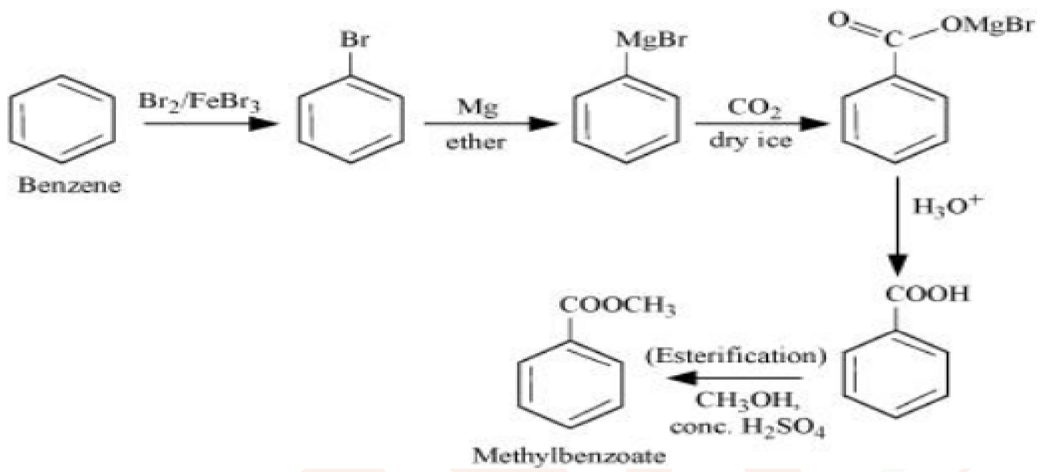
$$\underset{\text{Ethanal}}{CH_3CHO} + 3NaOI \rightarrow \underset{\substack{\text{Sodium}\\ \text{methanoate}}}{HCOONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2NaOH$$

Q. 14. **How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom**

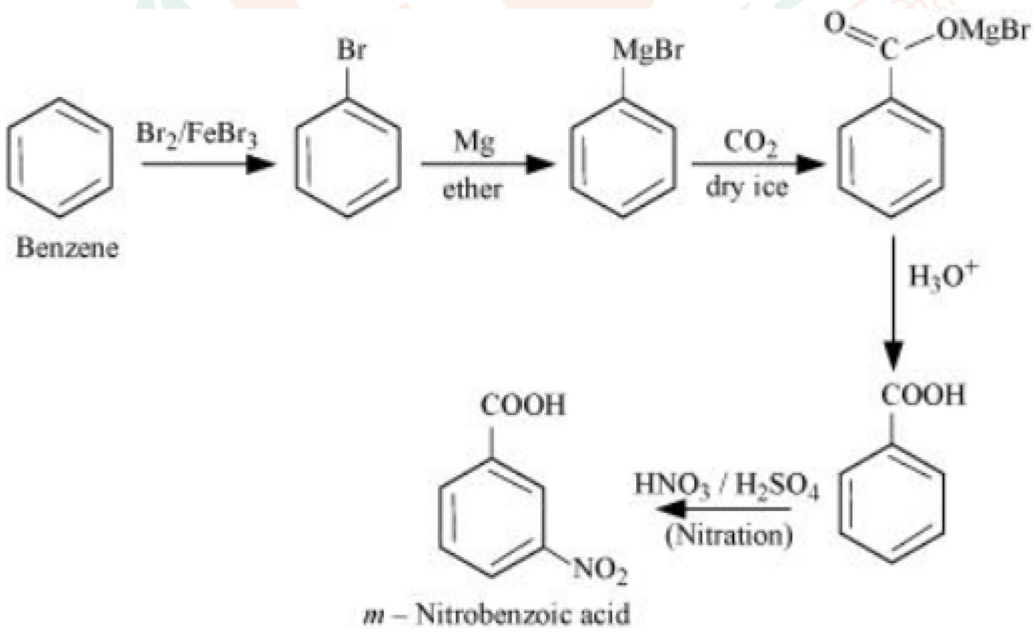
(i) **Methyl benzoate**
(ii) **m-Nitrobenzoic acid**
(iii) **p-Nitrobenzoic acid**
(iv) **Phenylacetic acid**
(v) **p-Nitrobenzaldehyde.**

ANSWER:-

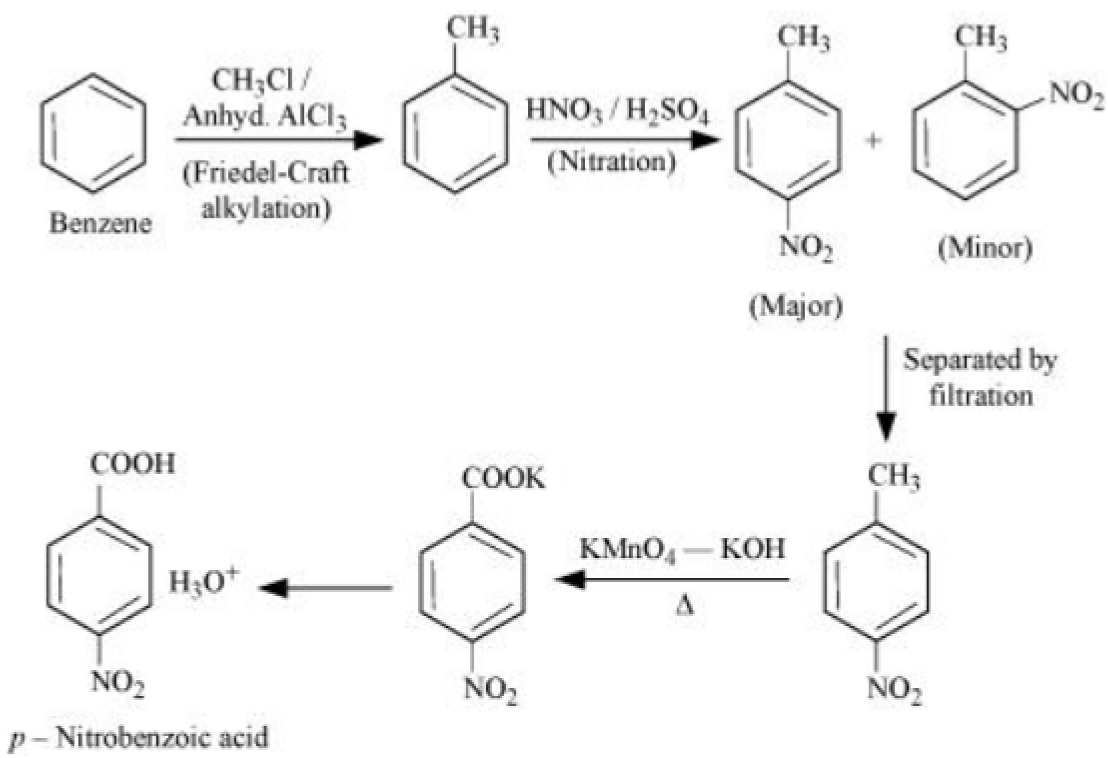
(i)



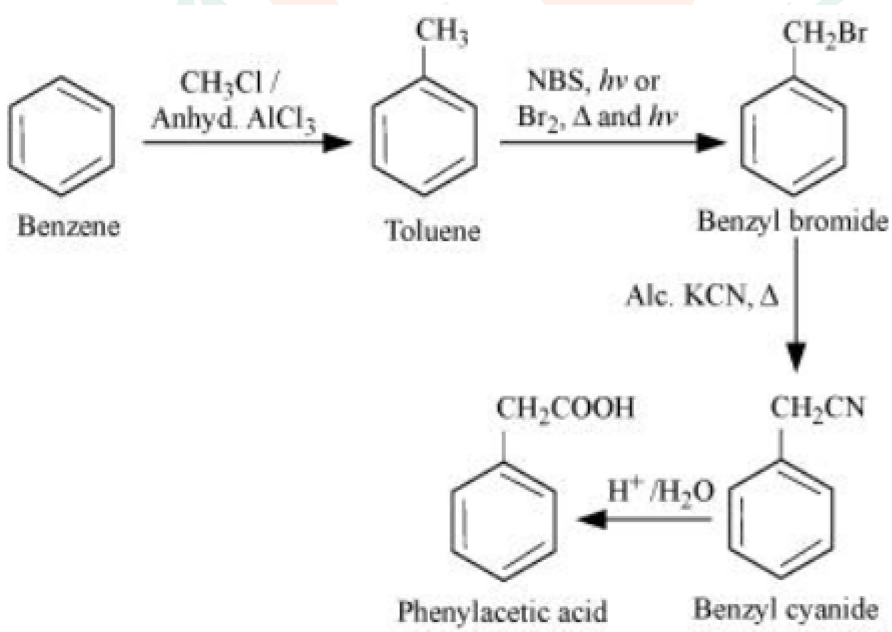
(ii)



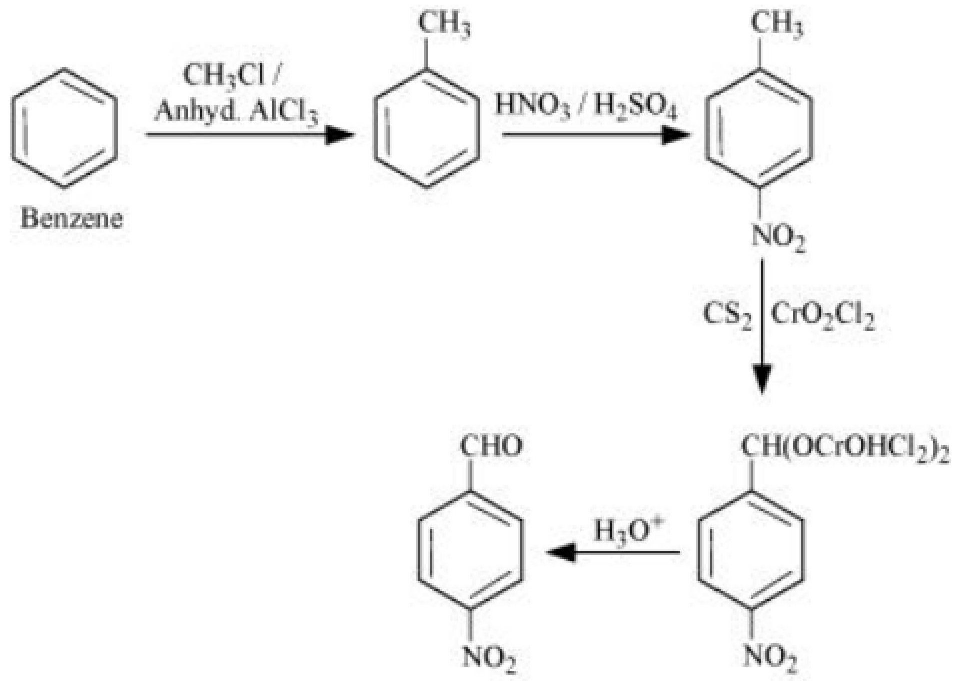
(iii)


Benzene
CH_3Cl / Anhyd. $AlCl_3$
(Friedel-Craft alkylation)
CH_3
HNO_3 / H_2SO_4
(Nitration)
CH_3
NO_2
(Major)
+
CH_3
NO_2
(Minor)
Separated by filtration
CH_3
NO_2
$KMnO_4$ — KOH
Δ
COOK
NO_2
H_3O^+
COOH
NO_2
p – Nitrobenzoic acid

(iv)


Benzene
CH_3Cl / Anhyd. $AlCl_3$
CH_3
Toluene
NBS, hv or Br_2, Δ and hv
CH_2Br
Benzyl bromide
Alc. KCN, Δ
CH_2CN
Benzyl cyanide
H^+ / H_2O
CH_2COOH
Phenylacetic acid

(v)



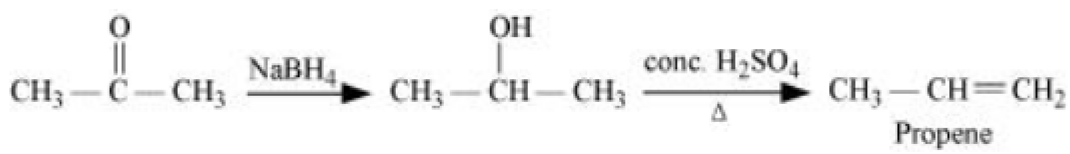
p – Nitrobenzaldehyde

Q. 15. **How will you bring about the following conversions in not more than two steps?**

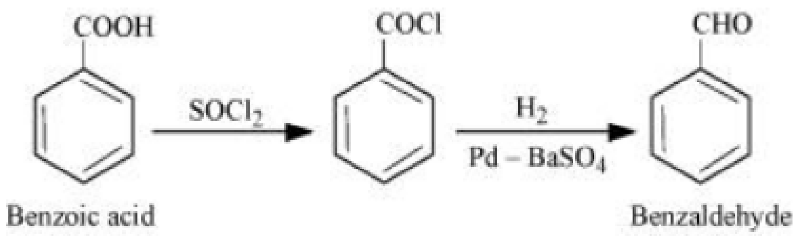
- (i) **Propanone to Propene**
- (ii) **Benzoic acid to Benzaldehyde**
- (iii) **Ethanol to 3-Hydroxybutanal**
- (iv) **Benzene to m-Nitroacetophenone**
- (v) **Benzaldehyde to Benzophenone**
- (vi) **Bromobenzene to 1-Phenylethanol**
- (vii) **Benzaldehyde to 3-Phenylpropan-1-ol**
- (viii) **Benazaldehyde to α-Hydroxyphenylacetic acid**
- (ix) **Benzoic acid to m- Nitrobenzyl alcohol**

ANSWER:-

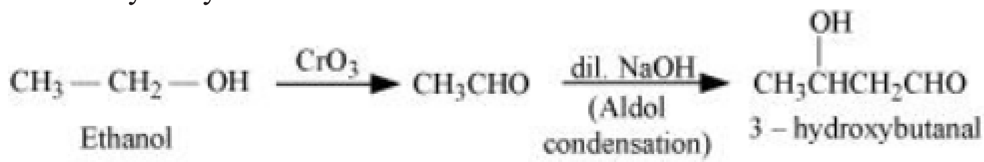
(i) Propanone to Propene



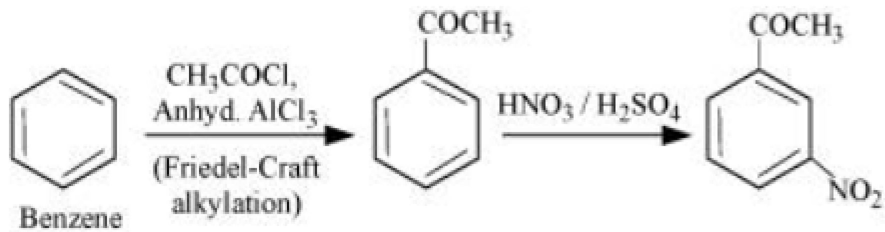
(ii) Benzoic acid to Benzaldehyde



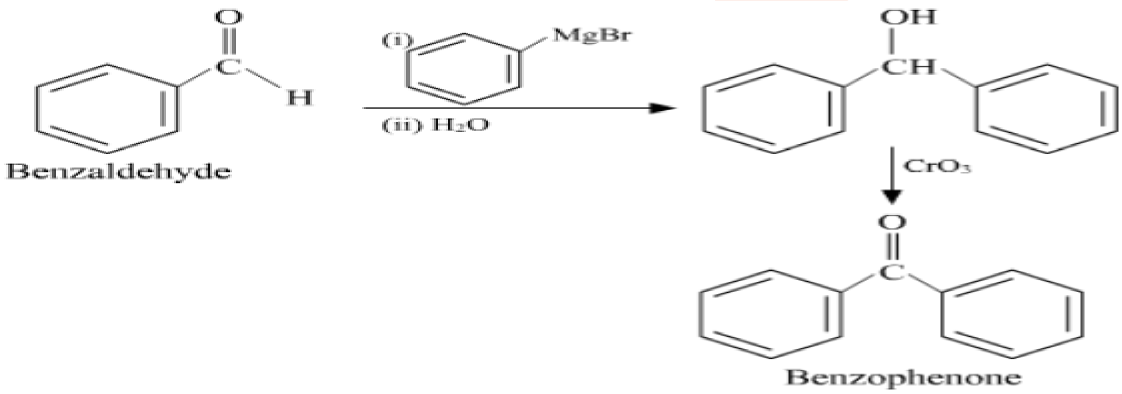
(iii) Ethanol to 3-Hydroxybutanal



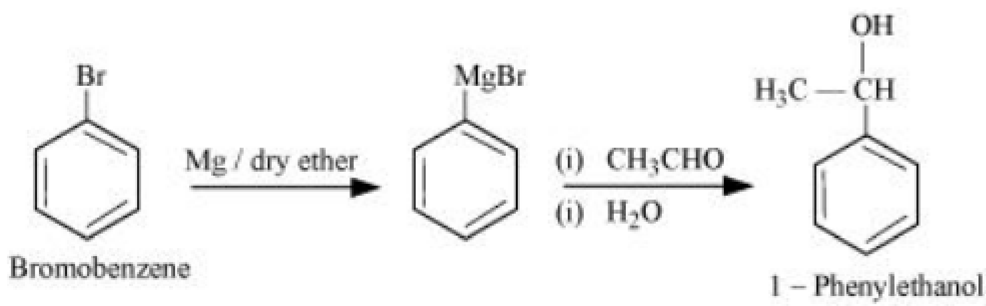
(iv) Benzene to m-Nitroacetophenone



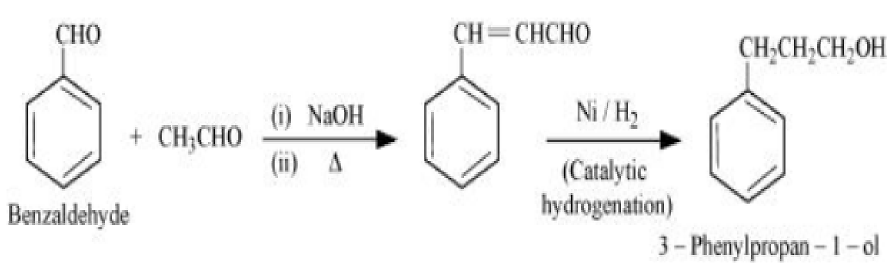
(v) Benzaldehyde to Benzophenone



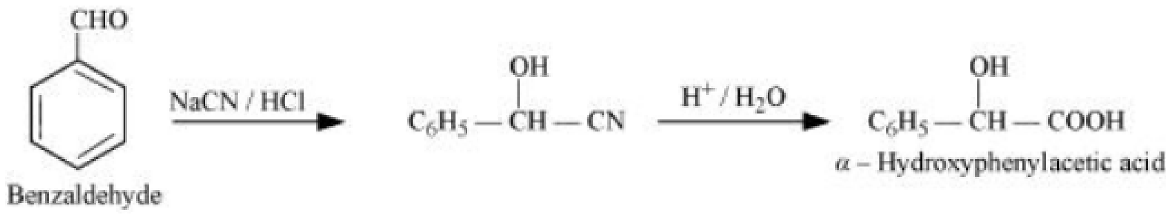
(vi) Bromobenzene to 1-Phenylethanol



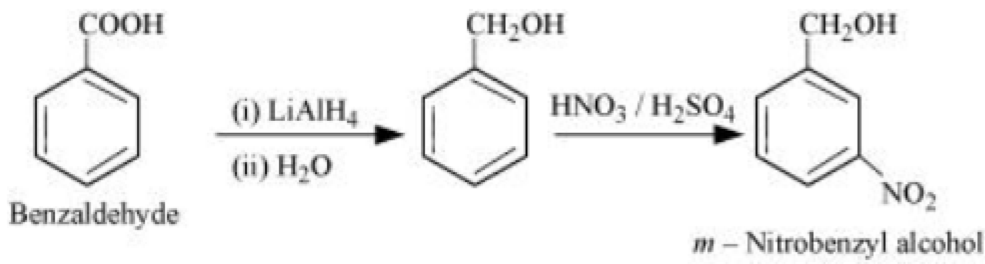
(vii) Benzaldehyde to 3-Phenylpropan-1-ol



(viii) Benazaldehyde to α-Hydroxyphenylacetic acid



(ix) Benzoic acid to m- Nitrobenzyl alcohol



Q. 16. **Describe the following:**

(i) **Acetylation** **(ii)** **Cannizzaro reaction**

(iii) **Cross aldol condaensation** **(iv)** **decarboxylation**

ANSWER:-

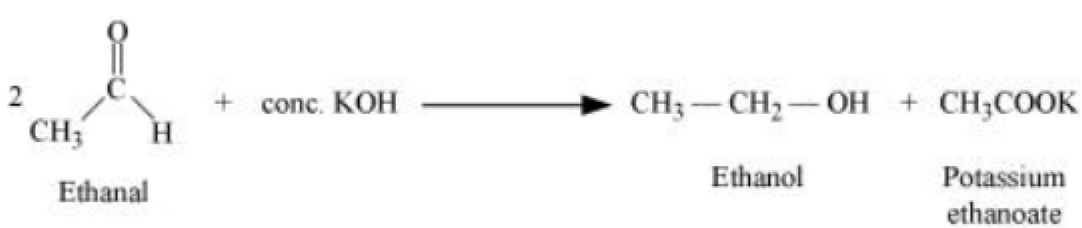
(i) Acetylation

Acetylation is the process of introducing an acetyl functional group into an organic compound. This reaction is typically carried out in the presence of a base like pyridine or dimethylaniline. It involves the replacement of an active hydrogen atom with an acetyl group. Acetyl chloride and acetic anhydride are commonly used as acetylating agents. For instance, acetylation of ethanol results in the formation of ethyl acetate.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Acetyl Chloride}}{CH_3COCl} \xrightarrow{\text{Pyridine}} \underset{\text{Ethylacetate}}{CH_3COOC_2H_5} + HCl$$

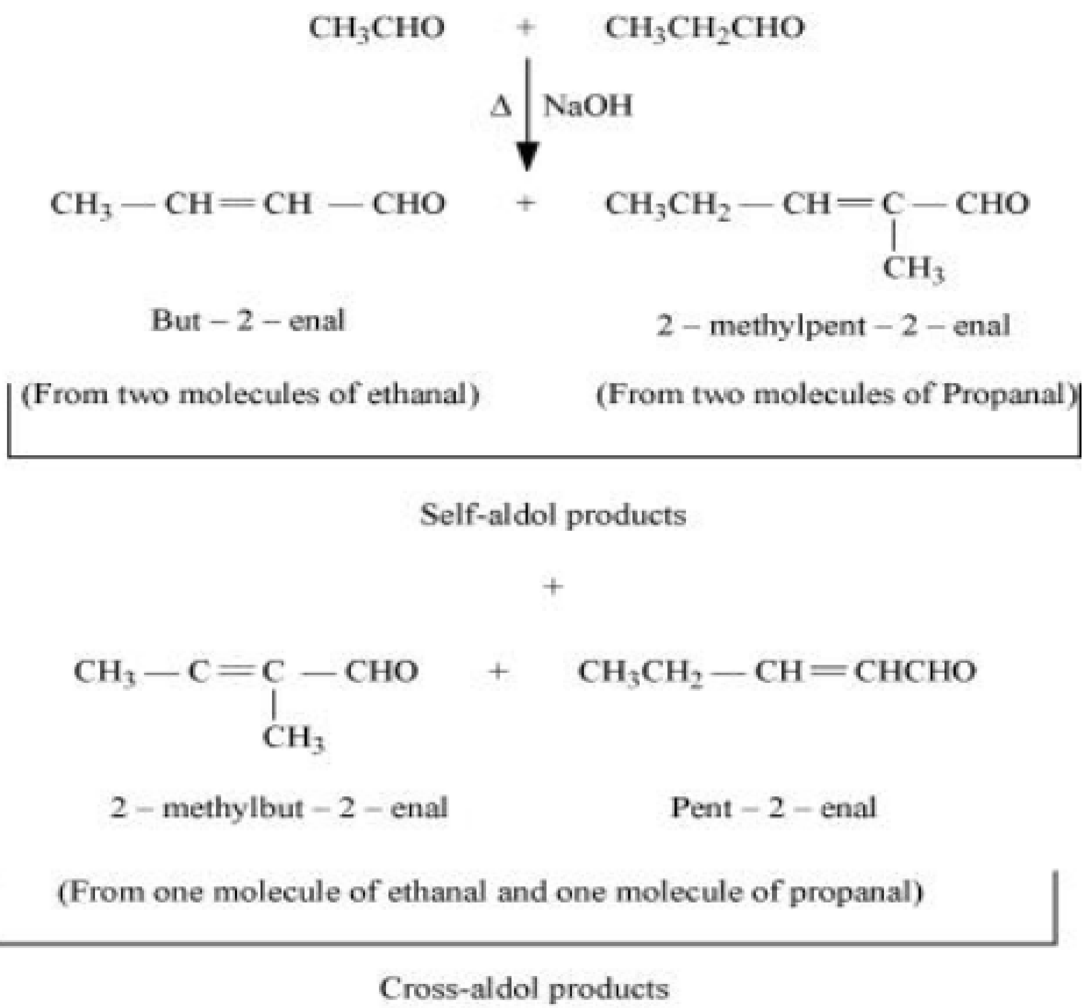
(ii) Cannizzaro reaction

The self-oxidation-reduction (disproportionation) reaction of aldehydes lacking α-hydrogens when treated with concentrated alkalis is known as the Cannizzaro reaction. In this reaction, two molecules of aldehyde are involved, with one being reduced to an alcohol and the other oxidized to a carboxylic acid. For example, when ethanal is treated with concentrated potassium hydroxide, ethanol and potassium ethanoate are formed.



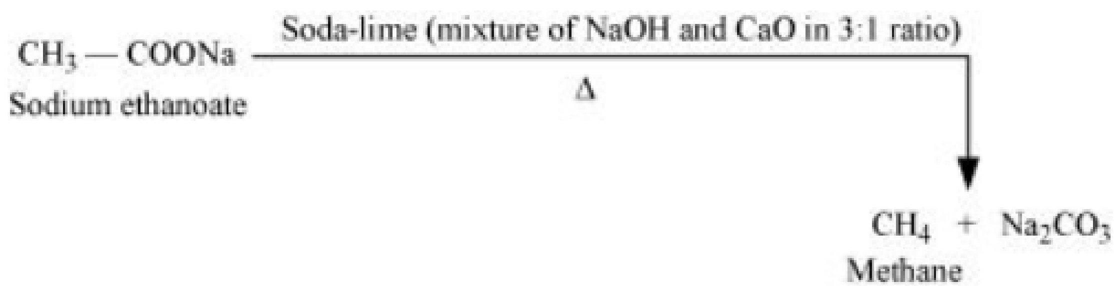
(iii) Cross aldol condaensation

When aldol condensation occurs between two different aldehydes, two different ketones, or an aldehyde and a ketone, the reaction is referred to as a cross-aldol condensation. If both reactants contain α-hydrogens, four products are formed. For instance, when ethanal and propanal react, they yield four products.



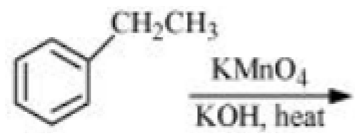
(iv) Decarboxylation

Decarboxylation refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime. Decarboxylation also takes place when aqueous solutions of alkali metal salts of carboxylic acids are electrolyzed. This electrolytic process is known as Kolbe's electrolysis.

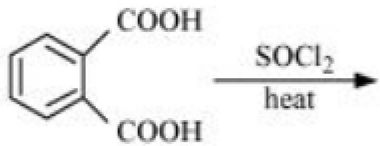


Q. 17. **Complete each synthesis by giving missing starting material, reagent or products**

(i)

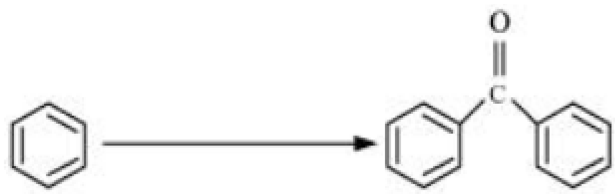


(ii)

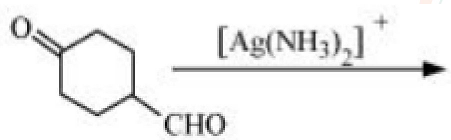


(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv)



(v)



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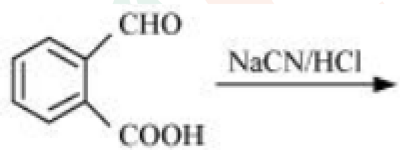
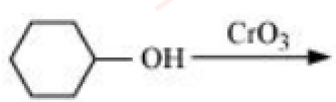


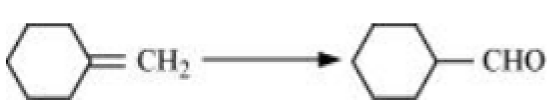
(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil. NaOH}}$

(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

(ix)



(x)



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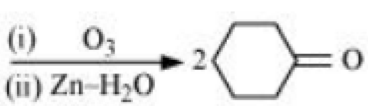
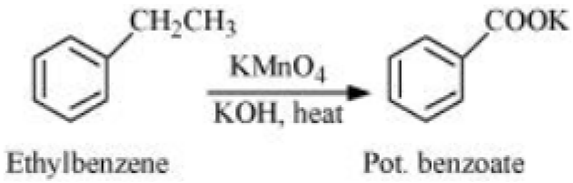
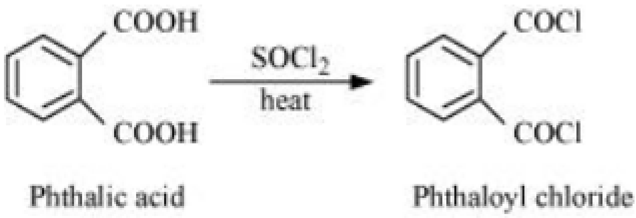


ANSWER:-

(i)



(ii)



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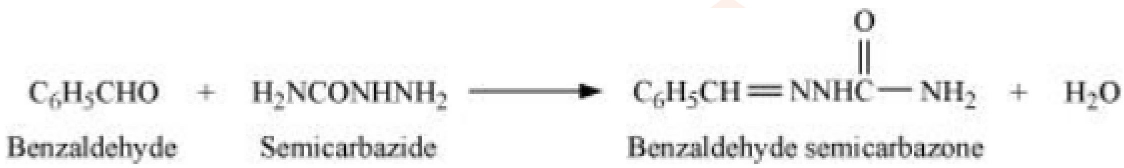

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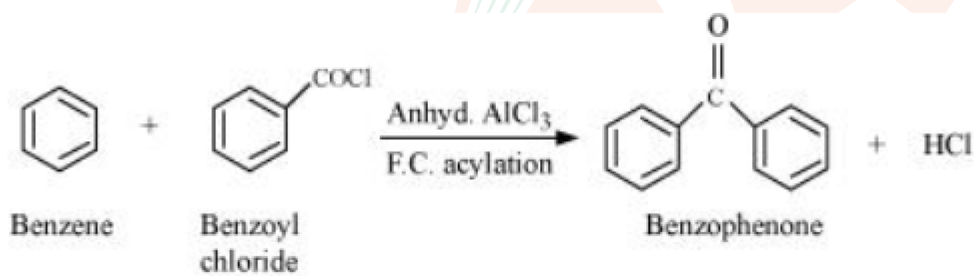
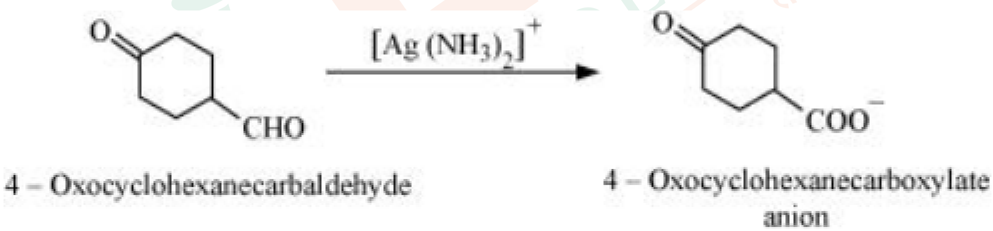
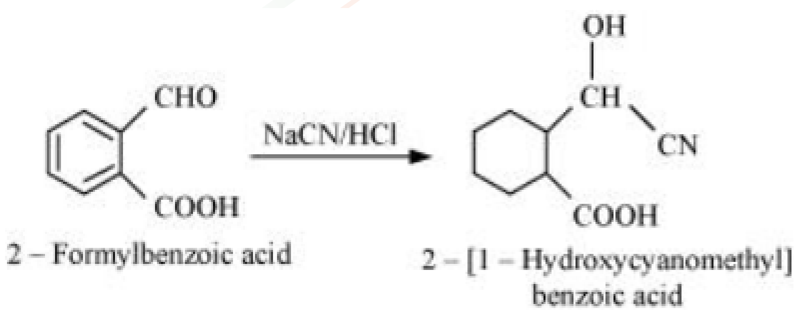


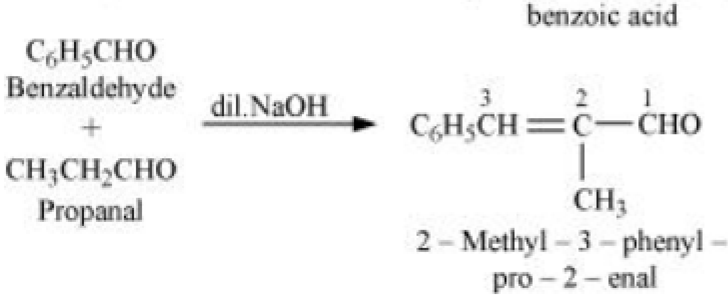
(v)



(vi)



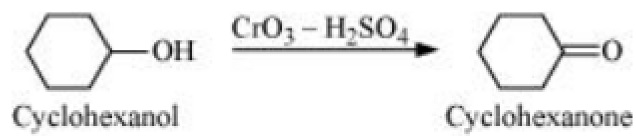
(vii)



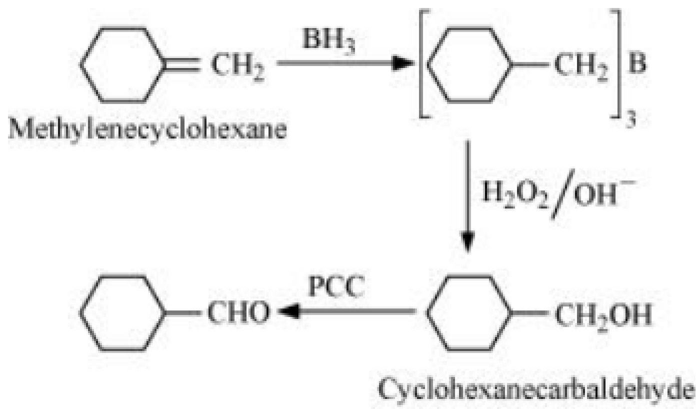
(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4} CH_3CH(OH)CH_2COOC_2H_5$

Ethyl 3 – oxobutanote Ethyl3 - hydroxybutanoate

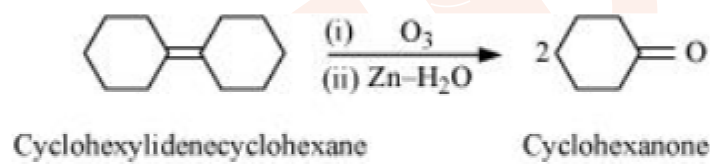
(ix)



(x)



(xi)



Q. 18. Give plausible explanation for each of the following:

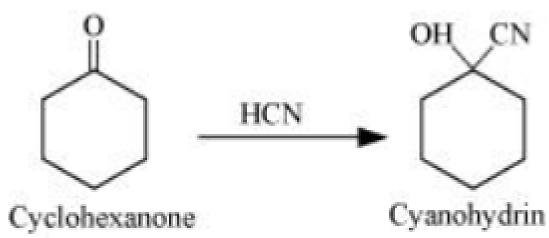
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

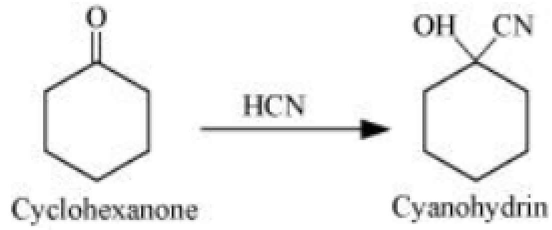
(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed

ANSWER:-

(i) Cyclohexanones react to form cyanohydrins as shown in the following equation.

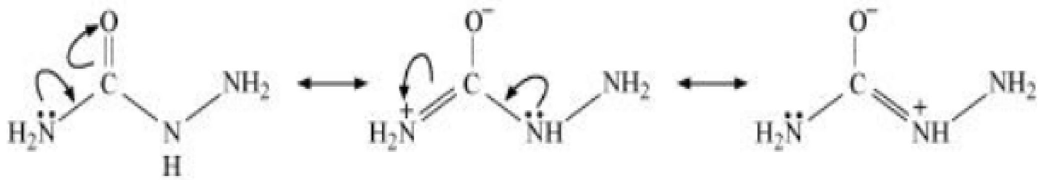


In this case, the nucleophile CN− can readily attack without any steric hindrance. However, in the case of 2, 2, 6-trimethylcyclohexanone, the methyl groups at the α-positions create steric hindrance, preventing the CN− from attacking effectively.



For this reason, it does not form a cyanohydrin.

(ii) Semicarbazide undergoes resonance involving only one of the two $-NH_2$ groups, specifically the one attached directly to the carbonyl carbon atom.



As a result, the electron density on the $-NH_2$ group involved in resonance decreases, preventing it from acting as a nucleophile. Since the other $-NH_2$ group is not involved in resonance, it retains its nucleophilic character and can attack the carbonyl carbon atoms of aldehydes and ketones, leading to the formation of semicarbazones.

(iii) Ester along with water is formed reversibly from a carboxylic acid and an alcohol in presence of an acid.

$$\underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \longrightarrow \underset{\text{Ester}}{RCOOR'} + \underset{\text{water}}{H_2O}$$

If water or ester is not removed promptly as it forms, it will react to regenerate the reactants, as the reaction is reversible. Therefore, to drive the equilibrium toward the formation of more ester, one of the two—water or ester—should be removed.

Q. 19. **An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.**

ANSWER:-

% of carbon = 69.77 % , % of hydrogen = 11.63 % ,% of oxygen = {100 − (69.77 + 11.63)}% = 18.6 % Thus, the ratio of the number of carbon, hydrogen, and oxygen atoms in the organic compound can be given as:

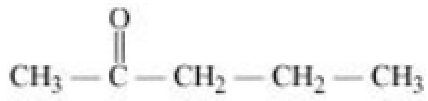
$$C:H:O = \frac{69.77}{12}:\frac{11.63}{1}:\frac{18.6}{16}$$

=5.81:11.63:1.16

=5:10:1

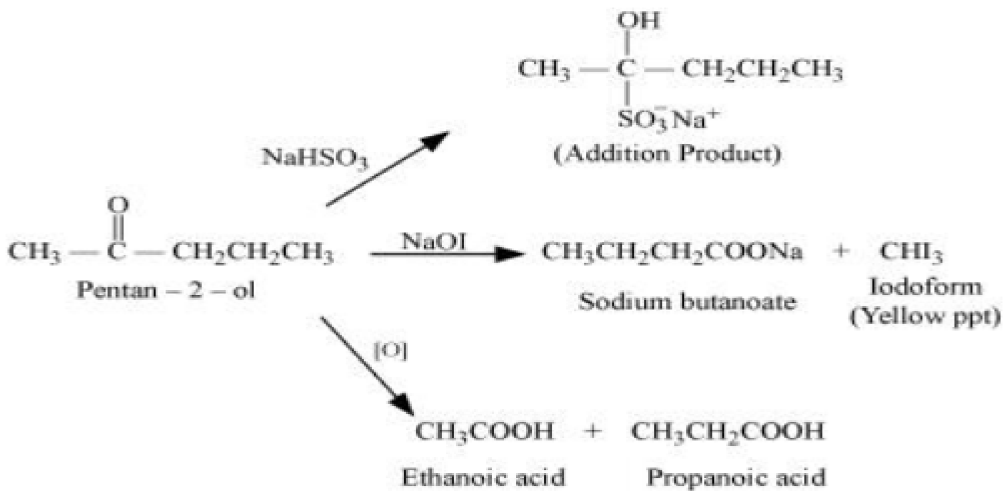
The empirical formula of the compound is $C_5H_{10}O$. The empirical formula mass can be calculated as:

$5 \times 12 + 10 \times 1 + 1 \times 16 = 86$. Since the molecular mass of the compound is 86, its molecular formula is $C_5H_{10}O$. As the compound does not reduce Tollen's reagent, it is not an aldehyde. Additionally, the compound forms sodium hydrogen sulfate addition products and gives a positive iodoform test. Since it is not an aldehyde, it must be a methyl ketone. The compound also yields a mixture of ethanoic acid and propanoic acid upon reaction. Therefore, the given compound is Pentan-2-one.



Pentan – 2 – ol

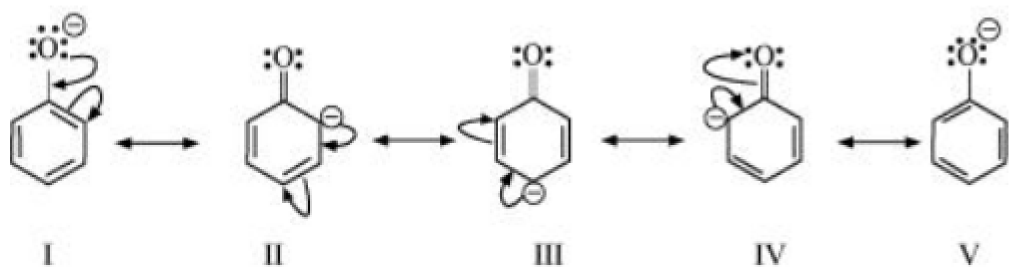
The following equations can explain the given reactions:



Q. 20. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

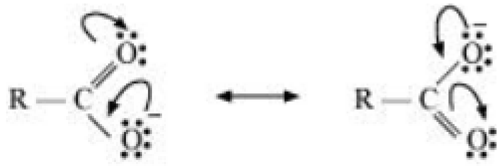
ANSWER:-

Resonance structures of phenoxide ion are:



From the resonance structures of the phenoxide ion, it can be observed that in structures II, III, and IV, the negative charge is placed on less electronegative carbon atoms. As a result, these structures contribute very little to the resonance stability of the phenoxide ion and can be disregarded. Only structures I and V place the negative charge on the more electronegative oxygen atom, making them the significant contributors.

Resonance structures of carboxylate ion are:



I'   II'

In the case of the carboxylate ion, the resonating structures I′ and II′ place the negative charge on more electronegative oxygen atoms, and the charge is delocalized over two oxygen atoms. In contrast, in the resonating structures I and V of the phenoxide ion, the negative charge is localized on the same oxygen atom. Therefore, the resonating structures of the carboxylate ion contribute more to its stability than those of the phenoxide ion. As a result, the carboxylate ion is more resonance-stabilized than the phenoxide ion, making carboxylic acid a stronger acid than phenol.