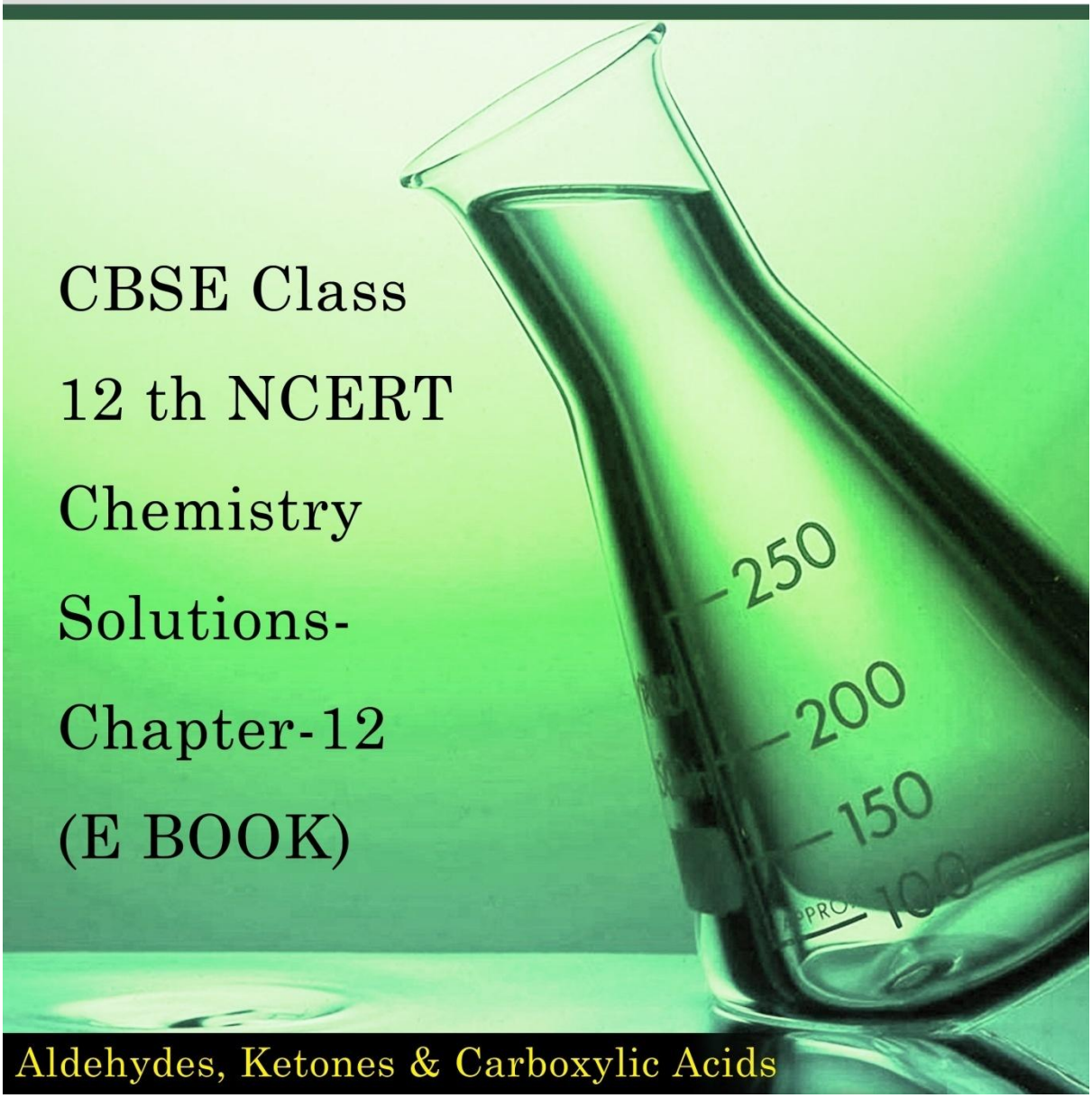
JAGRAN Josh
Simplifying Test Prep



Preface

This e-book is prepared by the CBSE board exam experts of jagranjosh.com, an online educational portal of Dainik Jagran.

The purpose of providing solutions for CBSE class 12th Science and Mathematics NCERT book is to explain the questions in an easy way and as per the CBSE marking scheme. This is a product exclusively for CBSE class 12th students which acts as a time-saver by providing a pattern for the solutions of NCERT based questions as per the CBSE curriculum. This document help to build a strong concept on the chapter mentioned in here and hence the students have been guided in the most appropriate way for their board examination

Chapter-12
Aldehydes, Ketones & Carboxylic Acids
Class-XII
Subject-Chemistry

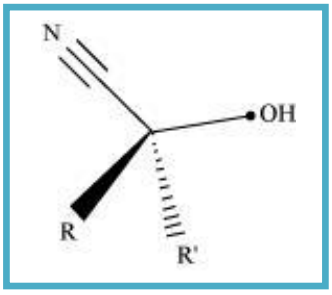
1. What is meant by the following terms? Give an example of the reaction in each case.

(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 12.1

(i) Cyanohydrin**: -**

Cyanohydrins are organic compounds having the formula RR′C(OH)CN, where R and R′ can be alkyl or aryl groups.



Cyanohydrin can be prepared from aldehydes and ketones. When they react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide (NaCN), cyanohydrins is produced. These reactions are known as cyanohydrin reactions.

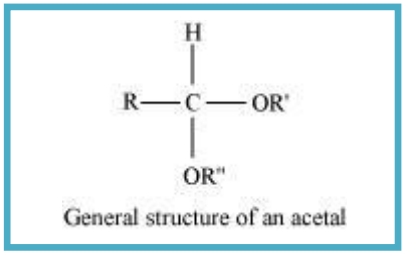
$$RR'C=O + HCN \xrightarrow{NaCN} RR'C(OH)CN$$

Ketone Cyanohydrin

Cyanohydrins are useful synthetic intermediates.

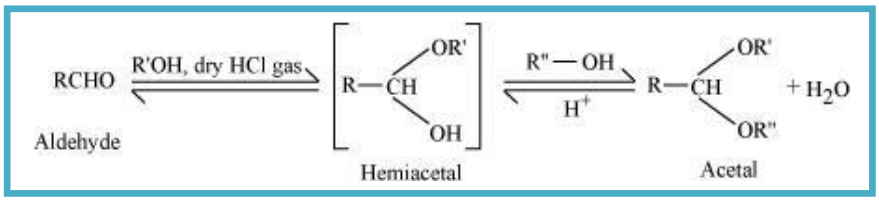
(ii) Acetal: -

Acetals are gem−dialkoxy alkanes in which two alkoxy groups are present on the terminal carbon atom. One bond is connected to an alkyl group while the other is connected to a hydrogen atom.



General structure of an acetal

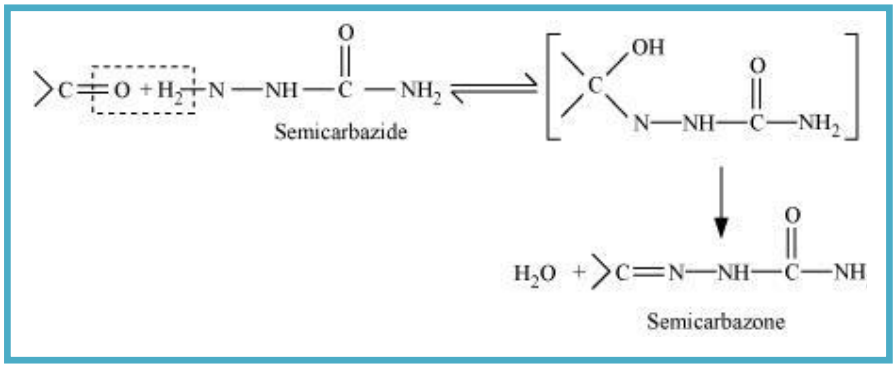
Hemiacetals can be produced by treating aldehydes with two equivalents of a monohydric alcohol in the presence of dry HCl gas, which further react with one more molecule of alcohol to yield acetal.



Aldehyde Hemiacetal Acetal

(iii) Semicarbarbazone**:**

Semicarbazones are the derivatives of aldehydes and ketones which can be produced by the condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazones are useful for identification and characterization of aldehydes and ketones.

(iv) Aldol**:**

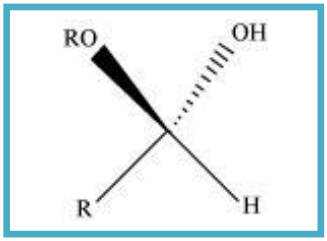
It is a β-hydroxy aldehyde or ketone is known as an aldol. It is produced by the condensation reaction of two molecules of the same or one molecule each of two different aldehydes or ketones in the presence of a base.

$$2CH_3CH_2-CHO \xrightleftharpoons{Dil.\ NaOH} CH_3-CH_2-CH(OH)-CH_2-CH_2-CHO$$

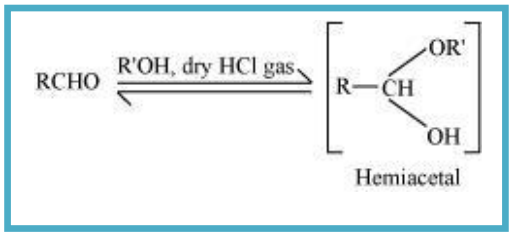
Propanal 4-Hydroxyhexanal (Aldol)

(v) Hemiacetal**:**

Hemiacetals are α−alkoxyalcohols



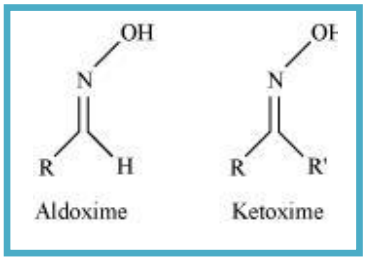
Aldehyde reacts with one molecule of a monohydric alcohol in the presence of dry HCl gas.

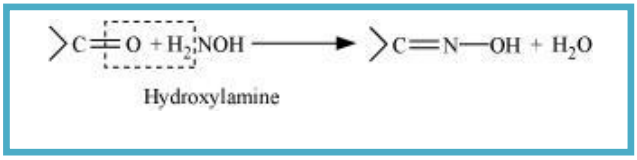


(vi) Oxime**:**

They have the general formula RR′CNOH, where R is an organic side chain and R′ is either hydrogen or an organic side chain. If R′ is H, then it is known as aldoxime and if R′ is an organic side chain, it is known as ketoxime.

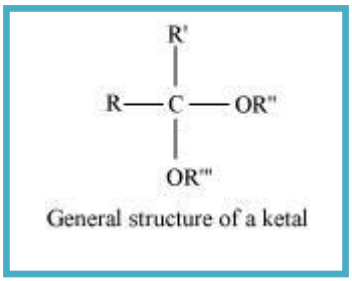
On treatment with hydroxylamine in a weakly acidic medium, aldehydes or ketones form oximes.



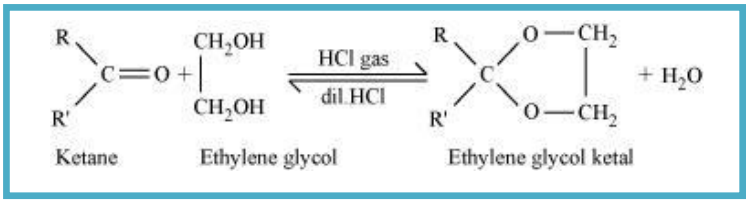


(vii) Ketal**:**

Ketals are gem−dialkoxyalkanes in which two alkoxy groups are present on the same carbon atom within the chain. The other two bonds of the carbon atom are connected to two alkyl groups.

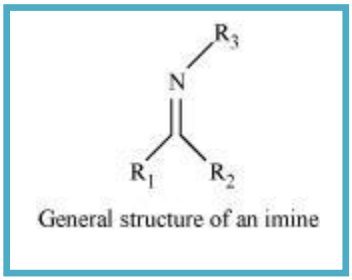


Ketones react with ethylene glycol in the presence of dry HCl gas to give a cyclic product known as ethylene glycol ketals.

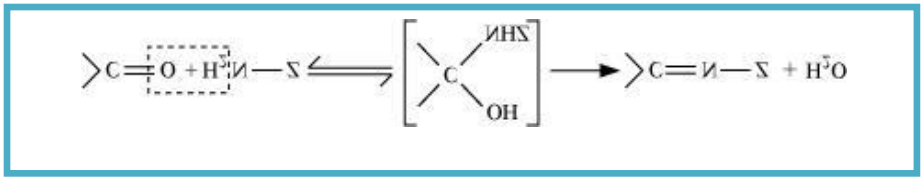


(viii) Imine**:**

Imines are chemical compounds containing a carbon nitrogen double bond.

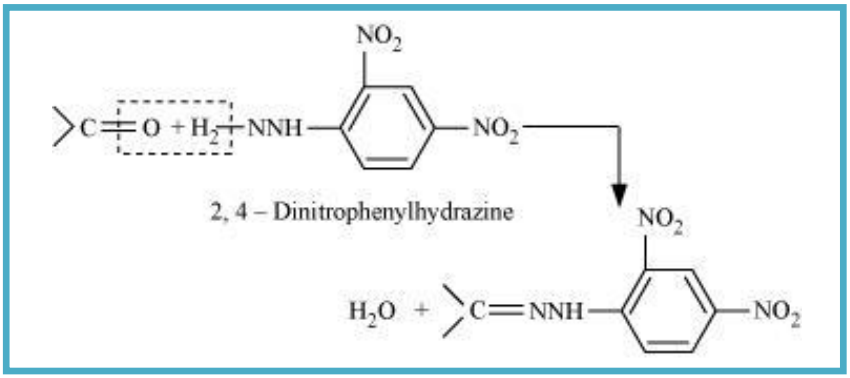


Imines are produced when aldehydes and ketones react with ammonia and its derivatives.



(ix) 2, 4−DNP−derivative:

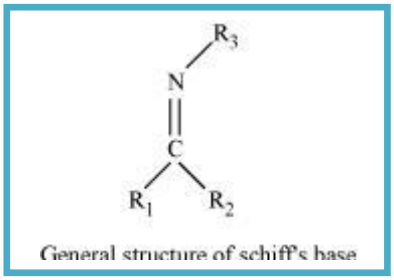
2, 4−dinitrophenylhydragones are 2, 4−DNP−derivatives, which are produced when aldehydes or ketones react with 2, 4−dinitrophenylhydrazine in a weakly acidic medium.



To identify and characterize aldehydes and ketones, 2, 4−DNP derivatives are used.

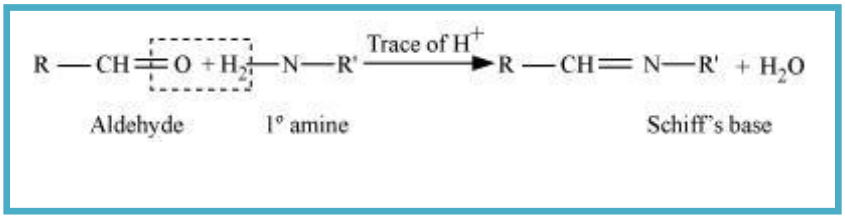
(x) Schiff's base:

It is a chemical compound which contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group-but not hydrogen. They have the general formula $R_1R_2C = NR_3$. Hence, it is an imine.



General structure of schiff's base

Aldehydes and ketones on treatment with primary aliphatic or aromatic amines in the presence of trace of an acid yields a Schiff's base.



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 12.2

(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

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**

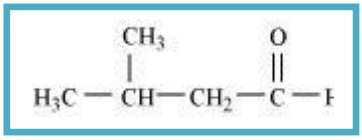
(vi) **3-Bromo-4-phenylpentanoic acid**

(vii) ***p,p'*-Dihydroxybenzophenone**

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

Answer 12.3

(i)



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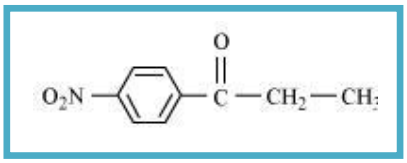

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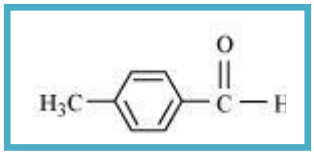

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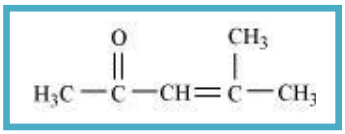

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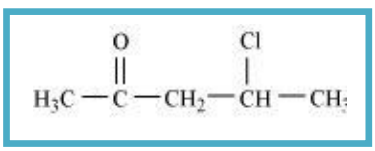

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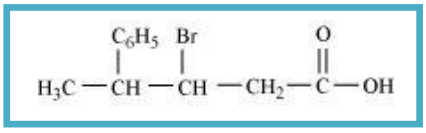

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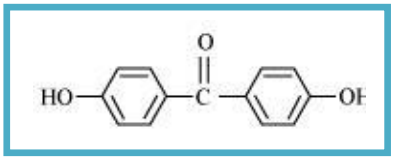

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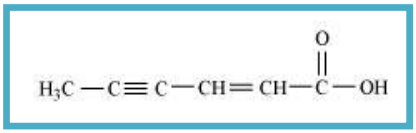


4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

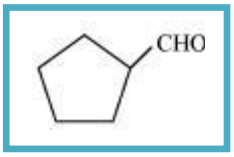
(i) $CH_3CO(CH_2)_4CH_3$

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(iii) $CH_3(CH_2)_5CHO$

(iv) Ph-CH=CH-CHO

(v)



(vi) PhCOPh

Answer 12.4

(i) $CH_3CO(CH_2)_4CH_3$

IUPAC name - Heptan-2-one

Common name - Methyl n-propyl ketone

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

IUPAC name - 4-Bromo-2-methylhaxanal

Common name- (γ-Bromo-α-methyl-caproaldehyde)

(iii) $CH_3(CH_2)_5CHO$

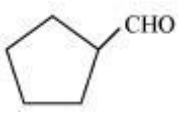
IUPAC name - Heptanal

(iv) Ph-CH=CH-CHO

IUPAC name - 3-phenylprop-2-enal

Common name - β-Pheynolacrolein

(v)



IUPAC name: Cyclopentanecarbaldehyde

(vi) PhCOPh

IUPAC name - Diphenylmethanone

Common name – Benzophenone

5. Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of Benzaldehyde

(ii) Cyclopropanone oxime

(iii) Acetaldehydedimethylacetal

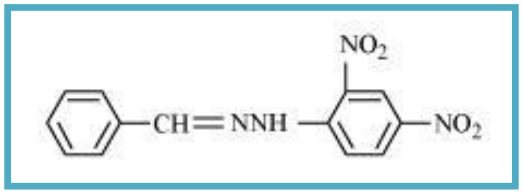
(iv) The semicarbazone of cyclobutanone

(v) The ethylene ketal of hexan-3-one

(vi) The methyl hemiacetal of formaldehyde

Answer 12.5

(i)



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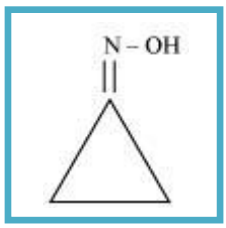

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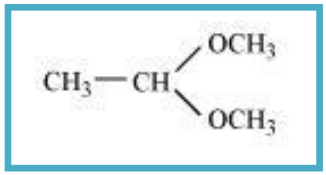

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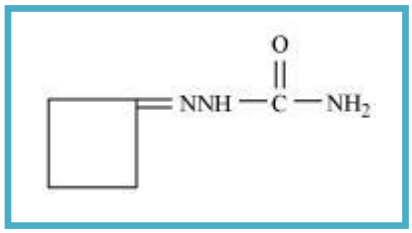

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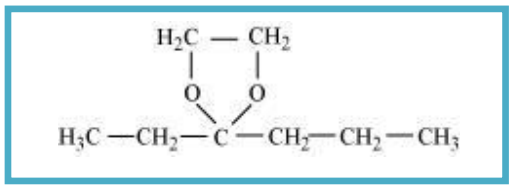

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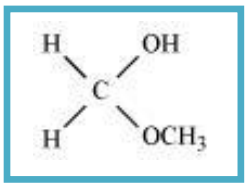


6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

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

(ii) **Tollens' reagent**

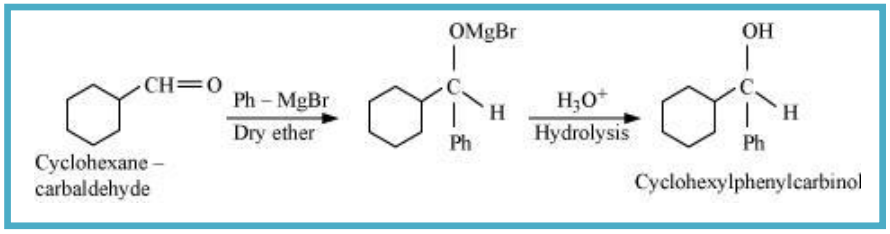
(iii) **Semicarbazide and weak acid**

(iv) **Excess ethanol and acid**

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

Answer 12.6

(i)



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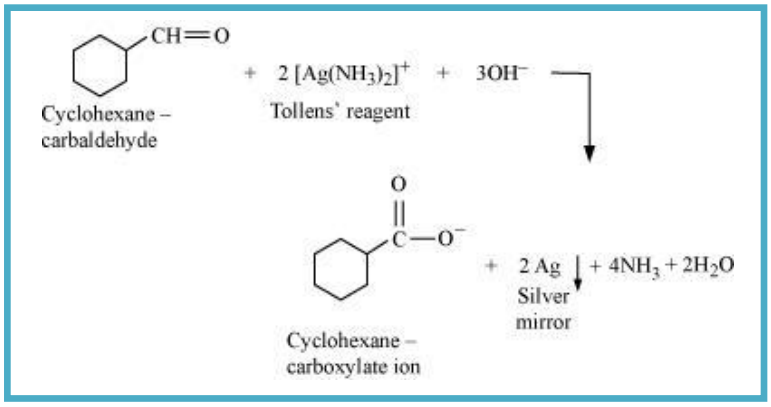

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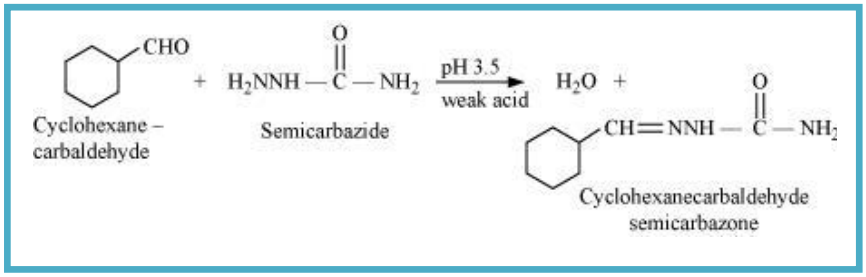

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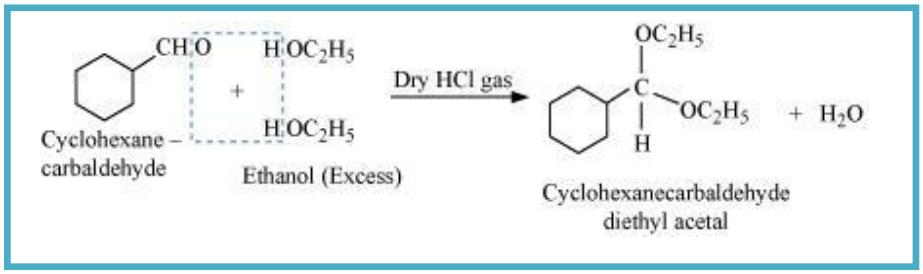

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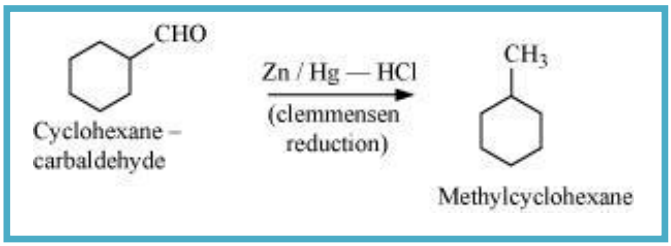


7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal

(ii) 2-Methylpentanal

(iii) Benzaldehyde

(iv) Benzophenone

(v) Cyclohexanone

(vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde

(viii) Butan-1-ol

(ix) 2, 2-Dimethylbutanal

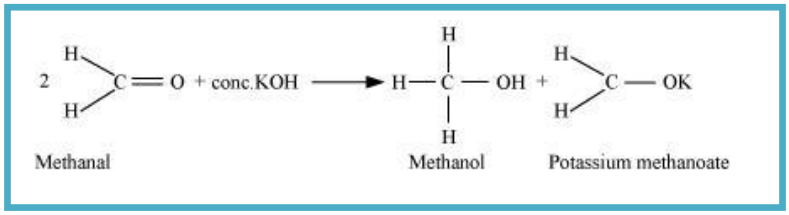
Answer 12.7

Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions. The compounds (i) Methanal, (iii) Benzaldehyde, and (ix) 2, 2-dimethylbutanal do not have any α-hydrogen. Thus, these undergo cannizzaro reactions.

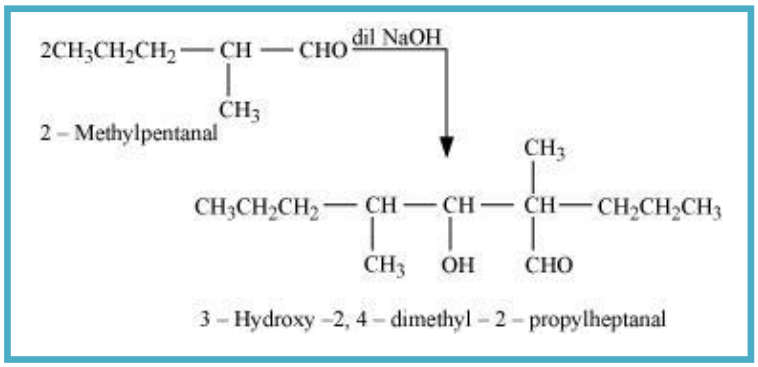
Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation. The compounds (ii) 2−methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vii) phenylacetaldehyde contain one or more α-hydrogen atoms. Hence, these undergo aldol condensation.

Compound (iv) Benzophenone is a ketone having no α-hydrogen atom and compound (viii) Butan-1-ol is an alcohol. Hence, these compounds do not undergo either aldol condensation or cannizzaro reactions.

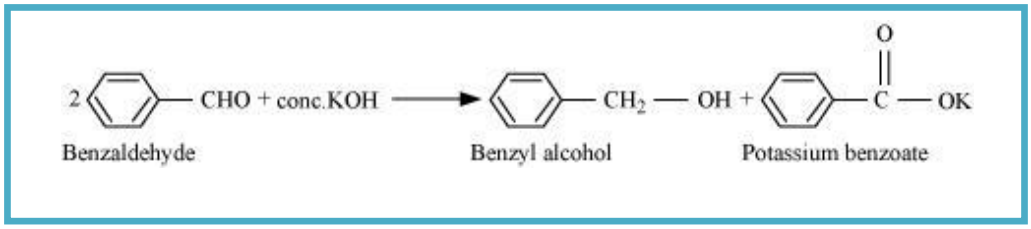
(i) Cannizzaro reaction



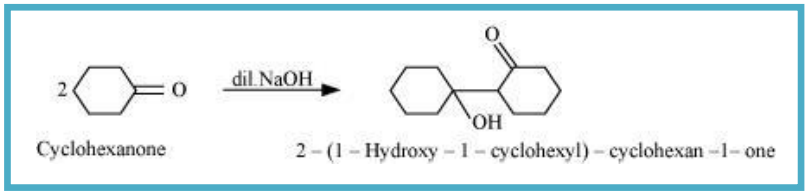
(ii) Aldol condensation



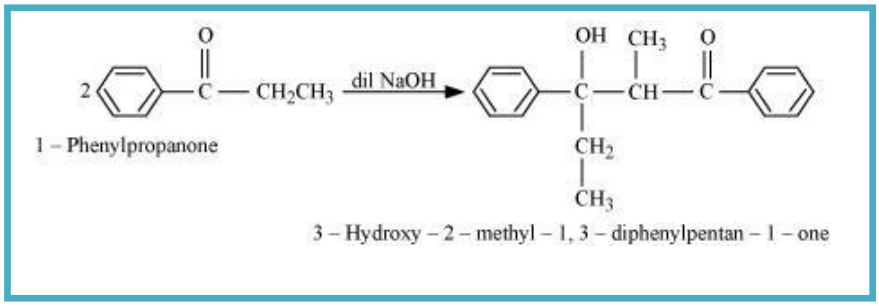
(iii) Cannizzaro reaction



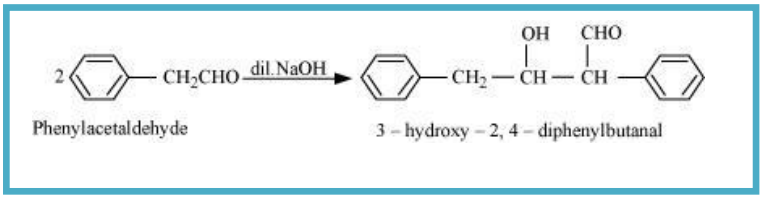
(v) Aldol condensation



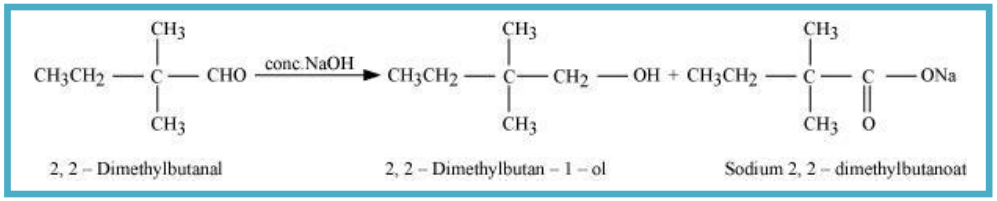
(vi) Aldol condensation



(vii) Aldol condensation



(ix) Cannizzaro reaction



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 12.8

(i) Ethanal to Butan-1,3-diol

$$CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3CH(OH)-CH_2-CHO \xrightarrow{NaBH_4} CH_3CH(OH)-CH_2CH_2OH$$

Ethanal 3-Hydroxybutanal Butan-1,3-diol

(ii) Ethanal to But-2-enal

$$CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3CH(OH) - CH_2 - CHO \xrightarrow{\Delta} CH_3CH = CH - CHO$$

Ethanal — 3-Hydroxybutanal — But-2-enal

(iii) Ethanal to but-2-enoic acid

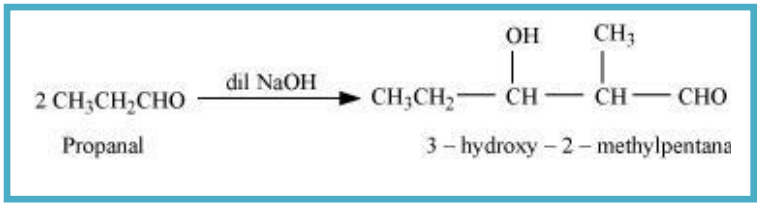
$$CH_3CH = CH - CHO \xrightarrow{\text{Tollen's reagent}} CH_3CH = CHCOOH$$

But-2-enal — But-2-enoic acid

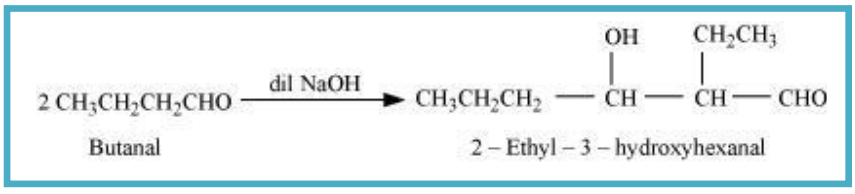
9. Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

Answer 12.9

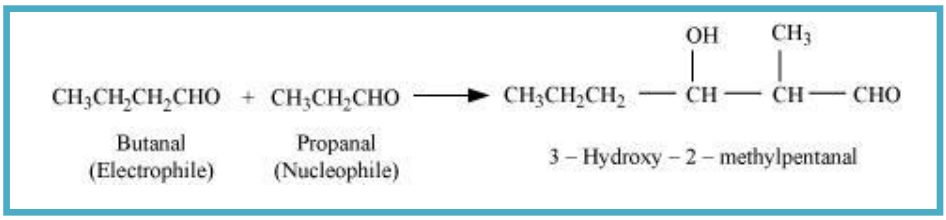
(i) Reaction of two molecules of propanal with dil. NaOH



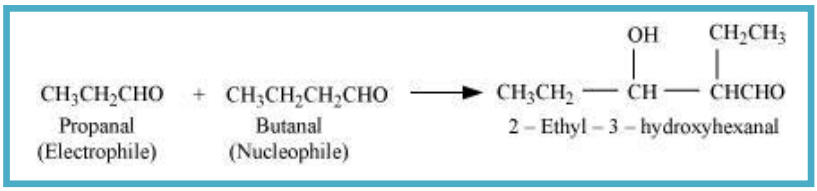
(ii) Reaction of two molecules of Butanal with dil. NaOH.



(iii) Taking one molecule each of propanal and butanal in which propanal acts as a nucleophile and butanal acts as an electrophile.



(iv) Taking one molecule each of propanal and butanal in which propanal acts as an electrophile and butanal acts as a nucleophile.

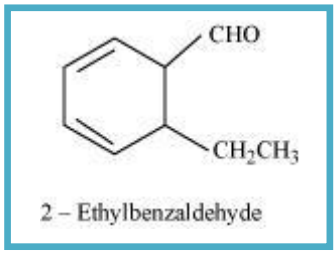


10. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

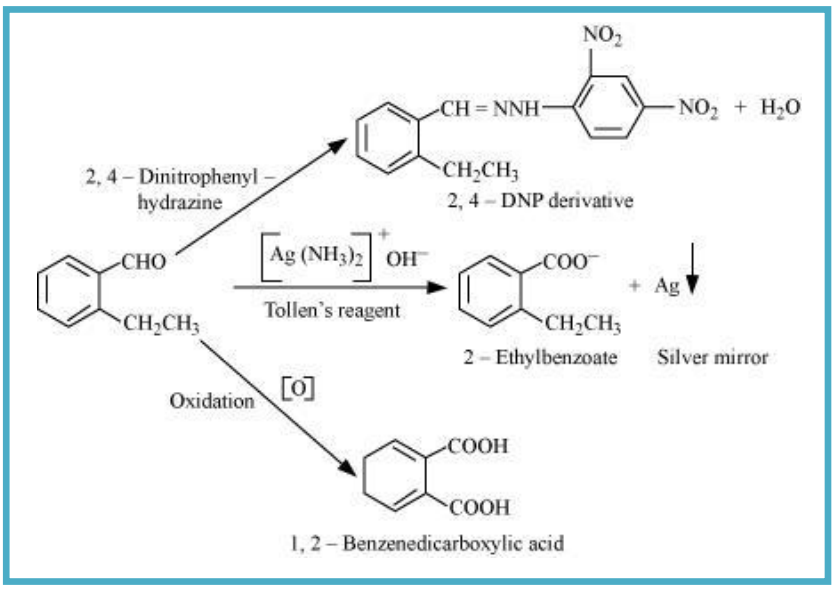
Answer 12.3

Given compound forms 2, 4-DNP derivative and reduces Tollen's reagent. Thus, the given compound must be an aldehyde.

Now, the compound undergoes cannizzaro reaction and on oxidation gives 1, 2-benzenedicarboxylic acid. Hence, the −CHO group is directly attached to a benzene ring and this benzaldehyde is ortho-substituted. Thus, the compound is 2-ethylbenzaldehyde.



Given reactions are:



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 12.3

Compound A ($C_8H_{16}O_2$) gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.

Now, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of 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.

Thus, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.

$$CH_3CH_2CH_2-COO-CH_2CH_2CH_2CH_3$$

Reactions are: -

$$\underset{\text{Butylbutanoate}}{CH_3CH_2CH_2-COO-CH_2CH_2CH_2CH_3} \xrightarrow{\text{Dil. } H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2-COOH} + \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-OH}$$

(A) (B) (C)

$$CH_3CH_2CH_2CH_2-OH \xrightarrow[\text{oxidation}]{CrO_3/CH_3COOH} \underset{(B)}{CH_3CH_2CH_2-COOH}$$

$$CH_3CH_2CH_2CH_2-OH \xrightarrow[-H_2O]{\text{dehydration}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

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

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

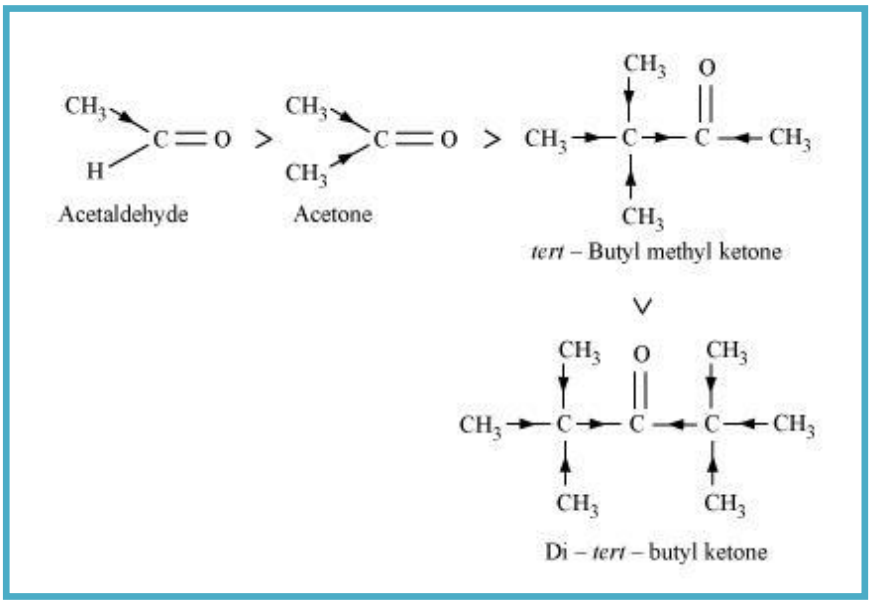
b) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)

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

Answer 12.12

a) When HCN reacts, CN^- acts as a nucleophile. Negative charge on the compound decreases its reactivity with HCN.

In the given compounds, the +I effect acts as follows. Here steric hindrance comes also in action.



Thus, order of their increasing reactivities toward HCN is:

Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde

b) Carboxylic acids gain negative charge after losing a proton

$$R-COOH \rightarrow R-COO^{-} + H^{+}$$

We know that, groups having +I effect will decrease the strength of the acids and groups having −I effect will increase the strength of the acids. In the given compounds, $-CH_3$ group has +I effect and Br^{-} group has −I effect. Thus, acids containing Br^{-} are stronger.

Thus, the strengths of the given acids increase as:

$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

c) Here, methoxy group is an electron-donating group, so 4-methoxybenzoic acid is a weaker acid than benzoic acid.

Nitro group is an electron-withdrawing group. It increases the strengths of acids. Thus, compound which contains two nitro groups will be slightly stronger acid than 4-nitrobenzoic acid.

Thus, the strengths of the given acids increase as:

4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

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 12.13

Propanal and propanone can be distinguished by tollen's test, fehling's test & Iodoform test.

a. Tollen's test

Propanal can be reduces Tollen's reagent. But, propanone does not reduce Tollen's reagent as it is a ketone.

$$CH_3CH_2CHO + 2\left[Ag\left(NH_3\right)_2\right]^+ + 3OH^- \rightarrow CH_3CH_2COO^- + Ag\downarrow \; + \; 4NH_3 + 2H_2O$$

Propanal Tollen's reagent Pranoate ion silver mirror

b. Fehling's test

Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu_2O, but propanone being a ketone does not.

$$CH_3CH_2CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_3CH_2COO^- + Cu_2O\downarrow + 3H_2O$$

Propanal Pranoate ion brown ppt

(i) Acetophenone and Benzophenone can be distinguished using the iodoform test.

Iodoform test:

Methyl ketones are oxidized by sodium hypoiodite to give yellow ppt. of iodoform. Acetophenone being a methyl ketone responds to this test, but benzophenone does not.

$$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3 + 2NaOH$$

Acetophenone Sodium benzoate yellow ppt

$$C_6H_5COC_6H_5 + NaOI \rightarrow \text{No yellow ppt}$$

Benzophenone

(ii) 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.

$$6C_6H_5OH + FeCl_3 \rightarrow \left[Fe\left(OC_6H_5\right)_6\right]^{3-} + 3H^+ + 3Cl^-$$

Phenol Iron-Phenol complex

But benzoic acid reacts with neutral $FeCl_3$ to give a buff coloured ppt. of ferric benzoate.

$$3C_6H_5COOH + FeCl_3 \rightarrow \left(C_6H_5COO\right)_3 Fe + 3HCl$$

Benzoic acid ferric benzoate $\left(\text{Buff coloured ppt}\right)$

(iii) Benzoic acid and Ethyl benzoate can be distinguished by sodium bicarbonate test.

Sodium bicarbonate test:

Acids react with $NaHCO_3$ to produce brisk effervescence due to the evolution of CO_2 gas.

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 \uparrow + H_2O$$

Benzoic acid Sodium benzoate

$$C_6H_5COOC_2H_5 + NaHCO_3 \rightarrow \text{No effervescence}$$

Benzoic acid being an acid responds to this test, but ethylbenzoate does not.

(iv) Pentan-2-one and pentan-3-one can be distinguished by iodoform test.

Iodoform test:

Pentan-2-one is a methyl ketone. Thus, it responds to this test. But pentan-3-one not being a methyl ketone does not respond to this test.

$$CH_3CH_2CH_2 - CO - CH_3 + 3NaOI \rightarrow CH_3CH_2CH_2COONa + CHI_3 \downarrow + 2NaOH$$

Pentan-2-one Sodium butanoate yellow ppt

$$CH_3CH_2 - CO - CH_2CH_3 + NaOI \rightarrow \text{No yellow ppt}$$

Pentan-3-one

(v) Benzaldehyde and acetophenone can be distinguished by the following tests.

a. Tollen's Test

Aldehydes respond to Tollen's test. Benzaldehyde being an aldehyde reduces Tollen's reagent to give a red-brown precipitate of Cu_2O. But acetophenone does not as it is a ketone.

$$C_6H_5CHO + 2\left[Ag\left(NH_3\right)_2\right]^+ + 3OH^- \rightarrow C_6H_5COO^- + Ag \downarrow + 4NH_3 + 2H_2O$$

Benzaldehyde Tollen's reagent Benzoate ion

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.

$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3 + 2NaOH$

Acetophenone Sodium benzoate

(vii) Ethanal and propanal can be distinguished by iodoform test.

$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3 + 2NaOH$

Acetophenone Sodium benzoate

Iodoform test

Ethanal having one methyl group linked to the carbonyl carbon atom responds to this test. But propanal does not have a methyl group linked to the carbonyl carbon atom and thus, it does not respond to this test.

$CH_3CHO + 3NaOI \rightarrow HCOONa + CHI_3 + 2NaOH$

Ethanal Sodium methanoate yellow ppt

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

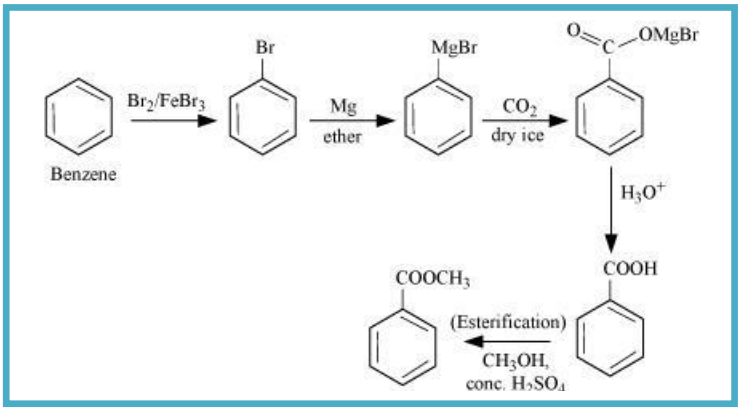
(iii) *p*-Nitrobenzoic acid

(iv) Phenylacetic acid

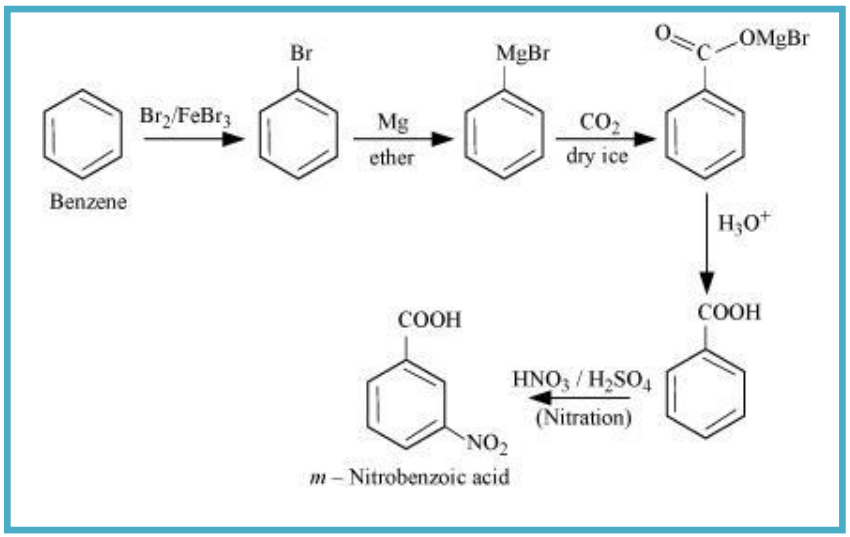
(v) *p*-Nitrobenzaldehyde.

Answer 12.14

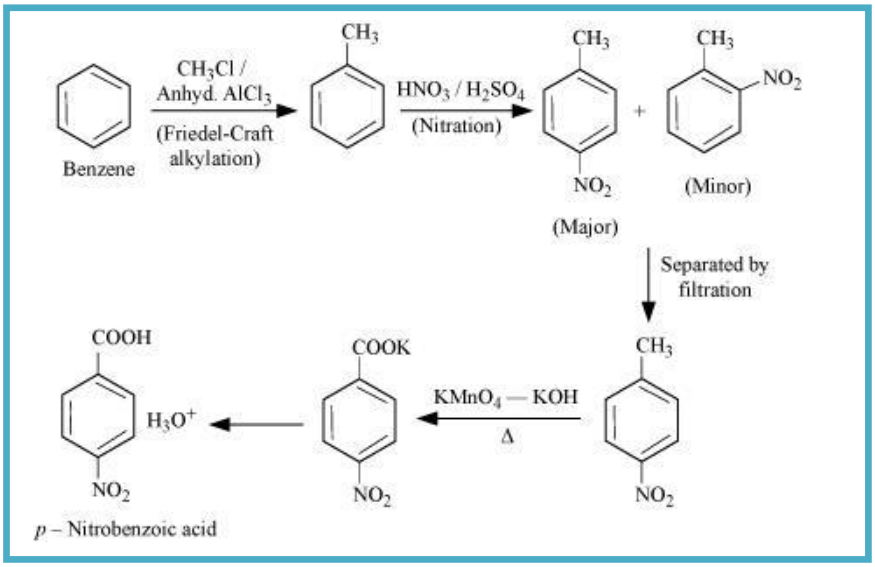
(i)



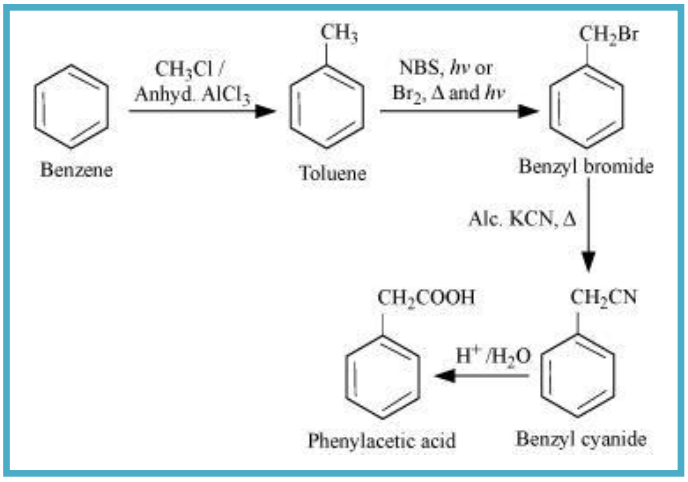
(ii)


Benzene
$Br_2/FeBr_3$
Br
Mg
ether
MgBr
CO_2
dry ice
O=C—OMgBr
H_3O^+
COOH
HNO_3 / H_2SO_4
(Nitration)
COOH
NO_2
m – Nitrobenzoic acid

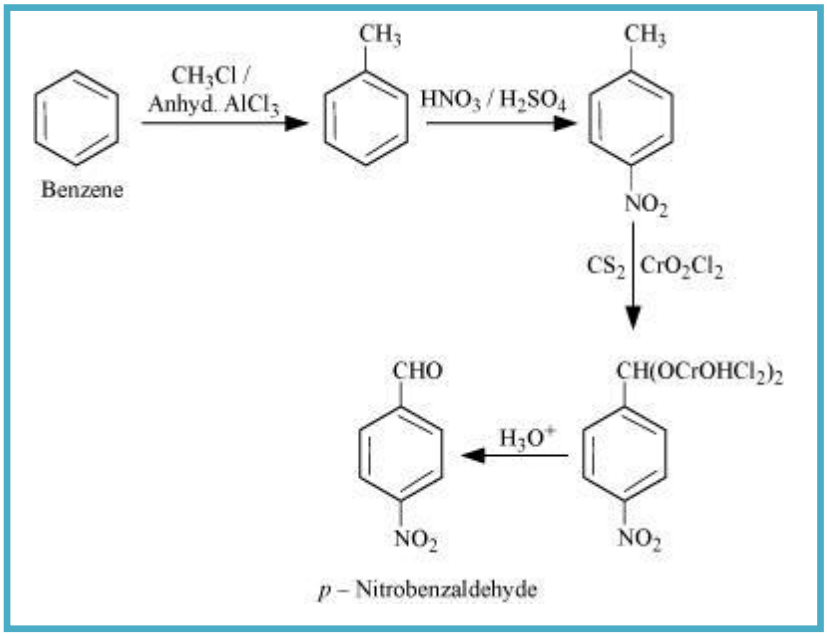
(iii)


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)



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**

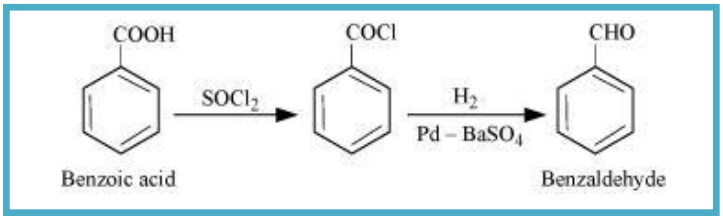
(vii) **Benzaldehyde to 3-Phenylpropan-1-ol**

(viii) **Benazaldehyde to α-Hydroxyphenylacetic acid**

(ix) **Benzoic acid to *m*- Nitrobenzyl alcohol**

Answer 12.15

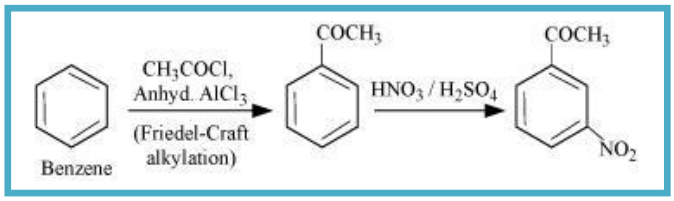
(i) $CH_3-CO-CH_3 \xrightarrow{NaBH_4} CH_3-CH(OH)-CH_3 \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_3-CH=CH_2$



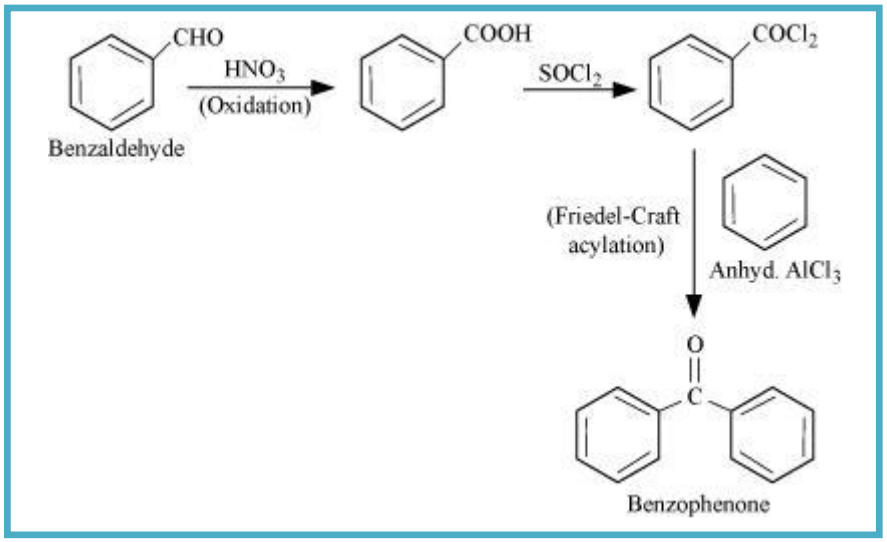
(ii)

$$CH_3-CH_2-OH \xrightarrow{CrO_3} CH_3CHO \xrightarrow{\text{dil. } H_2SO_4} CH_3CH(OH)CH_2CHO$$

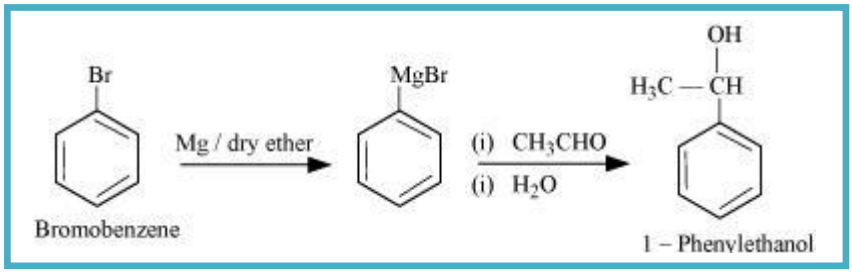
(iii)



(iv)



(v)



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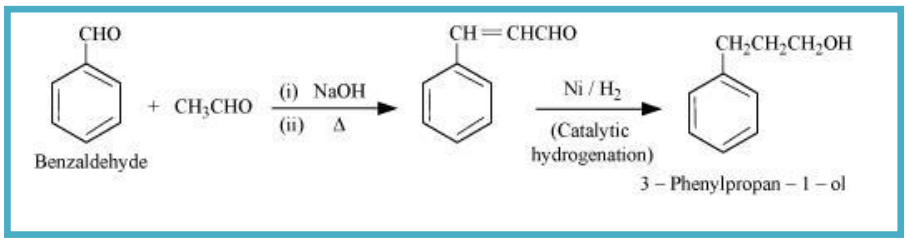
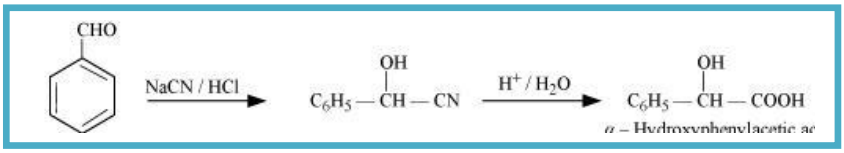
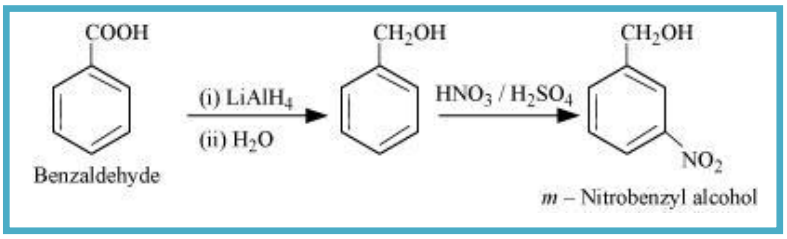


(vii)



(viii)



16. Describe the following:

(i) Acetylation

(ii) Cannizzaro reaction

(iii) Cross aldol condensation

(iv) Decarboxylation

Answer 12.16

(i) **Acetylation**

When an acetyl group is introduced into an organic compound, it is known as acetylation. It is usually carried out in the presence of a base such as pyridine, etc. Acetyl chloride and acetic anhydride are commonly used as acetylating agents.For example, acetylation of ethanol produces ethyl acetate.

$$CH_3CH_2OH + CH_3COCl \xrightarrow{Pyridine} CH_3COOC_2H_5 + HCl$$

Ethanol Acetyl chloride Ethyl acetate

(ii) **Cannizzaro reaction**:

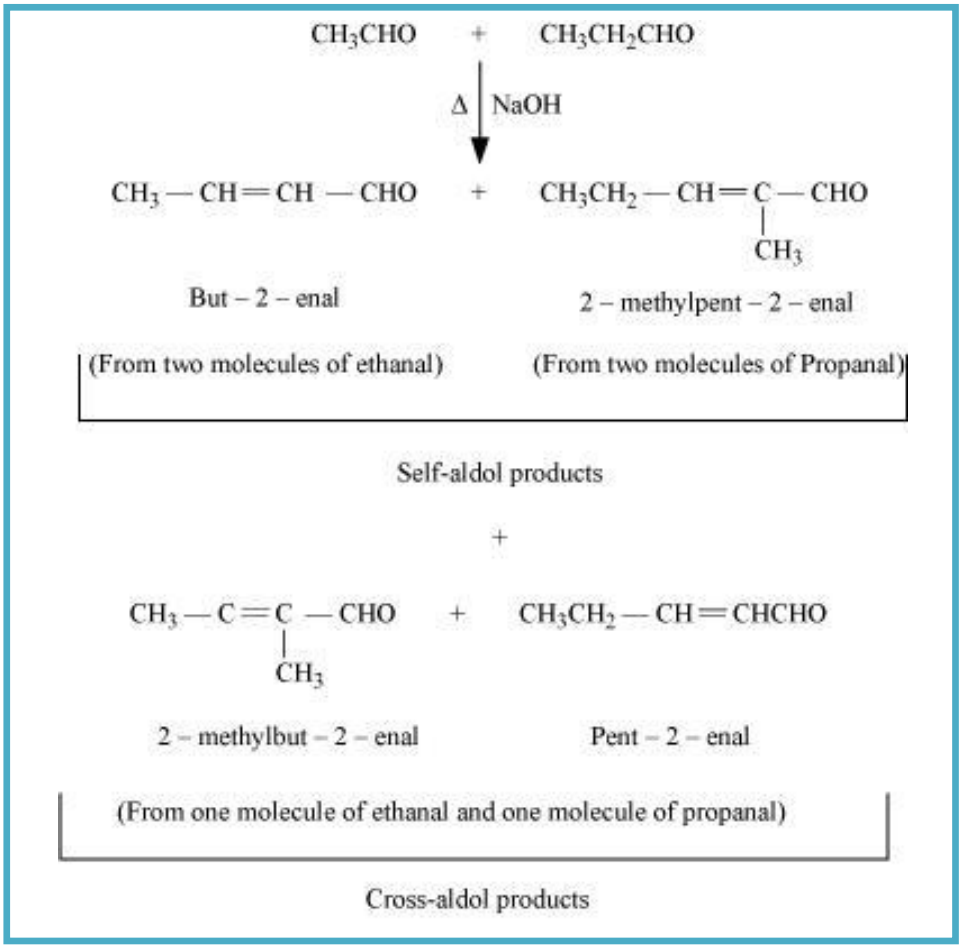
Aldehydes which have don't have α-hydrogen, they undergo this reaction. In this, aldehydes undergo self oxidation-reduction on treatment with concentrated alkalis. In this reaction, two molecules of aldehydes participate where one is reduced to alcohol and the other is oxidized to carboxylic acid. For example: -

$$2CH_3CHO + Conc.KOH \rightarrow CH_3CH_2OH + CH_3COOK$$

Ethanal Ethanol Potassium Ethanoate

(iii) **Cross-aldol condensation**:

It is carried out between two different aldehydes, or two different ketones, or an aldehyde and a ketone which contain α-hydrogen. In this reaction, four compounds are obtained as products. For example: -



(iv) **Decarboxylation**:

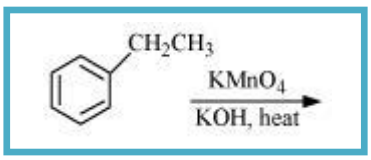
In this reaction, carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda-lime.

$$CH_3COONa \xrightarrow[\Delta]{\text{Soda-lime}(NaOH:CaO=3:1)} CH_4 + Na_2CO_3$$

Sodium ethanoate Methane

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

(i)



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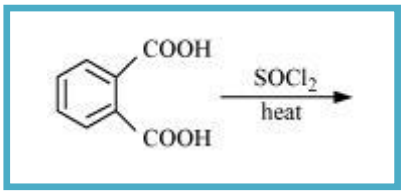
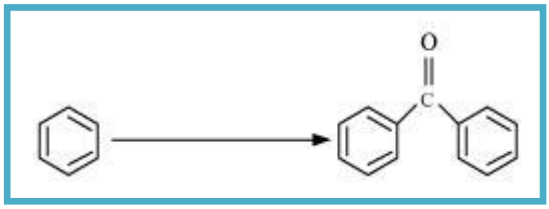


(iii)

(iv)



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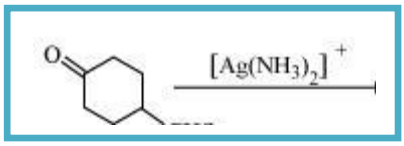

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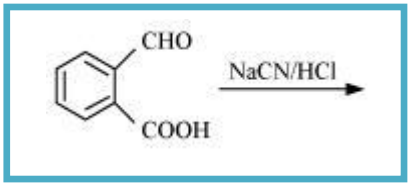
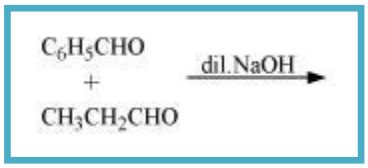


(vii)



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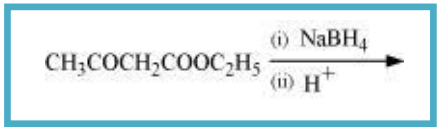

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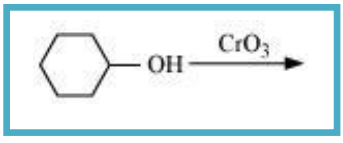
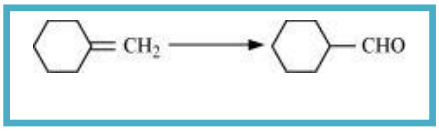
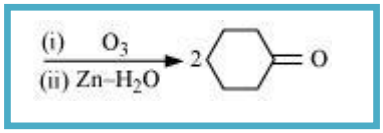


(x)

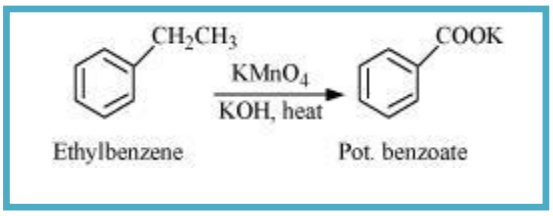


(xi)



Answer 12.17

(i)



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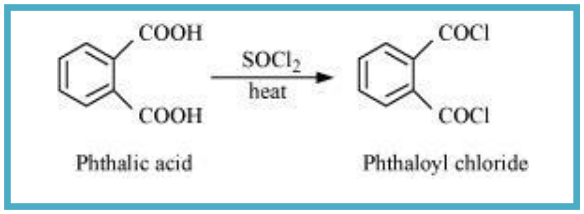
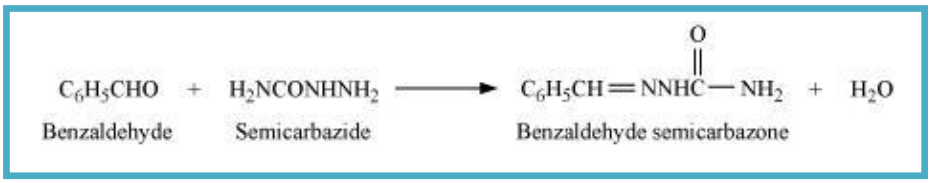
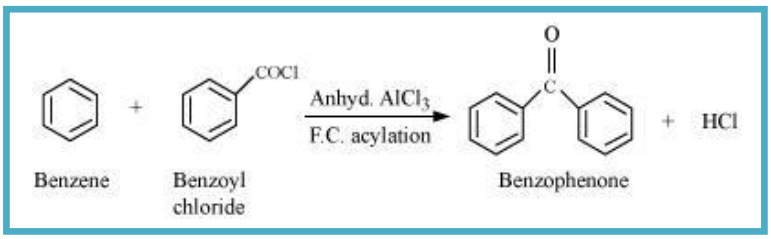


(iii)



(iv)



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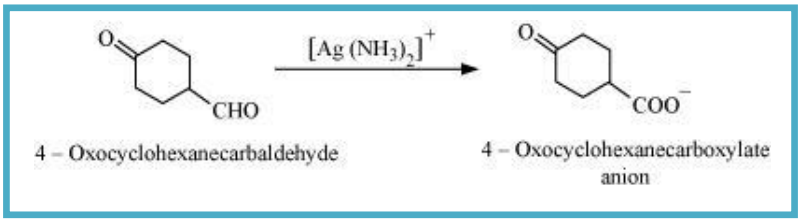

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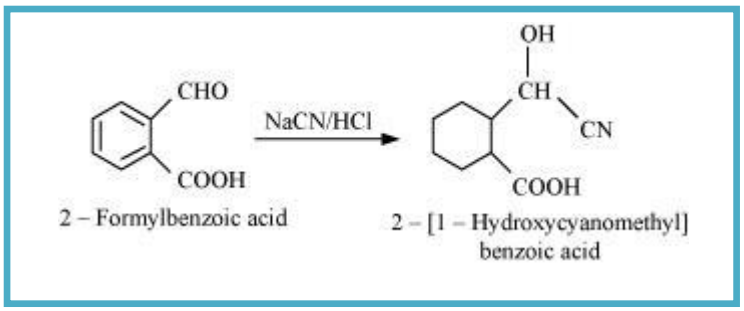
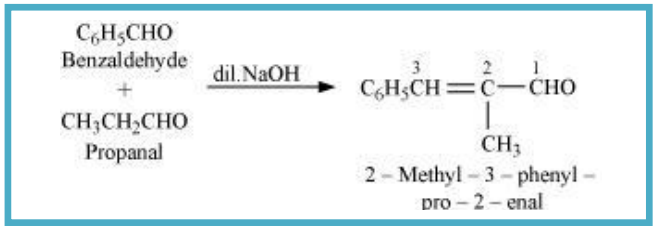


(vii)



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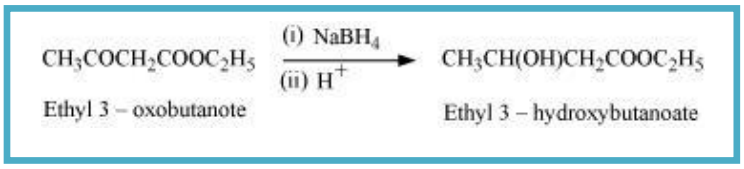

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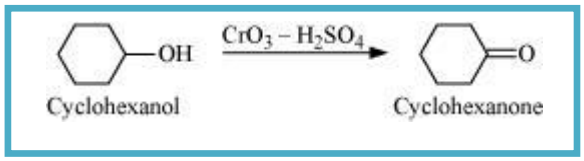

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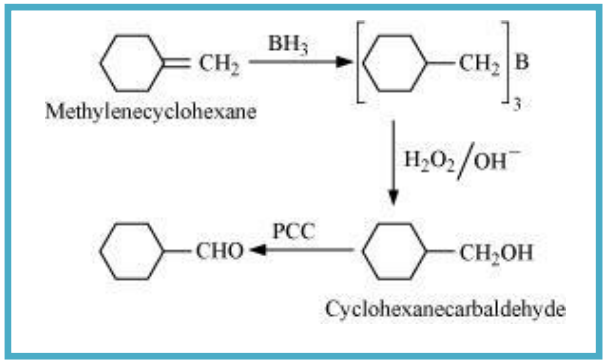
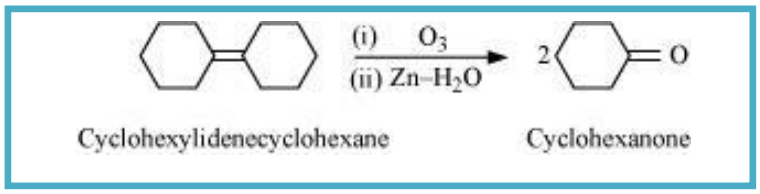


(xi)



18. Give plausible explanation for each of the following:

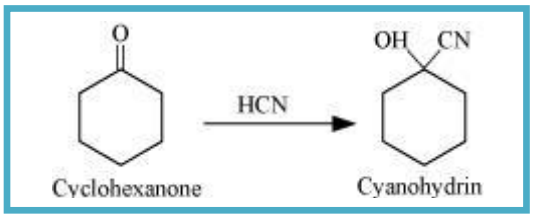
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

(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.

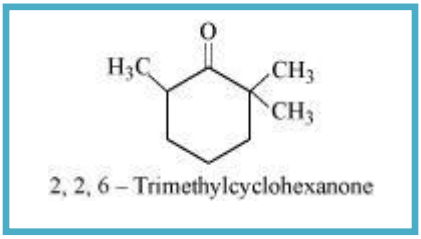
Answer 12.18

(i) Cyclohexanones form cyanohydrins:



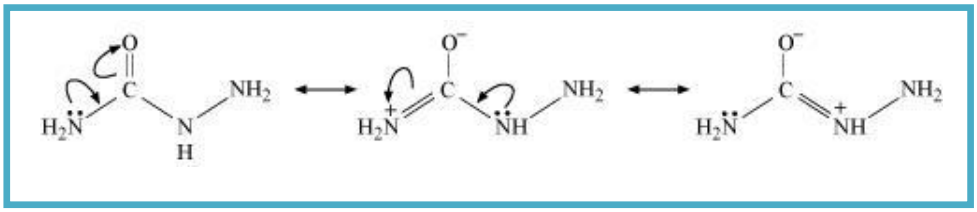
In this, CN^- can easily attack without any steric hindrance.

But, in the case of 2, 2, 6 trimethylcydohexanone, methyl groups at α-positions offer steric hindrances and as a result, CN^- cannot attack effectively.



Thus, it does not form a cyanohydrin.

(ii) Semicarbazide undergoes resonanceas follows:



Therefore, the electron density on $-NH_2$ group involved in the resonance also decreases. As a result, it won't be able to act as a nucleophile. Since the other $-NH_2$ group is not involved in resonance; it can act as a nucleophile and can attack carbonyl-carbon atoms of aldehydes and ketones to produce semicarbazones.

(iii) Formation of ester: -

$$R-COOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

If we don't remove water or ester as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible.

Thus, in order to produce more ester, it is required to shift the equilibrium in the forward direction.

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 12.19

% of carbon = 69.77 %

% of hydrogen = 11.63 %

% of oxygen = {100 − (69.77 + 11.63)} %

= 18.6 %

Ratio of the number of carbon, hydrogen, and oxygen atoms in the organic compound is:

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

$$=5.8:11.6:1.16$$
$$=5:10:1$$

Thus, the empirical formula of the compound is $C_5H_{10}O$.

Now, the empirical formula mass = 5 × 12 + 10 ×1 + 1 × 16

= 86

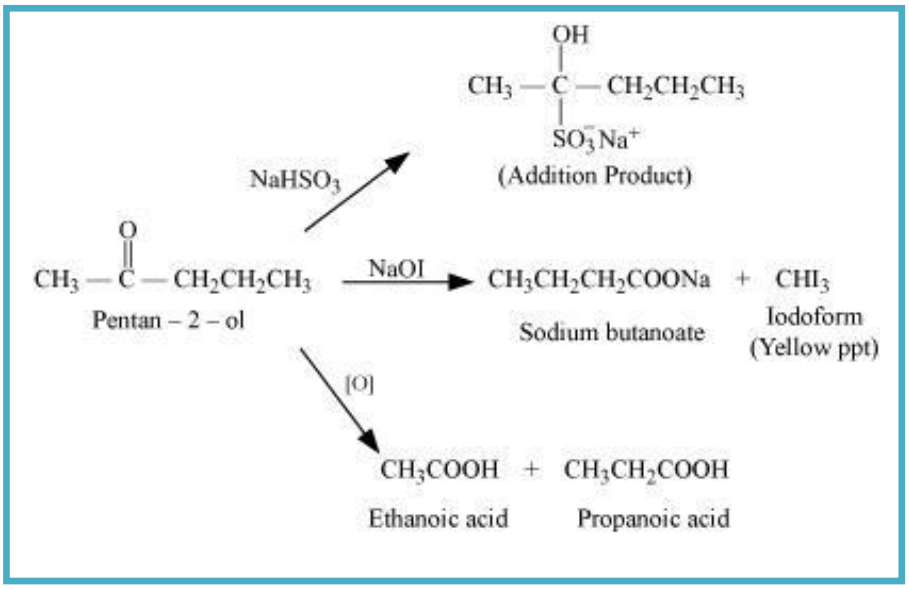
Molecular mass of the compound = 86

Therefore, the molecular formula of the compound is given by $C_5H_{10}O$.

- Now, the given compound does not reduce Tollen's reagent, so it is not an aldehyde.
- Also, the compound forms sodium hydrogen sulphate addition products and gives a positive iodoform test. Since the compound is not an aldehyde, it must be a methyl ketone.
- The given compound also gives a mixture of ethanoic acid and propanoic acid.

Hence, the given compound is pentan−2−ol.

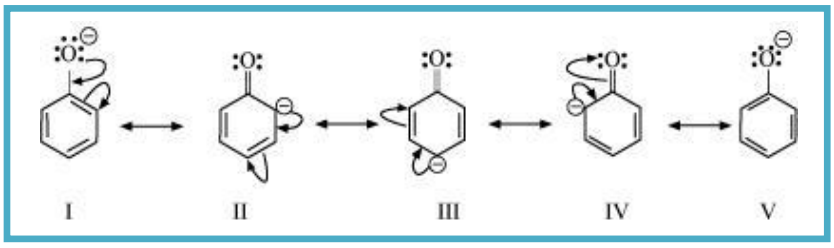
Given reactions are:



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

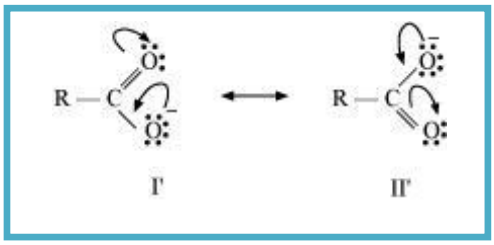
Answer 12.18

Resonance structures of phenoxide ion are:



We can observe from above structures that in II, III and IV, less electronegative carbon atoms carry a negative charge. Thus, these three structures contribute negligibly towards the resonance stability of the phenoxide ion. Hence, these structures can be eliminated. Only structures I and V carry a negative charge on the more electronegative oxygen atom.

Resonance structures of carboxylate ion are:



In resonating structures I′ and II′, the negative charge is delocalized over two oxygen atoms.

But in resonating structures I and V of the phexoxide ion, the negative charge is localized on the same oxygen atom. Thus, the resonating structures of carboxylate ion are more stable than phenoxide ion.

Hence, carboxylic acid is a stronger acid than phenol.