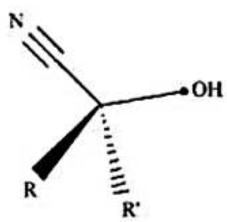
NCERT Exercise

Question 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
(vii) Imine
(ix) 2,4-DNP-derivative
(x) Schiff's base

Solution 1:
(i) Cyanohydrin:
Cyanohydrins are organic compounds having the formula RR′C(OH)CN, where R and R′can be alkyl or aryl groups.



Aldehydes and ketones react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide ($NaCN$) as a catalyst to field cyanohydrin. These reactions are known as cyanohydrin reactions.

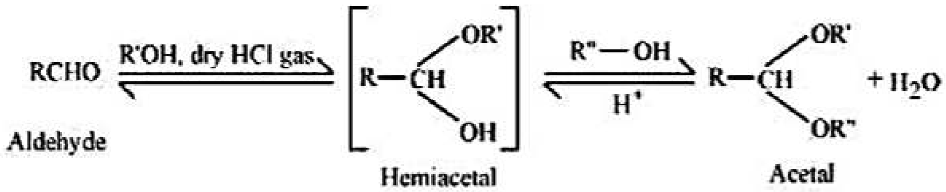
$$\underset{Ketone}{RR'C = O} + HCN \xrightarrow{NaCN} \underset{Cyanodydrin}{RR'C(OH)CN}$$

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.

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OR''}{|}}{C}}-OR'$$

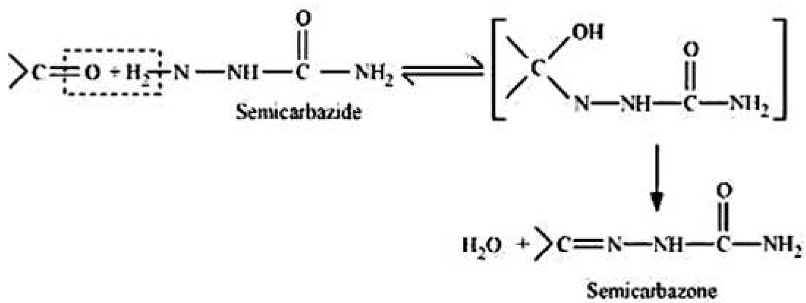
General Structure of an acetal

When aldehydes are treated with two equivalents of a monohydric alcohol in the presence of dry HCl gas, hemiacetals are produced that further react with one more molecule of alcohol to yield acetal.



(iii) Semicarbarbazone:

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



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

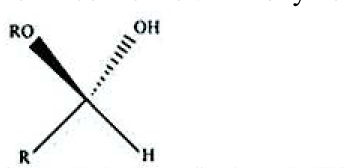
(iv) Aldol:

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.

$$\underset{\text{Propanal}}{2CH_3CH_2-CHO} \xrightleftharpoons{\text{dil NaOH}} \underset{4-\text{Hydroxyhexanal (Aldol)}}{CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-CHO}$$

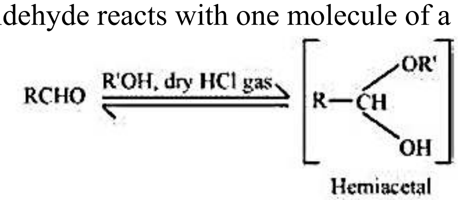
(v) Hemiacetal:

Hemiacetals are α−alkoxyalcohols



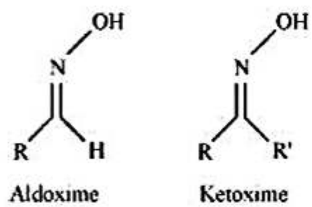
General structure of a hemiacetal

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

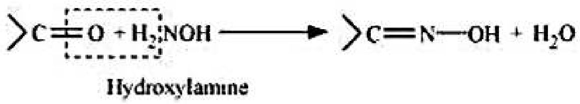


(vi) Oxime:

Oximes are a class of organic compounds having 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.

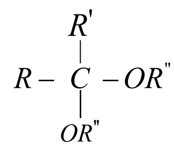


On treatment with hydroxylamine in a weakly acidic medium, aldehydes or ketones formoximes.



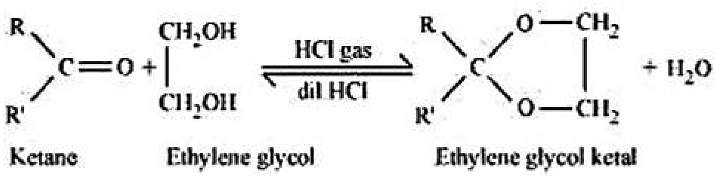
(vii) Ketal:

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.



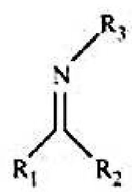
General structure of a ketal

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



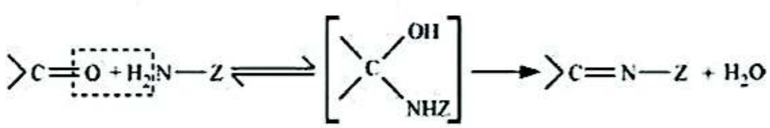
(viii) Imine:

Imines are chemical compounds containing a carbon nitrogen double bond.



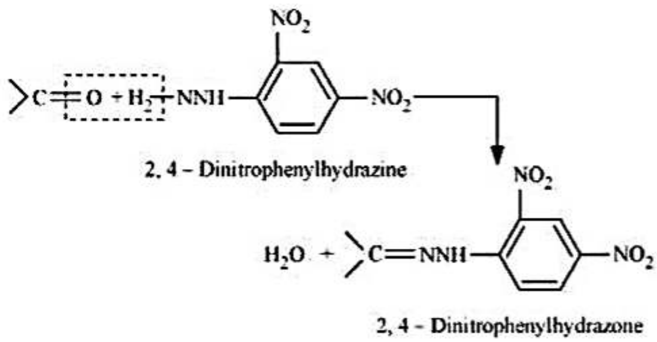
General structure of an imine

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



(ix) 2, 4−DNP−derivative:

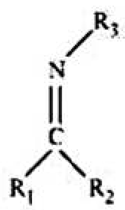
2, 4−dinitrophenylhydrazones are 2, 4−DNP−derivatives, which are produced when aldehydes or ketones react with 2, 4−dinitrophenylhydrazine in a weakly acidic medium.



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

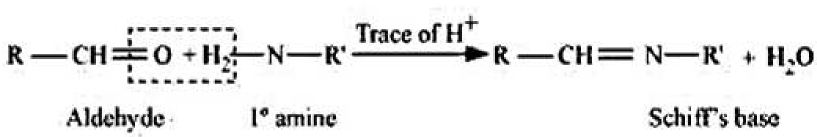
(x) Schiff's base:

Schiff's base (or azomethine) is a chemical compound containing 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. It is named after a scientist, Hugo Schiff.



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.



Question 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) $OHCC_6H_4CHO-p$

Solution 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

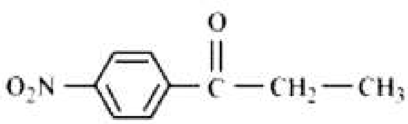
Question 3:

Draw the structures of the following compounds.
(i) 3-Methylbutanal **(ii)** *p*-Nitropropiophenone
(iii) *p*-Methylbenzaldehyde **(iv)** 4-Methylpent-3-en-2-one 4-chloropentan-2-one
(vi) 3-Bromo-4-phenylpentanoic acid **(vii)** p, p'-Dihydroxybenzophenone
(viii) Hex-2-en-4-ynoic acid

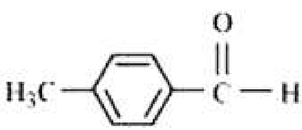
Solution 3:

$$(\text{i})\ H_3C-\underset{|}{\overset{CH_3}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

(ii)



(iii)

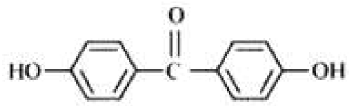


$$(\text{iv})\ H_3C-\overset{O}{\overset{\|}{C}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$$

$$(\text{v})\ H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$$

$$(\text{vi})\ H_3C-\overset{C_6H_5}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(vii)



(viii) $H_3C-C\equiv C-CH=CH-\overset{\overset{O}{\|}}{C}-OH$

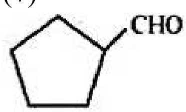
Question 4:

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

$(i) CH_3CO(CH_2)_4 CH_3$ $(ii) CH_3CH_2CHBrCH_2CH(CH_3)CHO$

$(iii) CH_3(CH_2)_5 CHO$ $(iv) Ph-CH=CH-CHO$

(v)



(vi) $PhCOPh$

Solution 4:

(i) $CH_3CO(CH_2)_4 CH_3$

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) $CH_3(CH_2)_5 CHO$

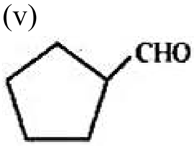
IUPAC name: Heptanal

(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

Question 5:

Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cyclopropanone oxime

(iii) Acetaldehydedimethylacetal

(iv) The semicarbazone of cyclobutanone

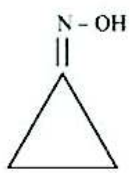
(v) The ethylene ketal of hexan-3-one

(vi) The methyl hemiacetal of formaldehyde

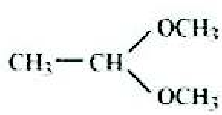
Solution 5:

(i)

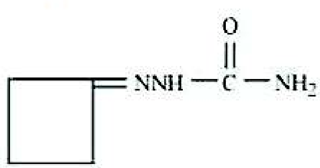
(ii)



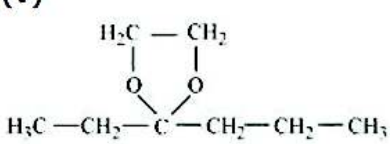
(iii)



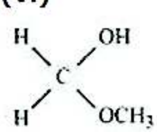
(iv)



(v)



(vi)



Question 6:

Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

(i) PhMgBr and then H_3O^+

(ii) Tollens' reagent

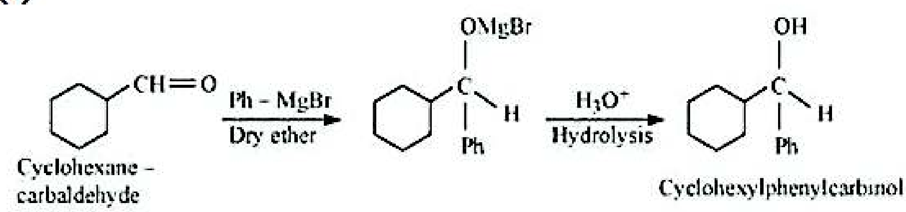
(iii) Semicarbazide and weak acid

(iv) Excess ethanol and acid

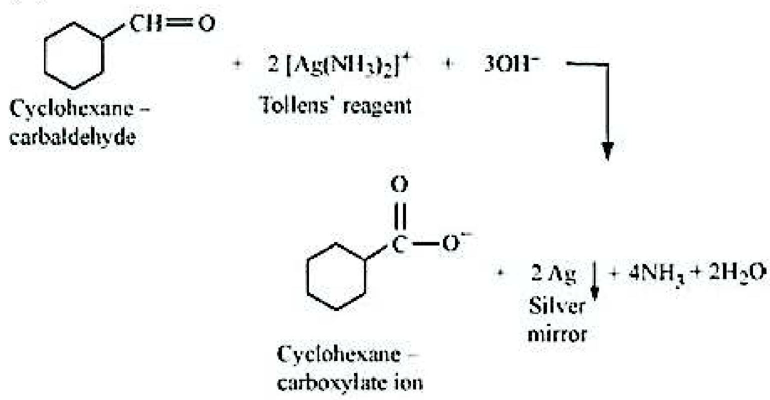
(v) Zinc amalgam and dilute hydrochloric acid

Solution 6:

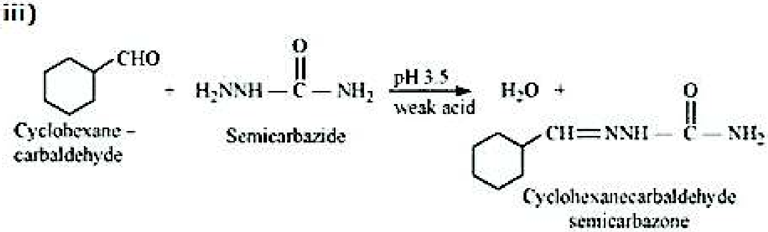
(i)



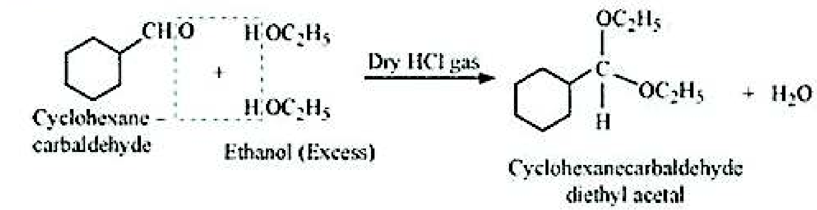
(ii)

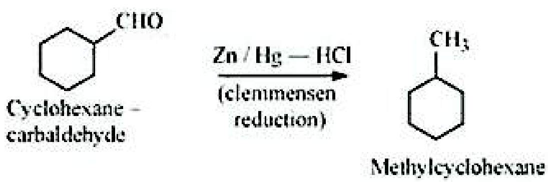


(iii)



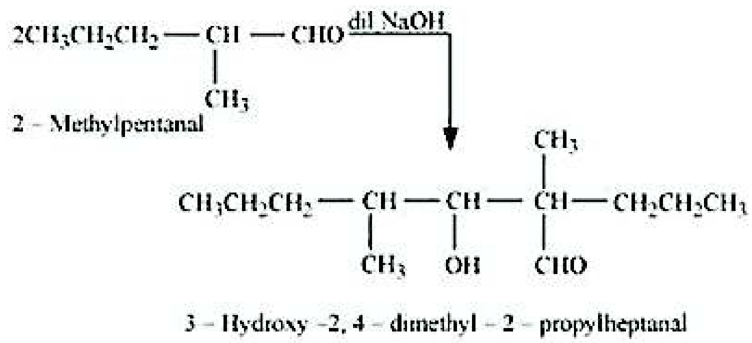
(iv)



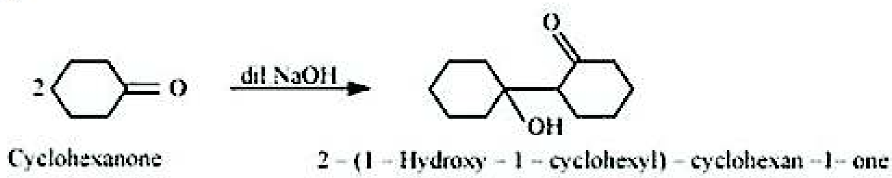


Question 7:
Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.
(i) Methanal
(ii) 2-Methylpentanal
(iii) Benzaldehyde
(iv) Benzophenone
(v) Cyclohexanone
(vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde
(viii) Butan-1-ol
(ix) 2, 2-Dimethylbutanal

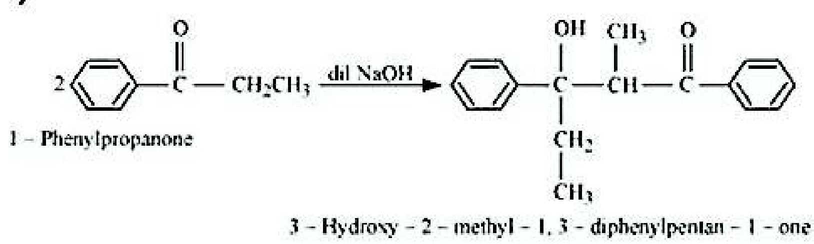
Solution 7:
Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation. The compounds (ii) 2−methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vii)phenylacetaldehyde contain one or more α-hydrogen atoms. Therefore, these undergo aldol condensation.
Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions. The compounds (i)Methanal,(iii) Benzaldehyde, and (ix) 2, 2-dimethylbutanal do not have any
α- hydrogen.Therefore, these undergo cannizzaro reactions. 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.
Aldol condensation (ii)



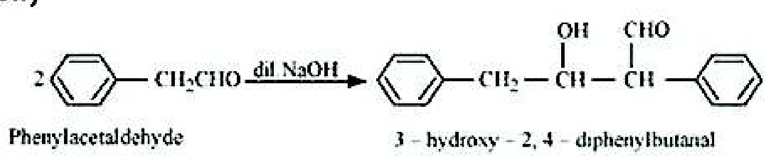
(v)



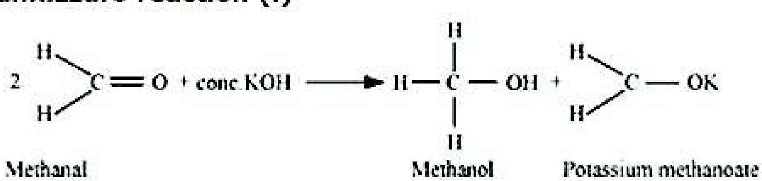
(vi)



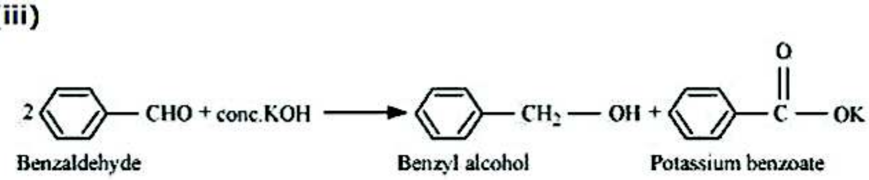
(vii)



Cannizzaro reaction (i)



(iii)



(ix)

$$\underset{2,2-dimethylbutanal}{CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO} \xrightarrow{\text{conc. NaOH}} \underset{\text{2,2-Dimethylbutan-1-o}}{CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OH} + \underset{\text{Sodium2,2-dimethylbutanoate}}{CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-ONa}$$

Question 8:
How will you convert ethanal into the following compounds?
(i) Butane-1, 3-diol **(ii)** But-2-enal **(iii)** But-2-enoic acid

Solution 8:
(i) On treatment with dilute alkali, ethanal produces 3-hydroxybutanal gives butane-1, 3-diol on reduction.

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{dil\ NaOH} \underset{\text{3-Hydroxybutanal}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO} \xrightarrow[(Reduction)]{NaBH_4} \underset{\text{Butane-1,3-diol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-OH}$$

(ii) On treatment with dilute alkali, ethanal gives 3-hydroxybutanal which on heating produces but-2-enal.

$$\underset{Ethanal}{CH_3CHO} \xrightarrow{dil\ NaOH} \underset{3-Hydrocybutanal}{CH_3-\overset{\overset{OH}{|}}{C}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{But-2-enal}{CH_3-CH=CH-CHO}$$

(iii) When treated with Tollen's reagent, But-2-enal produced in the above reaction produces but-2-enoic acid.

$$\underset{But-2-enal}{CH_3-CH=CH-CHO} \xrightarrow[Tollen's\ reagent]{[Ag(NH_3)_2]^+OH^-} \underset{But-2-enoic\ acid}{CH_3CH=CHCOOH}$$

Question 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.

Solution 9:
(i) Taking two molecules of propanal, one which acts as a nucleophile and the other as an electrophile.

$$\underset{Propanal}{2CH_3CH_2CHO} \xrightarrow{dil\ NaOH} \underset{3-hydroxy-2-methylpentanal}{CH_3CH_2-\overset{\overset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CHO}$$

(ii) Taking two molecules of butanal, one which acts as a nucleophile and the other as an electrophile.

$$\underset{Butanal}{2CH_3CH_2CH_2CHO} \xrightarrow{dil\ NaOH} \underset{2-Ethyl-3-hydroxyhexanal}{CH_3CH_2CH_2-\overset{OH}{\overset{|}{C}H}-\overset{CH_2CH_3}{\overset{|}{C}H}-CHO}$$

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

$$\underset{\substack{Butanal \\ (Electrophile)}}{CH_3CH_2CH_2CHO} + \underset{\substack{Propanal \\ (Nucleophile)}}{CH_3CH_2CHO} \longrightarrow \underset{3-Hydroxy-2-methylpentanal}{CH_3CH_2CH_2-\overset{OH}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CHO}$$

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

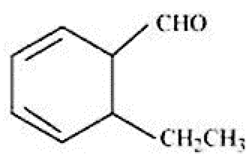
$$\underset{\substack{Propanal \\ (Electrophile)}}{CH_3CH_2CHO} + \underset{\substack{Butanal \\ (Nucleophile)}}{CH_3CH_2CH_2CHO} \longrightarrow \underset{2-Ethyl-3-hydroxyhexanal}{CH_3CH_2CH_2-\overset{OH}{\overset{|}{C}H}-\overset{CH_2CH_3}{\overset{|}{C}H}-CHO}$$

Question 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.

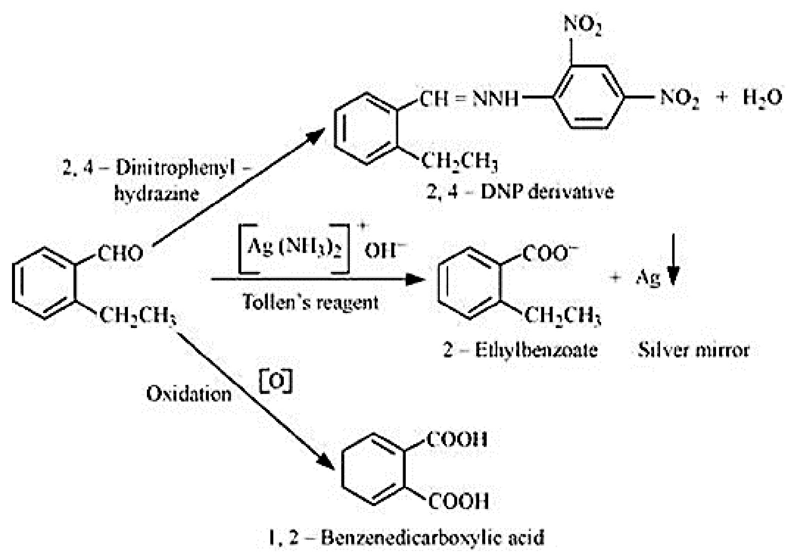
Solution 10:

It is given that the compound (with molecular formula $C_9H_{10}O$) forms 2, 4-DNP derivative and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde. Again, the compound undergoes cannizzaro reaction and on oxidation gives 1,2-benzenedicarboxylic acid. Therefore, the −CHO group is directly attached to a benzene ring and this benzaldehyde is ortho-substituted. Hence, the compound is 2-ethylbenzaldehyde.



2 – Ethylbenzaldehyde

The given reactions can be explained by the following equations.



Question 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.

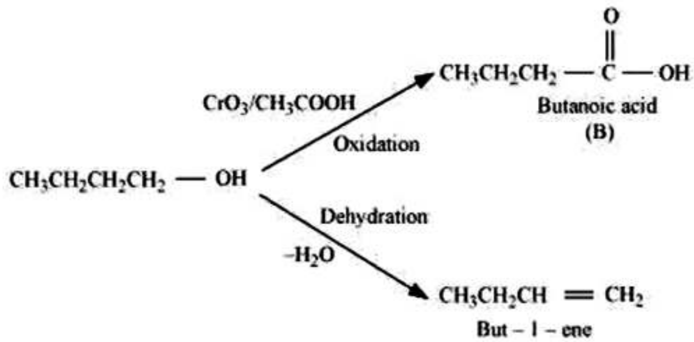
Solution 11:

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.

$$CH_3CH_2CH_2-\underset{\text{Butylbutanoate}}{\overset{\overset{\displaystyle O}{\|}}{C}}-OCH_2CH_2CH_2CH_3$$

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

$$\underset{\substack{\text{Butylbutanoate}\\(A)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3} \xrightarrow{dil\,H_2SO_4} \underset{\substack{\text{Butanoic acid}\\(B)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\substack{\text{Butan-1-ol}\\(C)}}{CH_3CH_2CH_2CH_2OH}$$



Question 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)

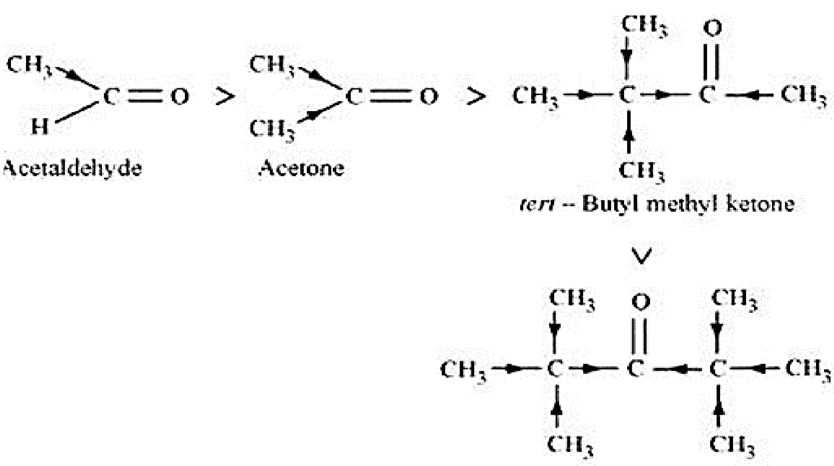
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$(acid strength)

(iii)

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

Solution 12:

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



Hence, the given compounds can be arranged according to their increasing reactivities toward HCN as:

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

(ii) After losing a proton, carboxylic acids gain a negative charge as shown:

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

Now, any group that will help stabilise the negative charge will increase the stability of the carboxyl ion and as a result, will increase the strength of the acid. Thus, groups having +Ieffect 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. Now, the +I effect of isopropyl group is more than that of *n*-propyl group.

Hence, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Also, the −I effect grows weaker as distance increases. Hence, $CH_3CH(Br)CH_2COOH$ is a weaker acid than $CH_3CH_2CH(Br)COOH$.

Hence, the strengths of the given acids increase as:

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

(iii) As we have seen in the previous case, electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid than 4-nitrobenzoic acid. Hence, the strengths of the given acids increase as:

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

Question 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

Solution 13:

(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.

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

(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.

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

(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.

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

(ii) 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.

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

$$\underset{\text{Benzophenone}}{C_6H_5COCH_3} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

(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.

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

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

$$\underset{\text{Benzonic acid}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\(\text{Buff coloured ppt})}}{\left(C_6H_5COO\right)_3Fe} + 3HCl$$

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

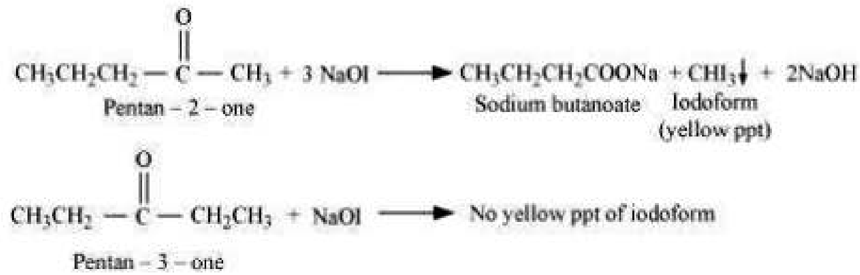
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + CO_2\uparrow + H_2O$$

$C_6H_5COOC_2H_5$ + $NaHCO_3$ ------------→ No effervercense due to evolution of CO_2 gas

(v) 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.



(vi) 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 being a ketone does not.

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

(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.

$$\underset{Acetophenone}{C_6H_5COCH_3} + 3NaOI \longrightarrow \underset{Sodium\ benzoate}{C_6H_5COONa} + \underset{\substack{Iodoform \\ (yellow\ ppt)}}{CHI_3} + 2NaOH$$

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

Iodoform test

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom responds to the 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 state.

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

Question 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

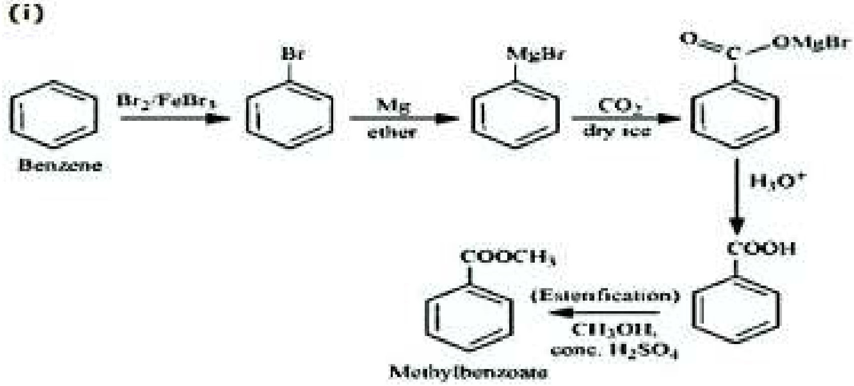
(i) Methyl benzoate **(ii)** *m*-Nitrobenzoic acid

(iii) *p*-Nitrobenzoic acid **(iv)** Phenylacetic acid

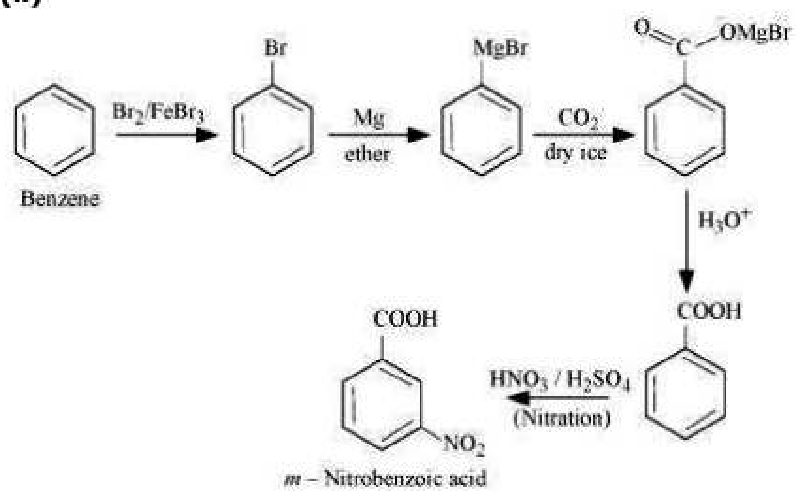
(v) *p*-Nitrobenzaldehyde.

Solution 14:

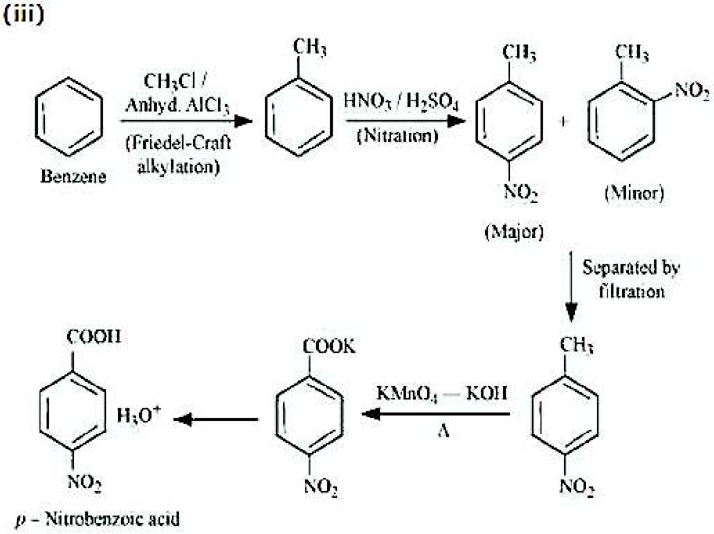
(i)


Br
MgBr
O=C—OMgBr
Br2/FeBr3
Mg
ether
CO2
dry ice
Benzene
H3O+
COOH
COOCH3
(Esterification)
CH3OH,
conc. H2SO4
Methylbenzoate

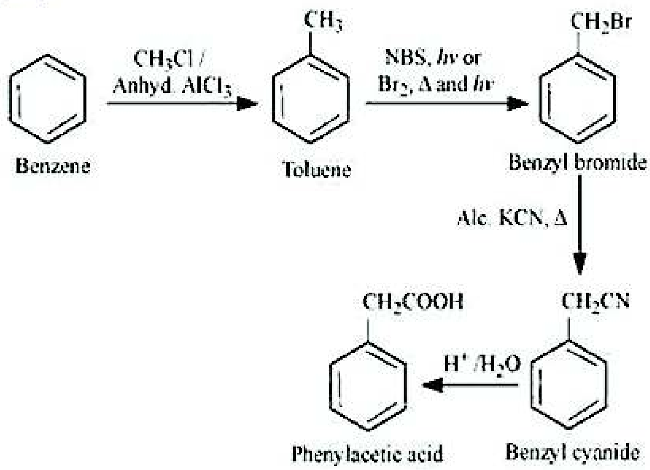
(ii)


Br
MgBr
O=C—OMgBr
Br2/FeBr3
Mg
ether
CO2
dry ice
Benzene
H3O+
COOH
COOH
HNO3 / H2SO4
(Nitration)
NO2
m – Nitrobenzoic acid

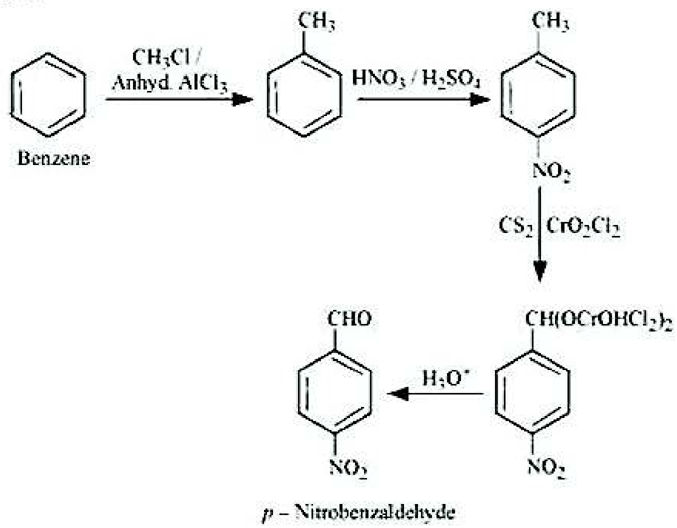
(iii)


CH3
CH3
CH3
CH3Cl /
Anhyd. AlCl3
(Friedel-Craft
alkylation)
Benzene
HNO3 / H2SO4
(Nitration)
NO2
NO2
(Minor)
(Major)
Separated by
filtration
COOH
COOK
CH3
KMnO4 — KOH
Δ
H3O+
NO2
NO2
NO2
p – Nitrobenzoic acid

(iv)



(v)



Question 15:

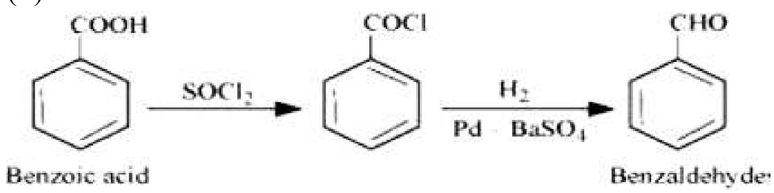
How will you bring about the following conversions in not more than two steps?

(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

Solution 15:

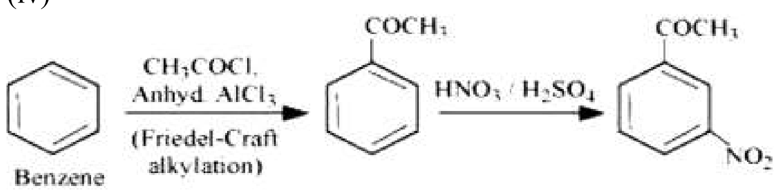
$$(i)\ CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{NaBH_3} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[\Delta]{conc.H_2SO_4} \underset{Propene}{CH_3-CH=CH_2}$$

(ii)

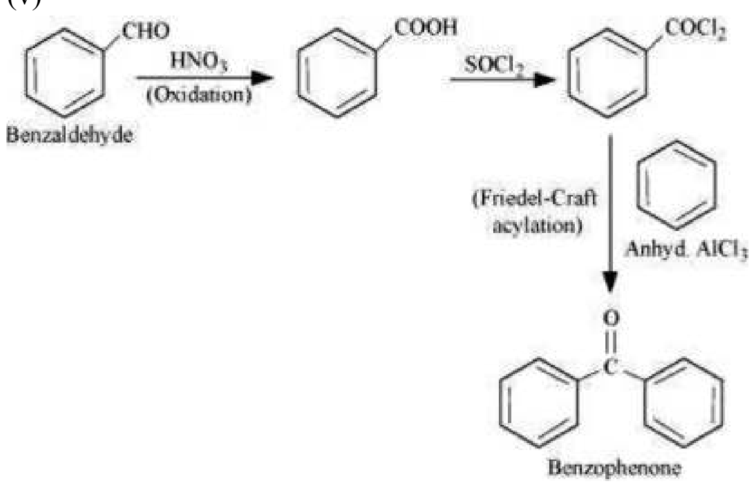


$$(iii)\ CH_3-\underset{Ethanol}{CH_2}-OH \xrightarrow{CrO_3} CH_3CHO \xrightarrow[(Aldol\ condensation)]{dil.NaOH} \underset{3-hydroxybutanal}{CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CHO}$$

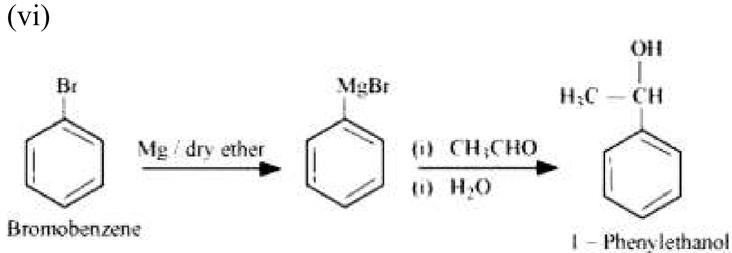
(iv)



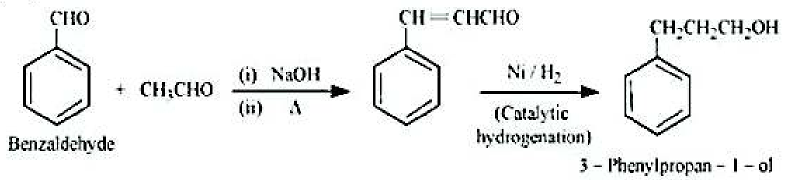
(v)



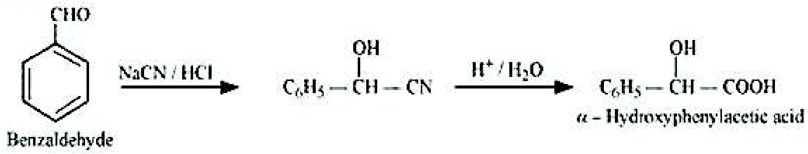
(vi)



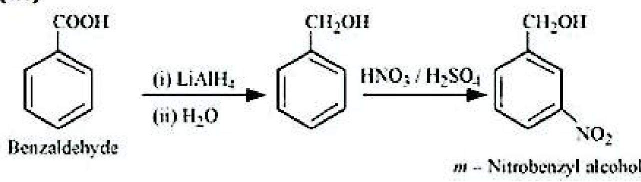
(vii)



(viii)



(ix)



Question 16:
Describe the following:
(i) Acetylation
(ii) Cannizzaro reaction
(iii) Cross aldol condensation
(iv) Decarboxylation

Solution 16:
(i) Acetylation
The introduction of an acetyl functional group into an organic compound is known as acetylation. It is usually carried out in the presence of a base such as pyridine, dimethylaniline, etc. This process involves the substitution of an acetyl group for an active hydrogen atom. Acetyl chloride and acetic anhydride are commonly used as acetylating agents.
For example, acetylation of ethanol produces ethyl acetate.

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

(ii) Cannizzaro reaction:
The self oxidation-reduction (disproportionation) reaction of aldehydes having no α -hydrogen's on treatment with concentrated alkalis is known as the Cannizzaro reaction. In this reaction, two molecules of aldehydes participate where one is reduced to alcohol and the other is oxidized to carboxylic acid.
For example, when ethanol is treated with concentrated potassium hydroxide, ethanol and potassium ethanoate are produced.