EXERCISE QUESTIONS

CHAPTER-12 Aldehydes, Ketones and Carboxylic Acids

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

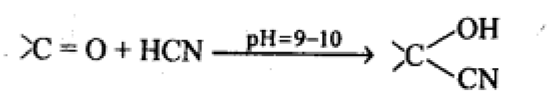
(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone

(iv) Aldol (v) Hemiacetal (vi) Oxime

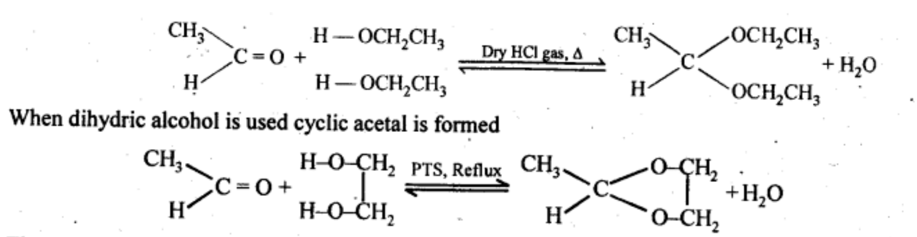
(vii) Ketal (vii) Imine (ix) 2,4-DNP-derivative

(x) Schiff's base

Ans - (i) Cyanohydrins are gem-Hydroxynitriles, which are substances with hydroxyl and cyano groups on the same carbon atom. In a weakly basic media, they are made by adding HCN to aldehydes or ketones.

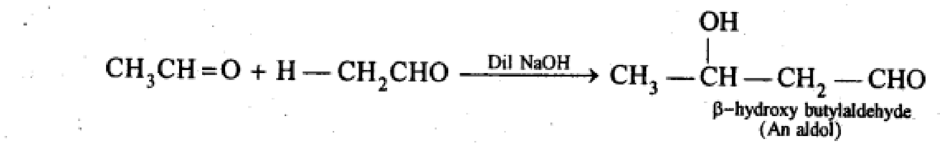


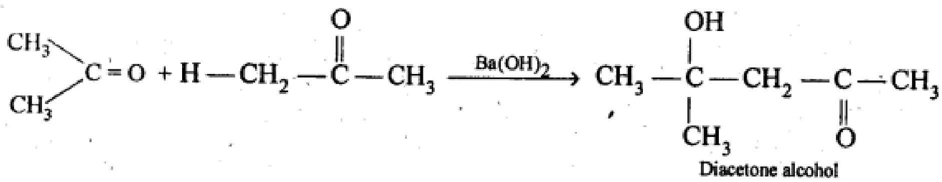
(ii) Acetals are dialkoxy compounds that have two alkoxy groups attached to the terminal carbon atom. These are created when two equivalents of a monohydric alcohol react with an aldehyde in the presence of dry HCl gas.



(iii) Semicarbazides, which are derived from aldehydes and ketones, act on them in an acidic solution to form semicarbazones.

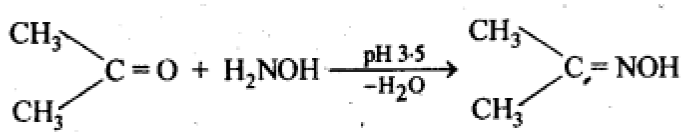
(iv) P-hydroxy aldehydes or ketones, known as aldols, are created when two molecules of the same compound or one molecule of each of two separate compounds are combined in the presence of a diluted aqueous base.



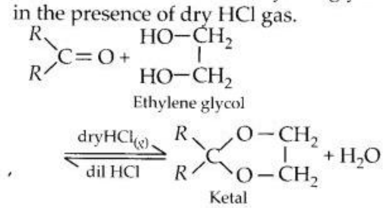


(v)Alkoxyalcohols are referred to as hemiacetals in gem. These are made by mixing one molecule of a monohydric alcohol with an aldehyde while dry HCl gas is present.

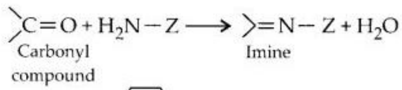
(vi)Oximes are created when hydroxyl amine and aldehydes or ketones combine in a mildly acidic media.

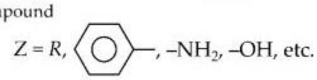


(vii) Ketals are cyclic products formed by the reaction of ketones with ethylene glycol in the presence of dry HCl gas.

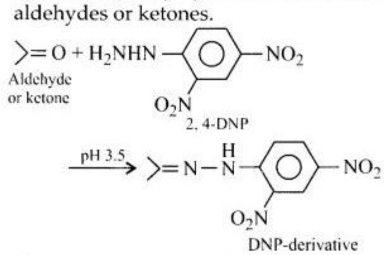


(viii) Imines are formed when carbonyl compounds react with ammonia derivative.





(ix) 2, 4-DNP derivatives are formed when 2, 4-dinitrophenylhydrazine reacts with aldehydes or ketones.



(x) Reaction between aldehydes or ketones with 1° aliphatic or aromatic amines yields a Schiff's base.

$R\text{—CHO} + H_2N\text{—}R'$

$\xrightarrow{\text{very dil } H^+} RCH\text{=N—}R' + H_2O$

Schiff's base

12.2 Name the following compounds according to IUPAC system of nomenclature:

(i) CH3CH(CH3)CH2CH2CHO

(ii) CH3CH2COCH(C2H5)CH2CH2Cl

(iii) CH3CH=CHCHO

(iv) CH3COCH2COCH3

(v) CH3CH(CH3)CH2C(CH3)2COCH3

(vi) (CH3)3CCH2COOH

(vii) OHCC6H4CHO-p

Ans - (i) 4-Methyl pentanal
(ii) 6-Chloro-4-ethylhexan-3-one
(iii) But-2-en-l-al
(iv) Pentane-2,4-dione
(v) 3,3,5-Trimethyl-hexan-2-one
(vi) 3,3-Dimethyl butanoic acid
(vii) Benzene-1,4-dicarbaldehyde

12.3 Draw the structures of the following compounds.

(i) 3-Methylbutanal

(ii) p-Nitropropiophenone

(iii) p-Methylbenzaldehyde

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

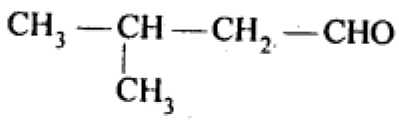
(v) 4-Chloropentan-2-one

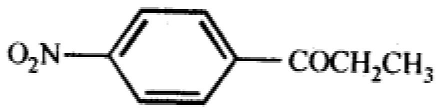
(vi) 3-Bromo-4-phenylpentanoic acid

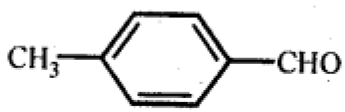
(vii) p,p'-Dihydroxybenzophenone

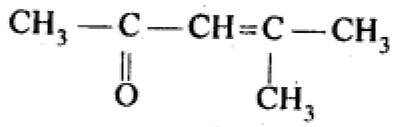
(viii) Hex-2-en-4-ynoic acid

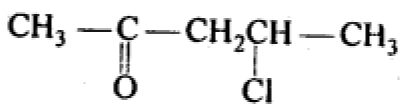
Ans – structures are:

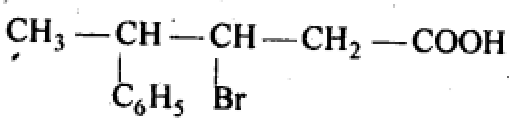
(i) 

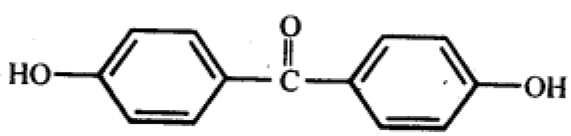
(ii) 

(iii) 

(iv) 

(v) 

(vi) 

(vii) 

(viii) $CH_3-C\equiv C-CH=CH-COOH$

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

(i) CH3CO(CH2)4CH3

(ii) CH3CH2CHBrCH2CH(CH3)CHO

(iii) CH3(CH2)5CHO

(iv) Ph-CH=CH-CHO

(v) CHO (vi) PhCOPh

Ans - (i) $CH_3CO(CH_2)_4CH_3$

IUPAC name is: Heptan-2-one

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

IUPAC name is: 4-Bromo-2-methylhaxanal

(iii) $CH_3(CH_2)_5CHO$

IUPAC name is: Heptanal

(iv) Ph-CH=CH-CHO

IUPAC name is: 3-phenylprop-2-enal

(v)

IUPAC name is: Cyclopentanecarbaldehyde

(vi) PhCOPh

IUPAC name is: Diphenylmethanone

12.5 Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cyclopropanone oxime

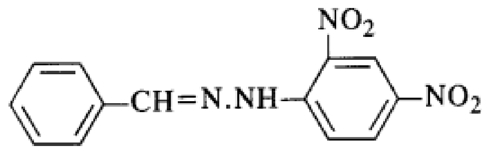
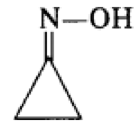
(iii) Acetaldehydedimethylacetal

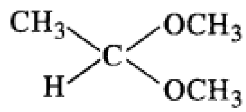
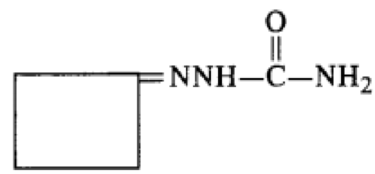
(iv) The semicarbazone of cyclobutanone

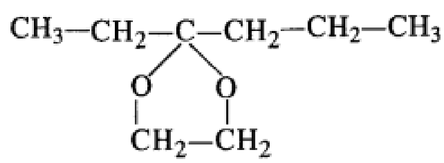
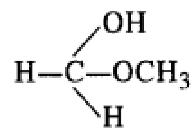
(v) The ethylene ketal of hexan-3-one

(vi) The methyl hemiacetal of formaldehyde

Ans -

(a)  (b) 

(c)  (d) 

(e)  (f) 

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

(i) PhMgBr and then H3O +

(ii) Tollens' reagent

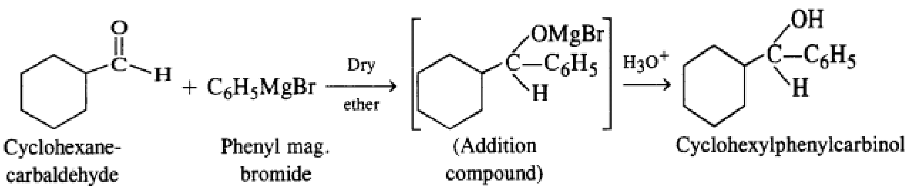
(iii) Semicarbazide and weak acid

(iv) Excess ethanol and acid

(v) Zinc amalgam and dilute hydrochloric acid

Ans -

(i)



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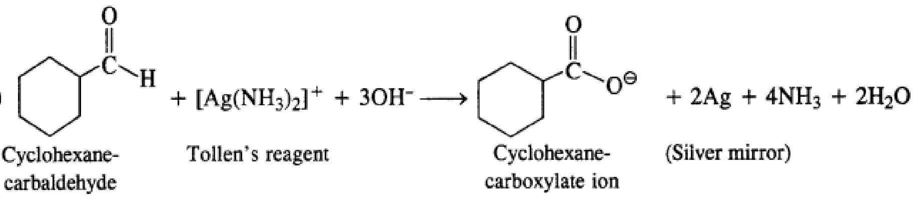

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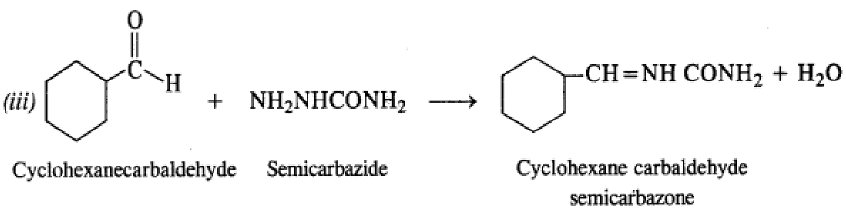

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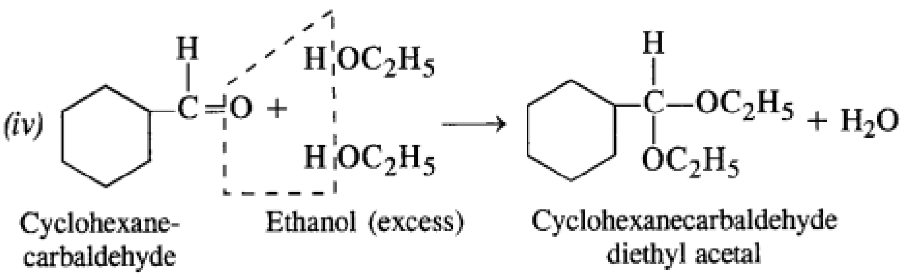

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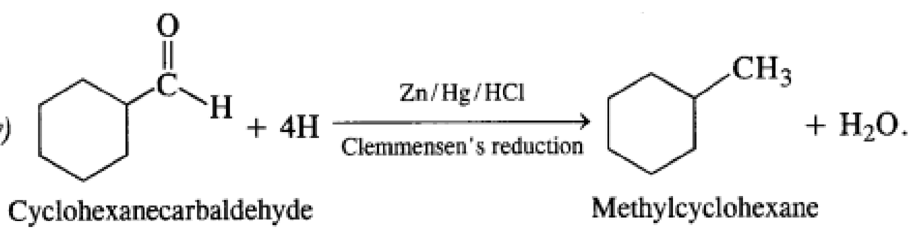


12.7 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde

(iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal

Ans - Aldol condensation happens with aldehydes and ketones that include at least one -hydrogen. One or more -hydrogen atoms can be found in the compounds (ii), 2-methylpentanal, (v), cyclohexanone, (vi), 1-phenylpropanone, and (vii), phenylacetaldehyde. These hence go through aldol condensation.

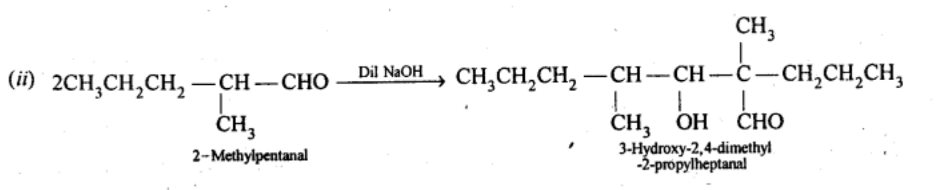
Cannizzaro reactions occur with aldehydes that don't include -hydrogen atoms. Methanal, benzaldehyde, and 2, 2-dimethylbutanal are the only three substances that lack a -hydrogen. These therefore experience cannizzaro reactions.

Compound (iv) (iv) Benzophenone is an alcohol and compound (viii) butan-1-ol is a ketone with no -hydrogen atom. As a result, neither aldol condensation nor cannizzaro reactions occur in these molecules.

(i) Methanal (HCHO):

$$\underset{\text{Methanal}}{2HCHO} + NaOH \longrightarrow \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sod. methanoate}}{HCOONa}$$

(ii) 2-Methylpentanal:



(iii) **Benzaldehyde** :

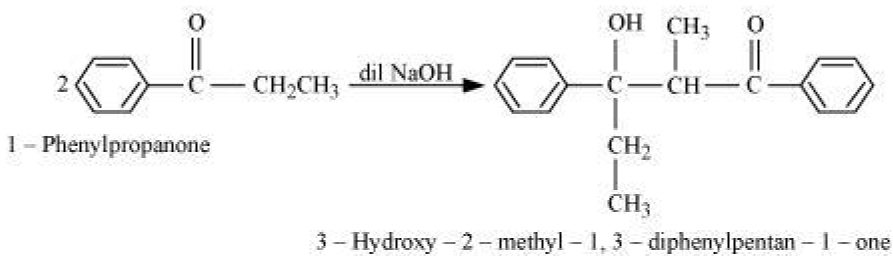
$$\underset{\text{Benzaldehyde}}{2\,C_6H_5CHO} + NaOH\ (\text{Conc.}) \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. benzoate}}{C_6H_5COONa}$$

(iv) Benzophenone : It will not give any of the two reactions aldol nor cannizaro.

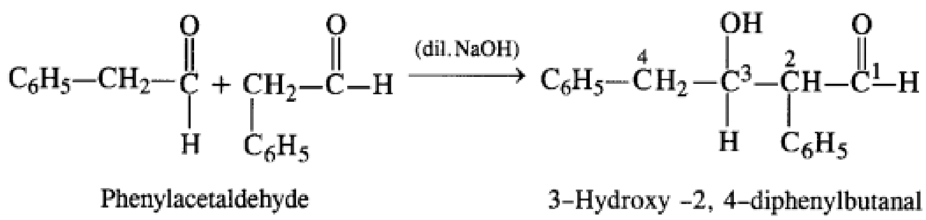
(v)

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

(vi)



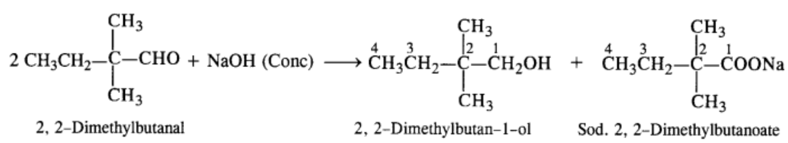
(vii)



(viii) Butan-1-ol: It will not give any of the reactions.

(ix)

(ix) **2, 2–Dimethylbutanal ($CH_3-CH_2-C(CH_3)_2-CHO$).** It will give Cannizzaro's reaction since no α-hydrogen atom is present.



12.8 How will you convert ethanal into the following compounds?

(i) Butane-1,3-diol

(ii) But-2-enal

(iii) But-2-enoic acid

Ans - On treatment with dilute alkali

(i) $2CH_3CHO \xrightarrow{\text{Dil NaOH}} \underset{\text{3-Hydroxy butanal}}{CH_3CH(OH)CH_2CHO} \xrightarrow{NaBH_4} \underset{\text{Butan-1,3-diol}}{CH_3CHOHCH_2CH_2OH}$

(ii) $2CH_3CHO \xrightarrow{\text{Dil NaOH}} CH_3CH(OH)CH_2CHO \xrightarrow[-H_2O]{H_3O^+} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$

(iii) $\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i)Dil NaOH}} CH_3CH=CHCHO \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH=CHCO_2H}$

12.9 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.

Ans - Propanal and butane both contain a-hydrogen atoms. These can go through both self- and cross-aldol condensation to produce the following four compounds:

(a) Propanal acts as both nucleophile as well as electrophile.

$$CH_3CH_2CHO + CH_3CH_2CHO \longrightarrow \underset{\text{3-Hydroxy-2-methylpentanal}}{CH_3CH_2CH(OH)-CH(CH_3)-CHO}$$

(b) Propanal as electrophile and butanal as nucleophile.

$$CH_3CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow \underset{\text{2-Ethyl-3-hydroxypentanal}}{CH_3CH_2CH(OH)-CH(CH_2CH_3)-CHO}$$

(c) Butanal as electrophile and propanal as nucleophile.

$$CH_3CH_2CH_2CHO + CH_3CH_2CHO \longrightarrow \underset{\text{3-Hydroxy-2-methylhexanal}}{CH_3CH_2CH_2-CH(OH)-CH(CH_3)-CHO}$$

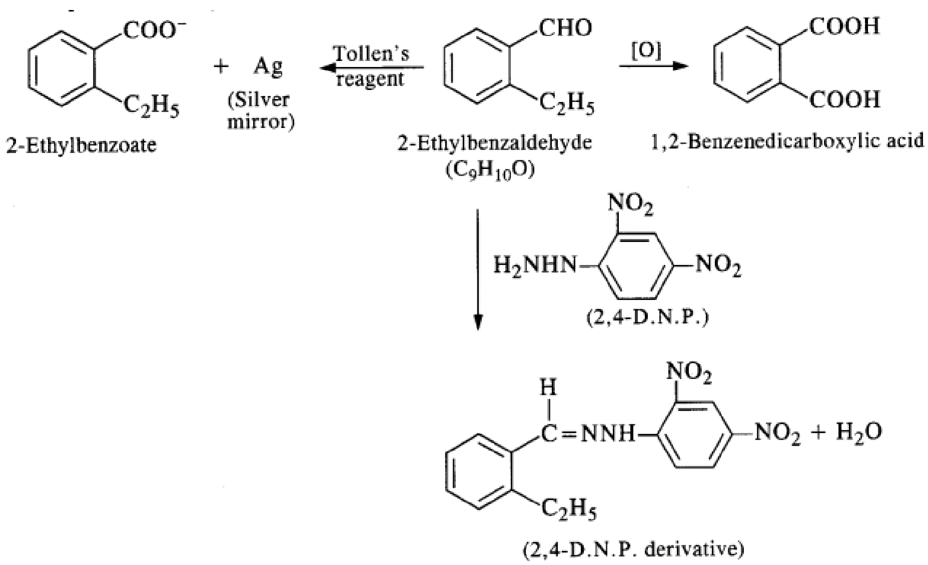
(d) Butanal acts as both nucleophile as well as an electrophile.

$$CH_3CH_2CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow \underset{\text{2-Ethyl-3-hydroxy hexanal}}{CH_3CH_2CH_2CH(OH)-CH(CH_2CH_3)-CHO}$$

12.10 An organic compound with the molecular formula C9H10O forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans - The provided substance, C9H10O, must be an aldehyde because it reduces Tollen's reagent and creates a derivative of 2,4-DNP. Because of the Cannizzaro reaction, the CHO group is consequently immediately linked to the benzene ring.

Since it produces 1, 2-benzene dicarboxylic acid upon severe oxidation, it must be an ortho- substituted benzaldehyde. O-ethyl benzaldehyde is the only o-substituted aromatic aldehyde with the chemical formula C9H10O. On the basis of this framework, all of the reactions can now be explained.



12.11 An organic compound (A) (molecular formula C8H16O2) 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.

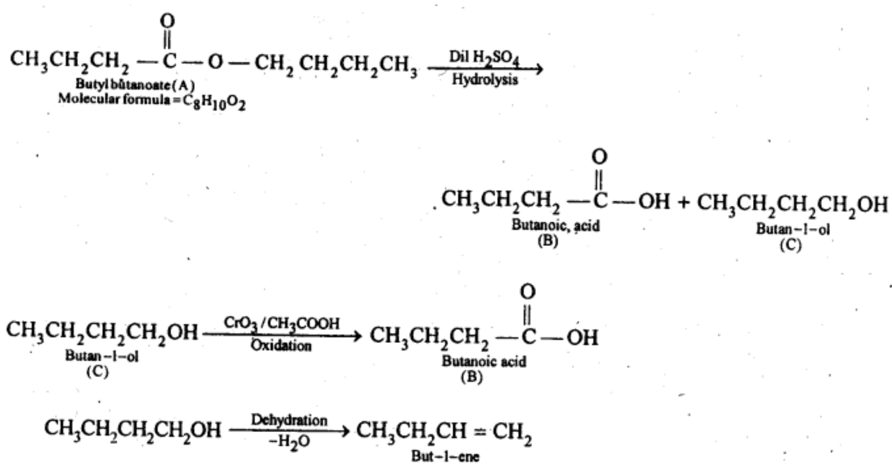
Ans - Since the carboxylic acid B and alcohol C are produced by the hydrolysis of an ester A with the chemical formula C8H16O2, and the acid B is produced by the oxidation of C with chromic acid, both the carboxylic acid B and alcohol C must have the same number of carbon atoms.

Furthermore, because ester A has eight carbon atoms, the carboxylic acid B and the alcohol C must each have four carbon atoms.

Since dehydration of alcohol C results in but-l-ene, C must be a straight chain alcohol, such as butan-l-ol.

If C is butanol, then the ester A must be butyl butanoate and the acid B must be butanoic acid.

The following are the chemical equations:



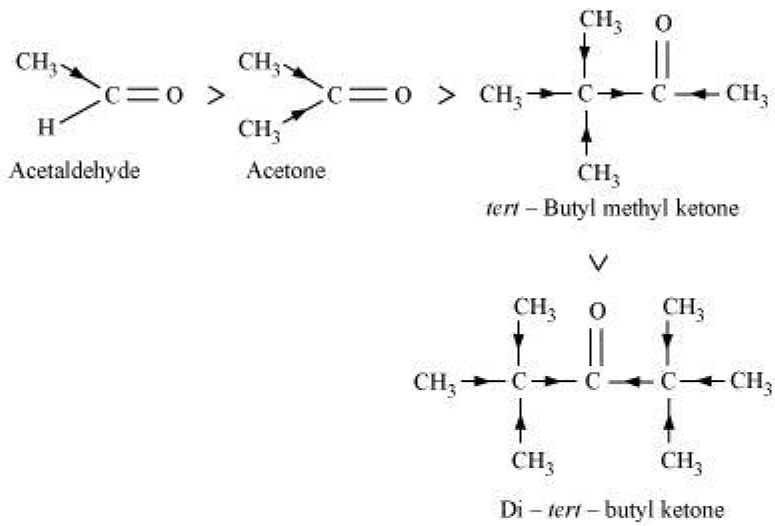
12.12 Arrange the following compounds in increasing order of their property as indicated:

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

(ii) CH3CH2CH(Br)COOH, CH3CH(Br)CH2COOH, (CH3)2CHCOOH, CH3CH2CH2COOH (acid strength)

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

Ans - (i)A nucleophile, or CN, attacks a chemical when HCN reacts with it. As a result, the compound's reactivity with HCN reduces as its negative charge rises. The +I effect grows in the compounds that are presented, as is demonstrated below. Steric impediment can be seen to rise in the similar way.



ii) We are aware that an alkyl group with the +I action weakens the acidity. Isopropyl groups have a greater +I impact than n-propyl groups. Similar to this, bromine (Br) with the -I action strengthens the acid. The greater the proximity of the carbon atom to the carboxyl (COOH) group, the greater the -I-effect and the more potent the acid. As a result, the ascending order of acidic strength is as follows:

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

(iii) Since the acidic strength is decreased by electron-donating groups, 4-methoxy benzoic acid is weaker than benzoic acid. Additionally, 3,4-dinitrobenzoic acid and 4-nitrobenzoic acid are stronger acids than benzoic acid because electron withdrawing groups increase the acidic strength. Additionally, 3,4-dinitrobenzoic acid is a stronger acid than 4-nitrobenzoic acid due to the existence of an additional -NO2 group at the /w-position with respect to a -COOH group. This results in an increase in total acidity in the following order: 4-methoxybenzoic acid, benzoic acid, 4-nitrobenzoic acid, and 3,4-dinitrobenzoic acid.

12.13 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

Ans -

(*i*) Propanal and Propanone can be distinguished by iodoform test.

$$CH_3COCH_3 + 3NaOI \longrightarrow \underset{\substack{\text{Iodoform} \\ \text{(Yellow ppt.)}}}{CH_3I\downarrow} + CH_3COONa + 2NaOH$$

This test is given by aldehydes containing —$COCH_3$ group. Propanal does not have —$COCH_3$ group thus it does not give iodoform test

(*ii*) Acetophenone and Benzophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\substack{\text{Iodoform} \\ \text{(Yellow ppt.)}}}{CH_3I\downarrow} + 2NaOH$$

$$C_6H_5COC_6H_5 \xrightarrow{NaOI} \text{No yellow ppt.}$$

This test is given by aldehydes and ketones containing –$COCH_3$ group

(*iii*) Phenol and Benzoic acid can be distinguished by $FeCl_3$ test

$$3C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{Buff-colouration ppt.}}{(C_6H_5COO)_3Fe} + 3HCl$$

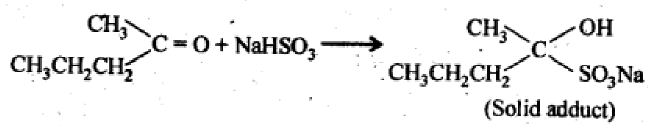
(*iv*) Benzoic acid and Ethyl benzoate— By $NaHCO_3$ test

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

Benzoic acid — Sodiumbenzoate

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No } CO_2 \text{ is formed}$$

(v) Pentan-2-one and Pentan-3-one can be distinguished by $NaHSO_3$ test



$$CH_3CH_2COCH_2CH_3 + NaHSO_3 \longrightarrow \text{No solid adduct.}$$

Only methyl and cyclic ketones react with $NaHSO_3$ to give solid adduct.

(vi) Benzaldehyde and Acetophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{(Yellow ppt.)}}{CH_3I \downarrow} + 2NaOH$$

$$C_6H_5CHO + NaOI \longrightarrow \text{No yellow ppt.}$$

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

$$CH_3CHO + 3NaOI \longrightarrow HCOONa + \underset{\text{(Yellow ppt.)}}{CH_3I \downarrow} + 2NaOH$$

$$CH_3CH_2CHO \xrightarrow{I_2/NaOH} \text{No yellow ppt.}$$

12.14 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

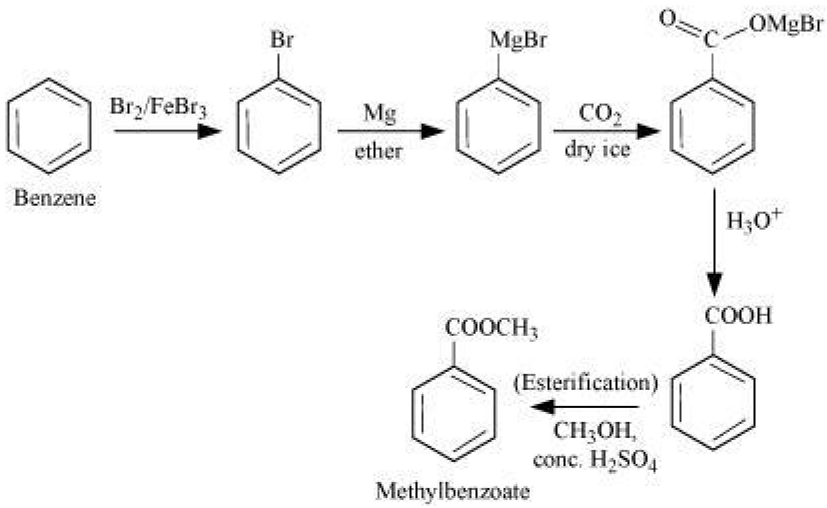
(ii) m-Nitrobenzoic acid

(iii) p-Nitrobenzoic acid

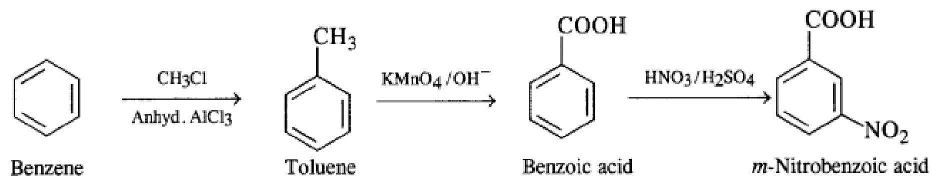
(iv) Phenylacetic acid

(v) p-Nitrobenzaldehyde.

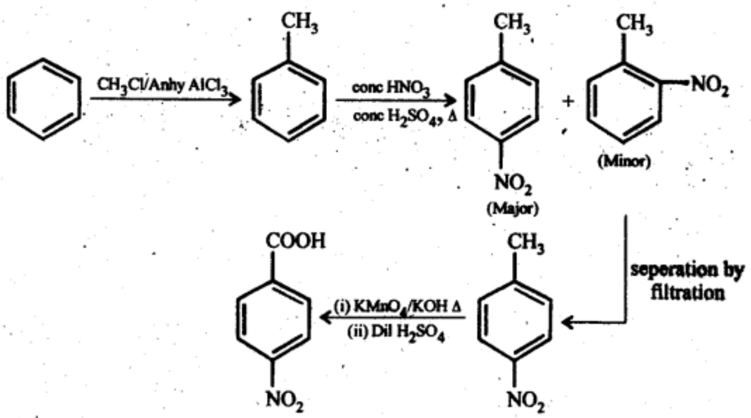
Ans -(i)


Br
MgBr
OMgBr
Benzene
$Br_2/FeBr_3$
Mg
ether
CO_2
dry ice
H_3O^+
COOH
$COOCH_3$
(Esterification)
CH_3OH,
conc. H_2SO_4
Methylbenzoate

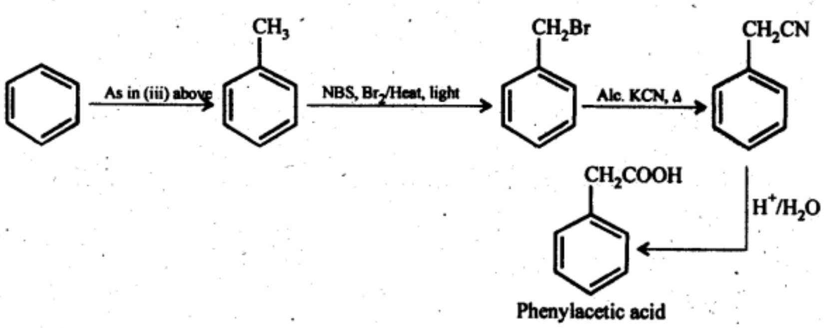
(ii)


CH_3
COOH
COOH
CH_3Cl
Anhyd. $AlCl_3$
$KMnO_4/OH^-$
HNO_3/H_2SO_4
NO_2
Benzene
Toluene
Benzoic acid
m-Nitrobenzoic acid

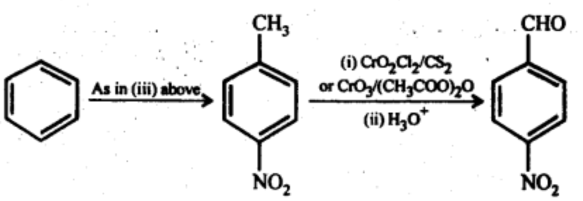
(iii)



(iv)



(v)



12.15 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

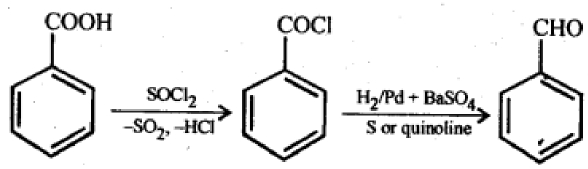
(viii) Benazaldehyde to α-Hydroxyphenylacetic acid

(ix) Benzoic acid to m- Nitrobenzyl alcohol

Ans - **(i) Propanone to propene**

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3\underset{\underset{OH}{|}}{C}HCH_3} \xrightarrow[\text{Heat}]{H_2SO_4\,(\text{conc.})} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

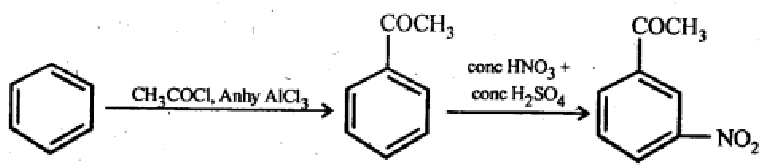
(*ii*) Benzoic acid to benzaldehyde:



(*iii*) Ethanol to 3-hydroxy butanal:

$$CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO \xrightarrow{\text{Dil NaOH}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CHO$$

(*iv*) Benzene to *m*-nitroacetophenone:



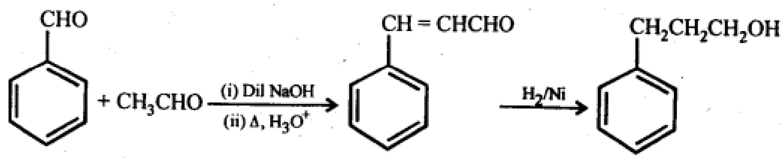
(*v*) Benzaldehyde to benzophenone:

$$C_6H_5CHO \xrightarrow[\text{(ii) } CaCO_3]{\text{(i) } K_2Cr_2O_7/H_2SO_4} (C_6H_5COO)_2Ca \xrightarrow[-CaCO_3]{\text{Dry Distillation}} (C_6H_5)_2CO$$

(*vi*) Bromobenzene to 1-phenylethanol

$$C_6H_5Br \xrightarrow{Mg/dry\ ether} C_6H_5MgBr \xrightarrow[(ii)H_3O^+]{(i)CH_3CHO} C_6H_5-\overset{\displaystyle OH}{\overset{|}{C}}H-CH_3$$

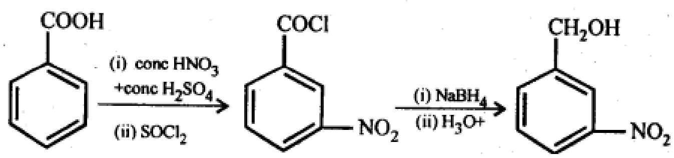
(*vii*) Benzaldehyde to 3-phenylpropan-1-ol



(*viii*) Benzaldehyde to α-hydroxyphenylacetic acid:

$$C_6H_5CHO \xrightarrow[pH,\ 9-10]{HCN} C_6H_5\overset{\displaystyle OH}{\overset{|}{C}}H-CN \xrightarrow{H^+/H_2O} C_6H_5-\overset{\displaystyle OH}{\overset{|}{C}}H-COOH$$

(*ix*) Benzoic acid to *m*-nitrobenzyl alcohol:



12.16 Describe the following:

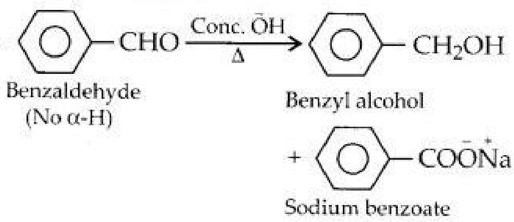
(i) Acetylation

(ii) Cannizzaro reaction

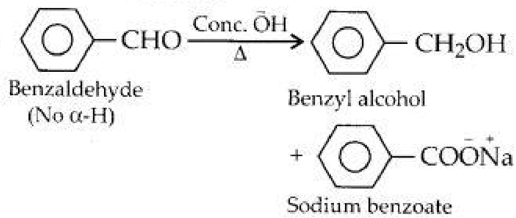
(iii) Cross aldol condensation

(iv) Decarboxylation

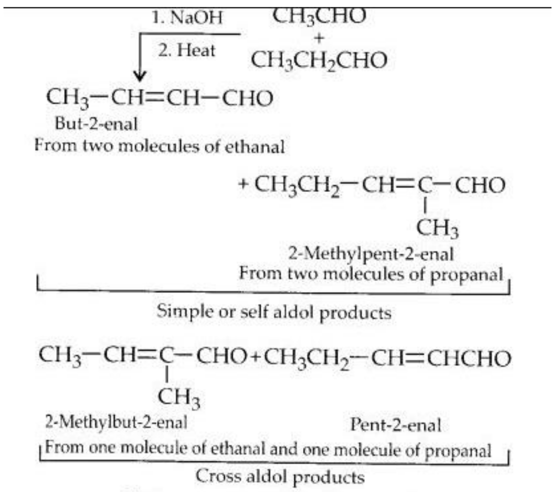
Ans - (i) Acetylation is the process of adding an acetyl group to a molecule, namely by replacing an active hydrogen atom with an acetyl group. The presence of a base, such as pyridine, dimethylanitine, etc., is typically required for acetylation to occur.

e.g., 

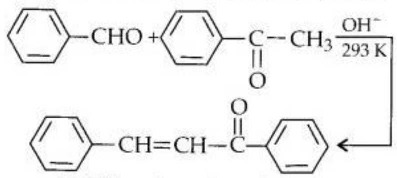
(ii) Cannizzaro reaction : Cannizzaro reaction is undergone by aldehydes or ketones that lack an α-hydrogen atom. Such carbonyl compounds in the presence of conc. NaOH and heat undergo disproportionation reaction to produce the corresponding carboxylate ion and alcohol.

e.g., 

(iii) Cross-aldol condensation : Aldol condensation is the reaction that takes place, when aldehydes or ketones with at least one α-H atom react in the presence of dilute alkali to produce β-hydroxy aldehydes or ketones. When two different aldehydes or ketones are taken, it gives a mixture of products. Such a reaction is called cross-aldol condensation.



Ketones can also be used as one component in the cross aldol reactions

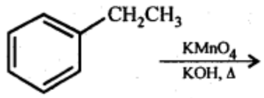


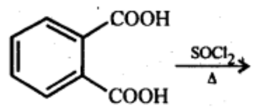
1,3-Diphenylprop-2-ene-1-one
(Benzalacetophenone) (Major product)

(iv) Decarboxylation : Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is

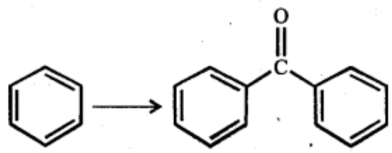
$$R\text{—COONa} \xrightarrow[\text{Heat}]{\text{NaOH + CaO}} R\text{—H} + Na_2CO_3$$

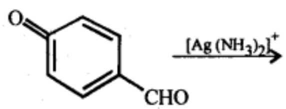
12.17 Complete each synthesis by giving missing starting material, reagent or products

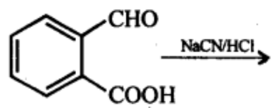
(*i*) 

(*ii*) 

(*iii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

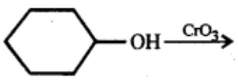
(*iv*) 

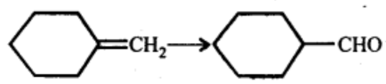
(*v*) 

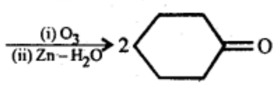
(*vi*) 

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

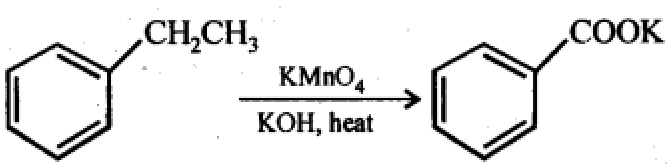
(*viii*) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

(*ix*) 

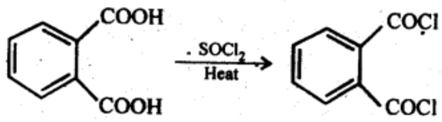
(*x*) 

(*xi*) 

Ans -

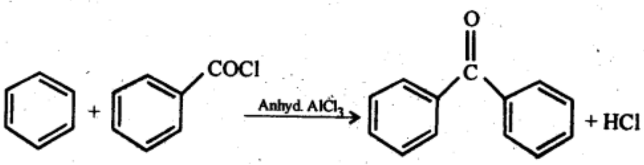
(*i*) 

(ii)

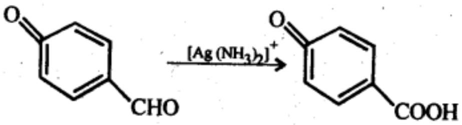


(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2} C_6H_5CH = NNHCONH_2 + H_2O$

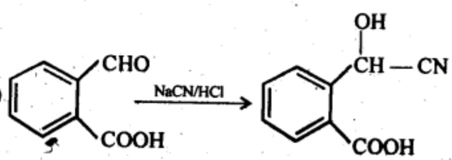
(iv)



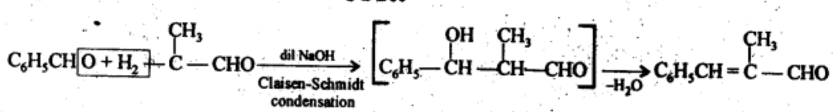
(v)



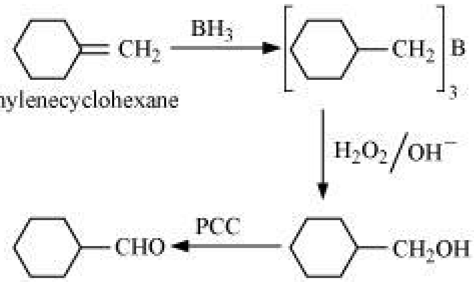
(vi)



(vii)



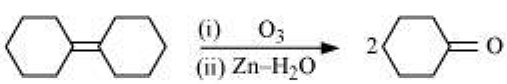
(x)



Methylenecyclohexane

Cyclohexanecarbaldehyde

(xi)



Cyclohexylidenecyclohexane Cyclohexanone

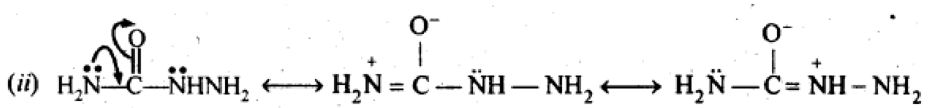
12.18 Give plausible explanation for each of the following:

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

(ii) There are two –NH2 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.

Ans - (i) The assault of a CN" ion (nucleophile) at the carbonyl carbon atom in cyclohexanone is simple to carry out. However, the three CH3 groups in 2, 4, and 6-trimethylcyclohexanone, which release electrons by nature (+ I effect), will significantly increase the electron density on the carbonyl carbon atom, making a nucleophile attack unlikely. Additionally, the two —CH3 substituents in the ortho locations will prevent the CN- ion from attacking the carbonyl group.



Despite the fact that semicarbazide has two - NH2 groups, only one of them—the one that is directly connected to C = O—is engaged in resonance, as seen above. As a result, this -NH2 group's N has less electron density, which prevents it from acting as a nucleophile. The lone pair of electrons on the N atom of the other -NH2 group, on the other hand, is not involved in resonance and is therefore available for nucleophilic attack on the C = O group of aldehydes and ketones.

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

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

12.19 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.

Ans -

$C = 69{\cdot}77\%, H = 11{\cdot}67\%$

$\therefore \quad O = 100 - (69{\cdot}77 + 11{\cdot}63)\% = 18{\cdot}6\%$

$\therefore \quad C:H:O = \frac{69\cdot77}{12} : \frac{11\cdot63}{1} : \frac{18\cdot6}{16} = 5\cdot88 : 11\cdot63 : 1\cdot16 :: 5 : 10 : 1$

The empirical formula of the given compound = $C_5H_{10}O$

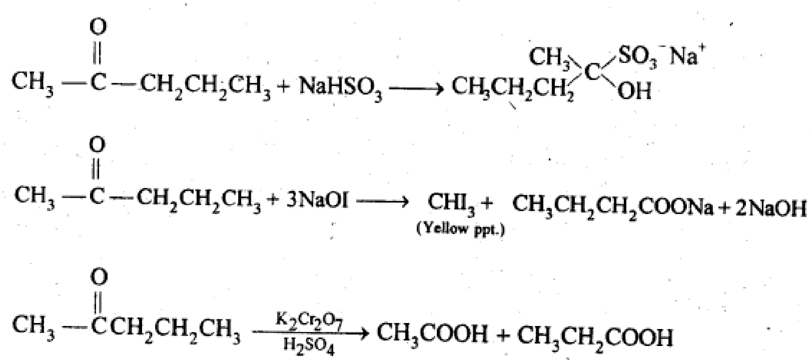
Empirical formula mass = $5 \times 12 + 10 \times 1 + 1 \times 16 = 86$

Molar mass = 86 (given)

$\therefore$ Molecular formula = $C_5H_{10}O$

Since the substance produces sodium hydrogen sulphite, it must either be an aldehyde or a methyl/cyclic ketone. It is impossible for the substance to be an aldehyde because it does not reduce Tollens' reagent. The supplied substance is a methyl ketone because the iodoform test results for the molecule are positive. The methyl ketone is pentan-2-one because the provided molecule undergoes strong oxidation to produce a combination of ethanoic acid and propanoic acid.

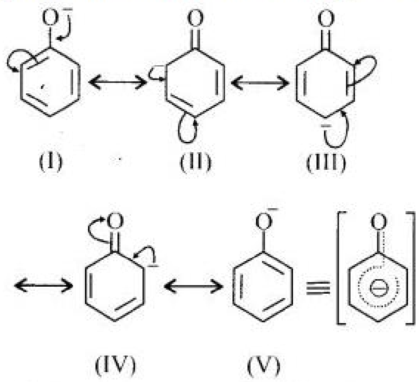
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$. The reactions involved are:



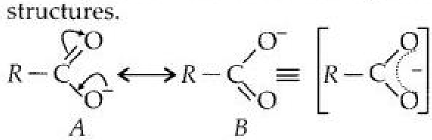
12.20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Ans -

(i) Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonance structures.



(ii) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

In the instance of the phenoxide ion, structures (V–VI) have a negative charge on the carbon atom that is less electronegative. They therefore make only a very minor contribution to the resonance stability of the phenoxide ion.

The negative charge on the oxygen atom is delocalized over two oxygen atoms in structures I and II (carboxylate ions), but it is still localised in structures III and IV just the electrons of the benzene ring are delocalized. The carboxylate ion is much more resonance stabilised than the phenoxide ion because delocalization of benzene electrons has a far smaller impact on the stability of the phenoxide ion. Therefore, it is significantly simpler to release a proton from carboxylic acids than from phenols. In other words, phenols are weaker acids than carboxylic acids.