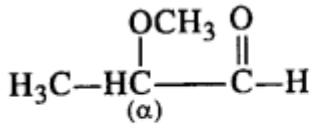
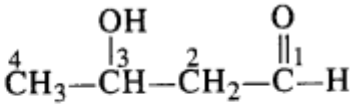
NCERT Solutions for Class 12 Chemistry

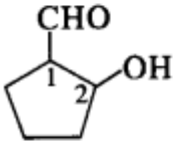
Chapter 12 Aldehydes, Ketones and Carboxylic Acids

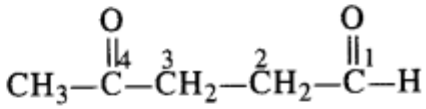
NCERT INTEXT QUESTIONS

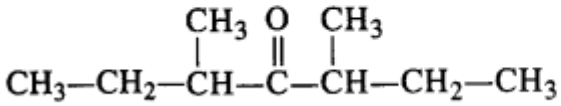
Question 1:
Write the structures of the following compoimds :
(i) α -Methoxypropionaldehyde
(ii) 3-Hydroxybutanal
(iii) 2-Hydroxycyclopentanecarbaldehyde
(iv) 4-Oxopentanal
(v) Di-sec butylketone
(vi) 4-Fluoroacetophenone
Answer:

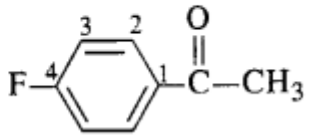
(i) 

(ii) 

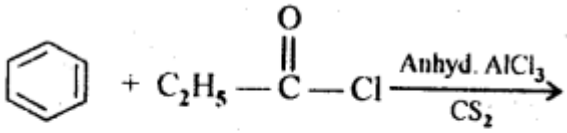
(iii) 

(iv) 

(v) 

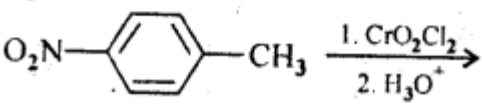
(vi) 

Question 2.
Write the structures of products of following reactions:

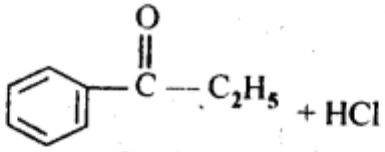
(i) 

(ii) $(C_6H_5CH_2)_2Cd + 2\,CH_3COCl \longrightarrow$

(iii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},H_2SO_4}$

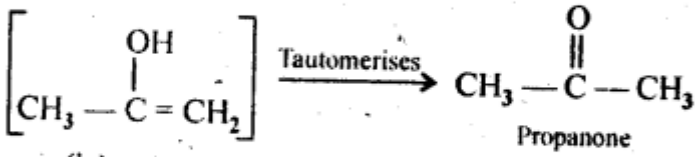
(iv) 

Answer:

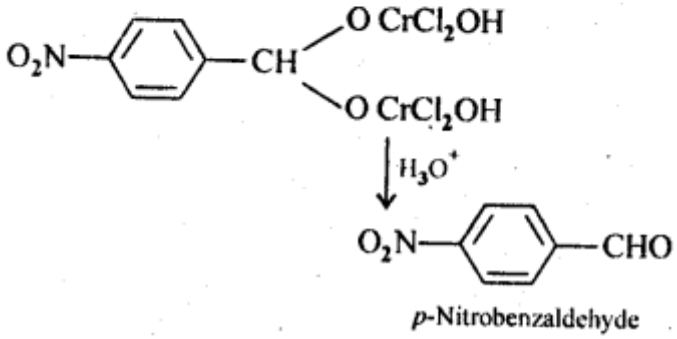
(i) 

Propiophenone

(ii) $2\,CH_3—\overset{O}{\overset{\|}{C}}—CH_2C_6H_5 + CdCl_2$
1 – Phenylpropanone

(iii) 

Propanone

(iv) 

p-Nitrobenzaldehyde

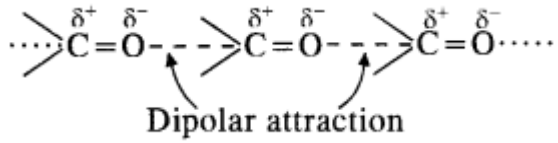
Question 3.
Arrange the following compounds in increasing order of their boiling points :
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$
Answer:
The increasing order of boiling points of all these compounds of comparable molecular masses is :

$$\underset{(213\ K)}{CH_3CH_2CH_3} < \underset{(249\ K)}{CH_3OCH_3} < \underset{(293\ K)}{CH_3CHO} < \underset{(351\ K)}{CH_3CH_2OH}$$

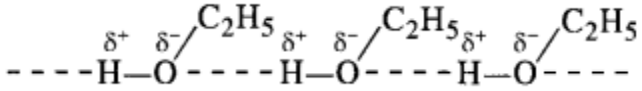
Explanation: We know that the boiling points of liquids are directly related to the magnitude of the intermolecular forces of attraction.

1. Hydrocarbons (alkanes) are completely non-polar. The only attractive forces in their molecules are Van der Waals forces which are quite weak. That is why propane ($CH_3CH_2CH_3$) has the least boiling point. It is a gas at room temperature.
2. Ethers have bent structures and are also polar. However, there is no hydrogen bonding in their molecules. The only attractive forces are dipolar forces. Therefore, boiling point of dimethyl ether (CH_3OCH_3) is higher than that of propane. However, it is also a gas at room temperature.

3. Aldehydes contain polar carbonyl group and have strong dipolar interactions in their molecules. It is more than in ethers. Therefore, the boiling point of acetaldehyde (CH_3CHO) is more than that of dimethyl ether.



4. Out of all the families listed, alcohols have maximum intermolecular forces in the form of hydrogen bonding

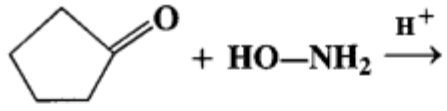


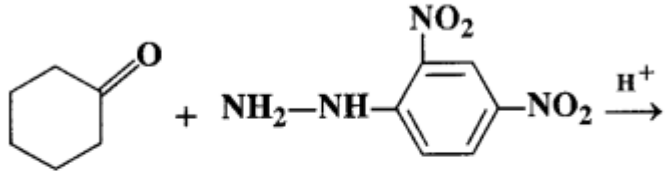
As a result, ethyl alcohol (C_2H_5OH) has the maximum boiling point.

Question 4.
Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions
(i) Ehtanal, propanaL, propanone, butanone
(ii) Benzaldehyde,p-Tolualdehyde, p-Nitrobenzaldehyde, acetophenone.
Ans: (i) Butanone < Propanone < Propanal < Ethanal .This is because as the no. of alkyl groups attached to carbonyl carbon increases, +I-effect increases. As a result, e^- density on C–atom of $-\overset{\overset{O}{\|}}{C}-$ group decreases and hence attack by Nu^- becomes slower and slower.

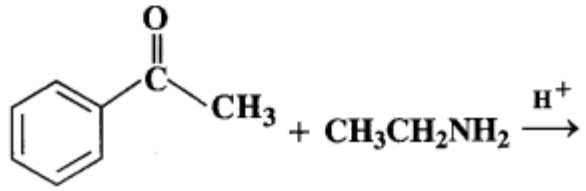
(ii) acetophenone < *p*–tolualdehyde < benzaldehyde < *p*–nitrobenzaldehyde
Acetophenone is ketone, rest all are aldehydes, hence it is the least reactive. In *p*–tolualdehyde, $-CH_3$ group at *p*–position increases e^- density on C–atom of $-\overset{\overset{O}{\|}}{C}-$ group thus making it less reactive than benzaldehyde. In *p*–nitrobenzaldehyde, $-NO_2$ groups with draw e^{-1}s by inductive and resonance effect thus rising e^- density on carbonyl C, thus making it more reactive than benzaldehyde.

Question 5.
Predict the products of the following reactions :

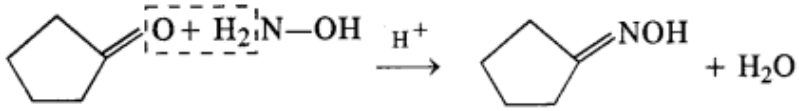
(i)  $+ HO-NH_2 \xrightarrow{H^+}$

(ii) 

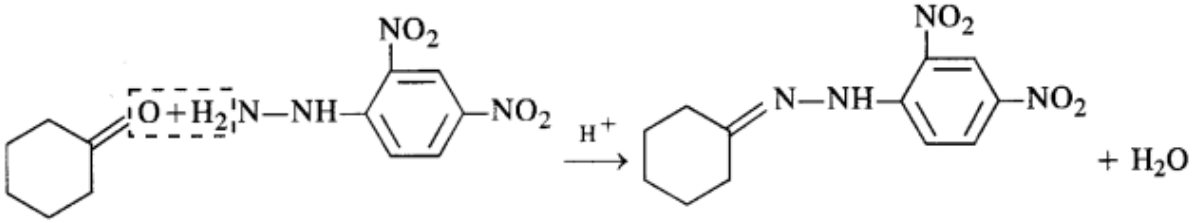
(iii) $R-CH=CH-CHO + NH_2-\underset{\underset{O}{\|}}{C}-NH-NH_2 \xrightarrow{H^+}$

(iv) 

Answer:

Ans. (i) 

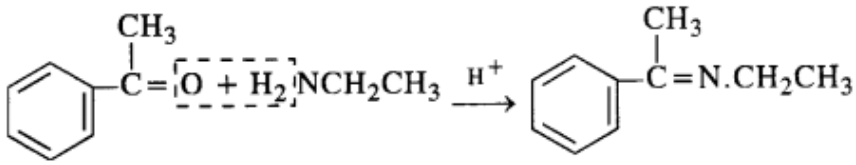
Cyclopentanone — Hydroxyl amine — Cyclopentanone oxime

(ii) 

Cyclohexanone — 2, 4-D.N.P — 2, 4-D.N.P derivative of cyclohexanone

(iii) $R-CH=CH-CH\overset{\oplus}{O}\overset{-}{+}H_2N-NH-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{H^+} R-CH=CH-CH=N-NH-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O$

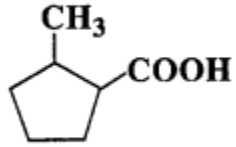
Unsaturated aldehyde — Semicarbazide — Semicarbazone

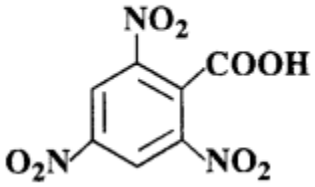
(iv) 

Acetophenone — Ethylamine — Schiff's base (Anil)

Question 6.
Give the IUPAC names of the following compounds:

(i) $C_6H_5CH_2CH_2COOH$ (ii) $(CH_3)_2C=CH\ COOH$

(iii) 

(iv) 

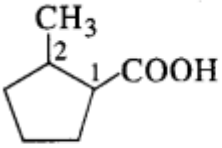
Answer:

(i) $C_6H_5\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$

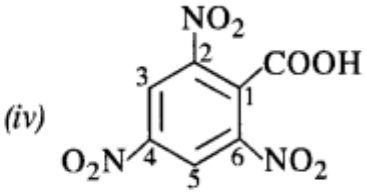
3-Phenylpropanoic acid

(ii) $\overset{4}{C}H_3-\overset{3}{C}=\overset{2}{C}H-\overset{1}{C}OOH$ (CH_3 on C-3)

3-Methylbut-2-enoic acid

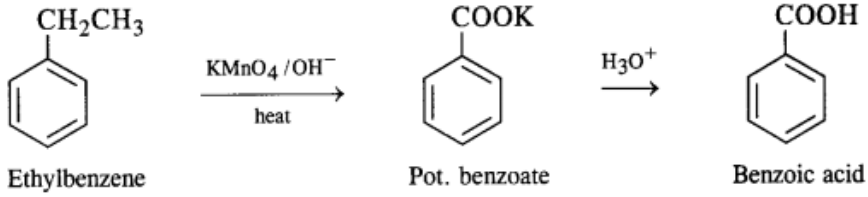
(iii) 

2-Methylcyclopentanecarboxylic acid

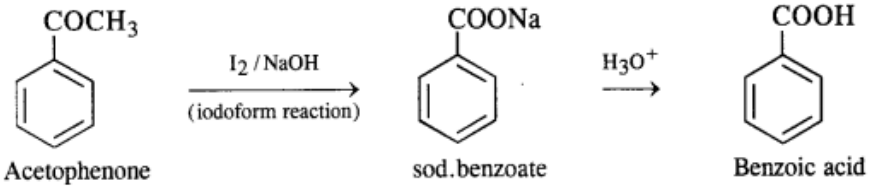
(iv) 

2,4,6-Trinitrobenzoic acid

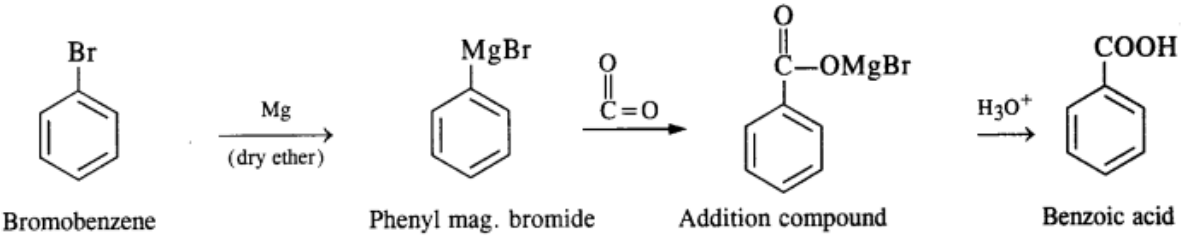
Question 7.
Show how each of the following compounds can be converted into benzoic acid?
(i) Ethylbenzene **(C.B.S.E. Outside Delhi 2017)**
(ii) Acetophenone **(C.B.S.E. Outside Delhi 2017)**
(iii) Bromobenzene
(iv) Phenylethene (Styrene)
Answer:

(i) 

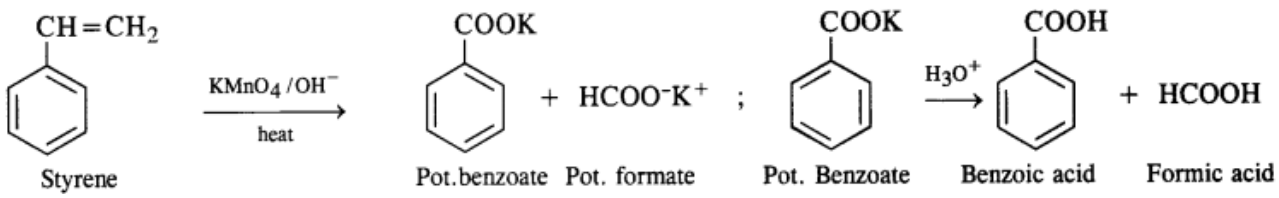
Ethylbenzene → Pot. benzoate → Benzoic acid

(ii) 

Acetophenone → sod.benzoate → Benzoic acid

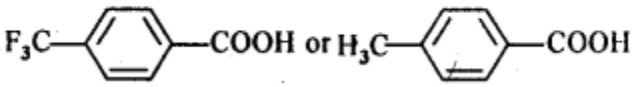
(iii) 

Bromobenzene → Phenyl mag. bromide → Addition compound → Benzoic acid

(iv) 

Styrene → Pot.benzoate + Pot. formate ; Pot. Benzoate → Benzoic acid + Formic acid

Question 8.
Which acid of each pair would you expect to be stronger?
(i) CH_3CO_2H or FCH_2CO_2H
(ii) FCH_2CO_2H or $ClCH_2CO_2H$
(iii) $FCH_2CH2CH_2CO_2H$ or $CH_3CH(F)CH_2CO_2H$
(iv)



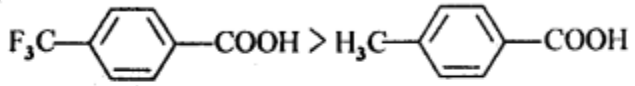
Answer:

(i) $FCH_2COOH > CH_3COOH$
(lesser e^- density in O–H bond and greater stability of FCH_2COO^- over CH_3COO^- ion.)

(ii) $FCH_2CO_2H > ClCH_2CO_2H$
(due to stronger – I effect of F over Cl)

(iii) $CH_3CH(F)CH_2CO_2H > FCH_2CH_2CH_2COOH$
(because I-effect decreases with distance)

(iv)



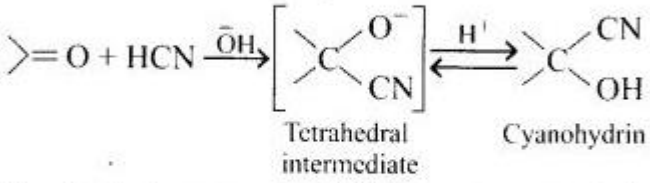
($F_3C-C_6H_4-COO^-$ ion is more stable due to delocalisation of charge whereas $CH_3-C_6H_4-COO^-$ ion is less stable due to increased intensity of –ve charge.

NCERT EXERCISE

Question 1.
What is meant by the following terms? Give an example in each case.
(a) Cyanohydrin
(b) Semicarbazone
(c) Acetal
(d) Oxime
(e) Cyanohydrin
(f) Ketal
(g) Aldol
(h) Schiff's base
(i) 2, 4-D.N.P.
(ii) Imine
Answer:

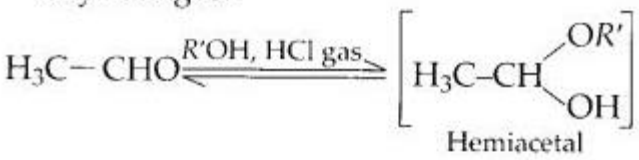
(i) Carbonyl compounds in the presence of an alkali, react with HCN to form an addition product called cyanohydrin.

$$HCN + \bar{O}H \rightleftharpoons H_2O + \bar{C}N$$

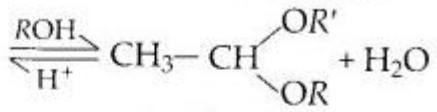


Tetrahedral intermediate — Cyanohydrin

(ii) Acetals are gem-dialkoxy compounds formed when aldehydes react with monohydric alcohols in the presence of dry HCl gas.

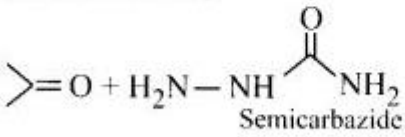


Hemiacetal

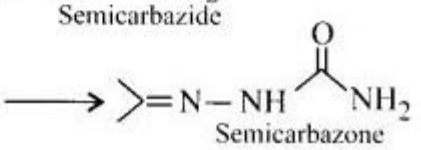


Acetal

(iii) Semicarbazone is formed by the reaction between carbonyl compounds and semicarbazide.



Semicarbazide



Semicarbazone

(iv) β-Hydroxy aldehydes are called aldol. Aldehydes and ketones containing at least one α-H atom undergo a reaction in the presence of dilute alkali to form aldol compounds. *e.g.*,

$$2CH_3CHO \xrightleftharpoons{\text{dil } \bar{O}H} \underset{\underset{\text{OH}}{|}}{CH_3CH}-CH_2CHO$$

3-Hydroxybutanal (aldol)

$$\xrightarrow[-H_2O]{\Delta} CH_3CH=CHCHO$$

But-2-enal

(v) Hemiacetals are gem-alkoxyalcohols which are produced from the addition of one molecule of monohydric alcohol to an aldehyde in the presence of HCl gas.

$$H_3C \diagdown \atop H \diagup C=O + H-OCH_3 \xrightleftharpoons{\text{Dry } HCl_{(g)}} CH_3 \diagdown \atop H \diagup C \diagup \atop \diagdown OCH_3 \diagup OH$$

Hemiacetal

(vi) Oximes are formed by reaction between aldehydes or ketones and hydroxylamine. The reaction is carried out in mildly acidic condition.

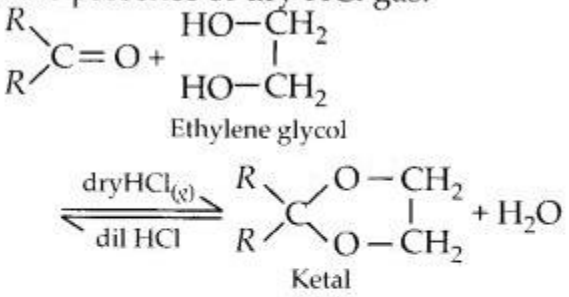
$$H_3C \diagdown \atop H \diagup >=O + H_2N-OH$$

Hydroxylamine

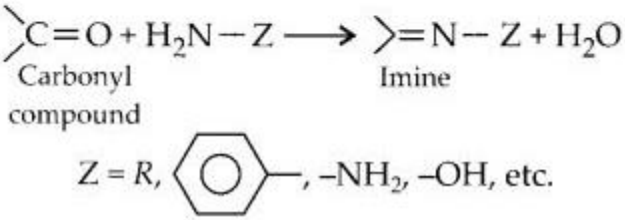
$$\xrightarrow{\text{pH } 3.5} H_3C \diagdown \atop H \diagup >=NOH + H_2O$$

Oxime

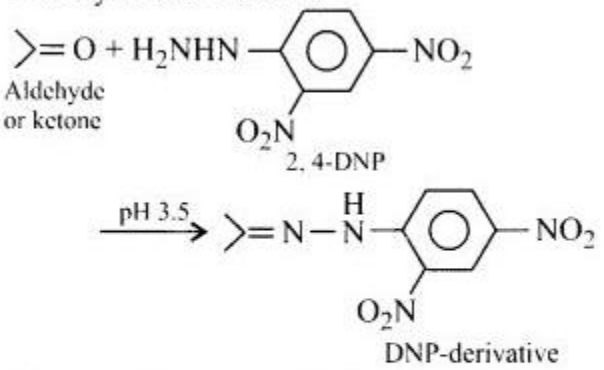
(vii) Ketals are cyclic products formed by the reaction of ketones with ethylene glycol in the presence of dry HCl gas.



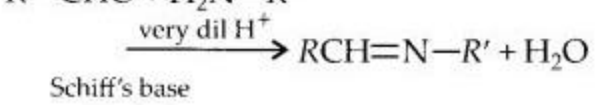
(viii) Imines are formed when carbonyl compounds react with ammonia derivative.



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



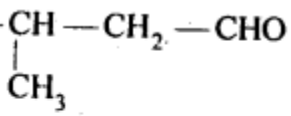
(x) Reaction between aldehydes or ketones with 1° aliphatic or aromatic amines yields a Schiff's base.

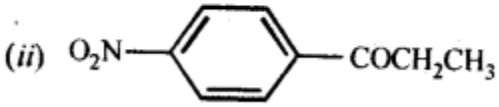


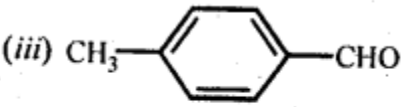
Question 2.
Name the following compounds according to IUPAC system of nomenclature.
(i) $CH_3CH(CH_3)CH_2CH_2CHO$
(ii) $CH_3CH=CHCHO$
(iii) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$
(iv) $OHCC_6H_4CHO(-p)$
(v) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(vi) $CH_3COCH_2COCH_3$

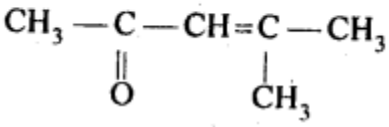
(vii) $(CH_3)_3CCH_2COOH$
(viii) $(CH_3)_2CHCH(CH_3)COCl$
Answer:
(i) 4-Methylpentanal
(ii) But-2-enal
(iii) 3 3 5-Trimethylhexan-2-one
(iv) Benzene- 1, 4-dicarbaldehyde
(v) 6-Chloro-4-ethylhexan-3-one
(vi) Pentane-2, 4-dione
(vii) 3, 3-Dimethylbutanoic acid
(viii) 2, 3-Dimethylbutanoyl chloride

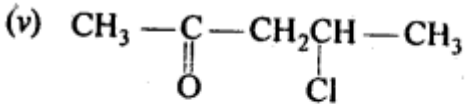
Question 3.
Draw the structures of the following compounds:
(i) 3-Methylbutanal
(ii) p-Nitropropiophenone
(iii) p-Methylbenzaldehyde
(iv) 4-Methylpent-3-en-2-one
(v) 4-Chloropentan-2-one
(vi) 3-Bromo-4-phenylpentanoic acid
(vii) pp'-Dihydroxybenzophenone
(viii) Hex-2-en-4-ynoic acid
Answer:

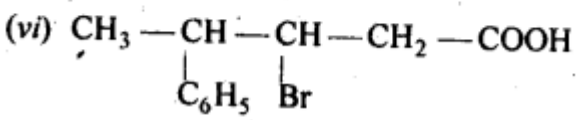
(i) 

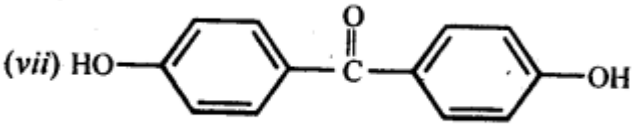
(ii) 

(iii) 

(iv) 

(v) 

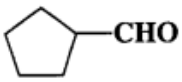
(vi) 

(vii) 

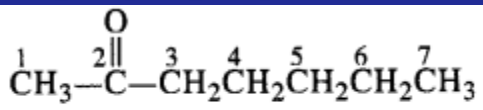
(viii)

Question 4.
Write the IUPAC names of the following aldehydes and ketones. Also give the common names wherever possible.

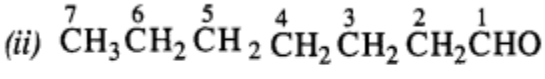
(i) $CH_3CO(CH_2)_4CH_3$ (ii) $CH_3(CH_2)_5CHO$ (iii) $C_6H_5CH=CH—CHO$

(iv) PhCOPh (v)  (vi) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

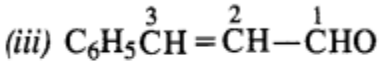
Answer:

(i) 

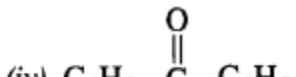
Heptan-2-one
(Methyl-*n*-pentyl ketone)

(ii) 

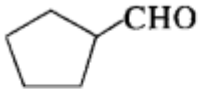
Heptanal

(iii) 

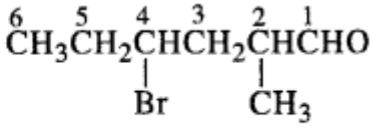
3-Phenylprop-2-enal
(Cinnamaldehyde)

(iv) 

Diphenylmethanone
(Benzophenone)

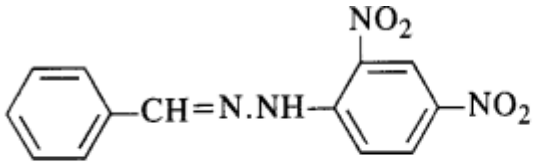
(v) 

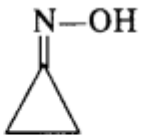
Cyclopentanecarbaldehyde

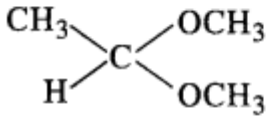
(vi) 

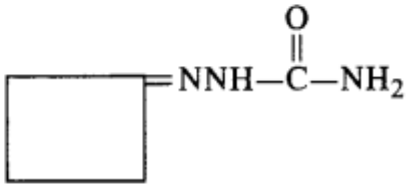
4-Bromo-2-methylhexanal

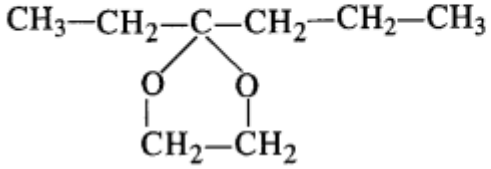
Question 5.
Draw the structures of the following compounds :
(a) 2, 4-dinitrophenylhydrazone of benzaldehyde
(b) Cyclopropanone oxime
(c) Acetaldehyde dimethyl acetal
(d) Semicarbazone of cyclobutanone
(e) Ethylene ketal of hexan-3-one
(f) Methyl hemiacetal of formaldehyde.
Answer:

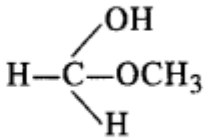
(a) 

(b) 

(c) 

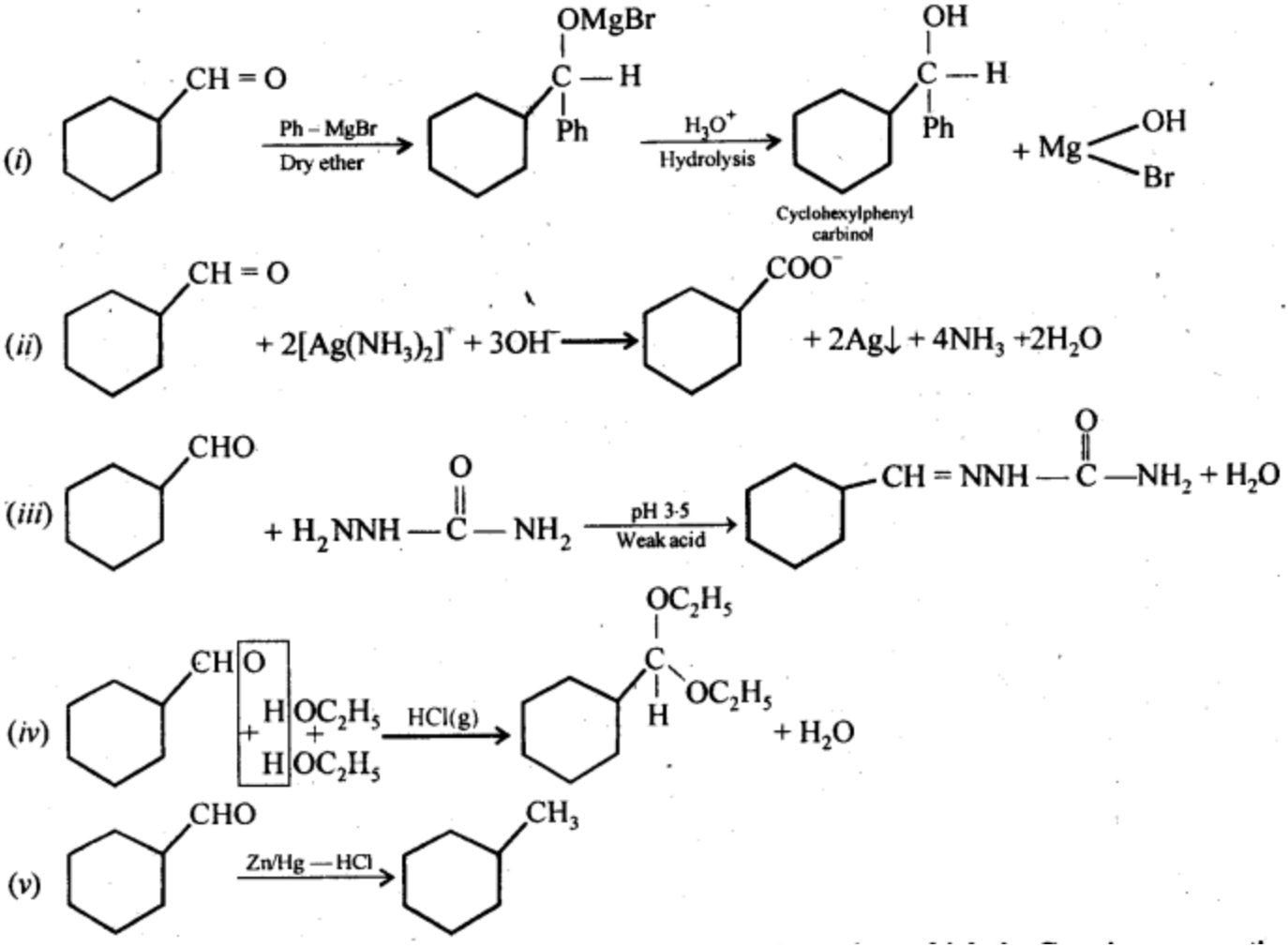
(d) 

(e) 

(f) 

Question 6.
Predict the products formed when cyclohexane carbaldehyde reacts with the following reagents.
(i) PhMgBr and then H_3O^+
(ii) Tollen reagent
(iii) Semicarbazide and weak acid
(iv) Excess ethanol and acid
(v) Zinc amalgam and dilute hydrochloric acid

Answer:



Question 7.

Which of the following will undergo Aldol condensation, which Cannizzaro's reaction, and which neither of these? Write the structures of the expected products in each case

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

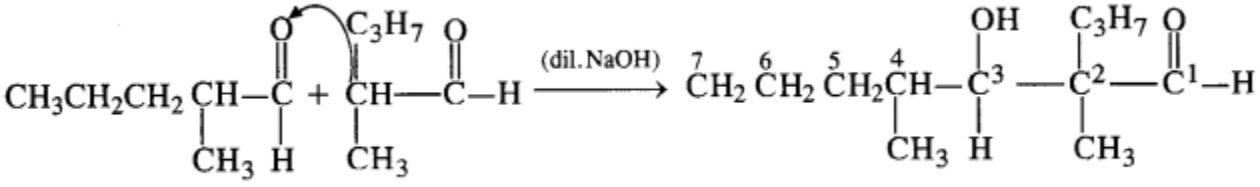
Answer:

(i) Methanal (HCHO): It will give Cannizzaro's reaction since the α-hydrogen atom is absent.

$$2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$$

Methanal — Methanol — Sod. methanoate

(ii) 2-Methylpentanal [$CH_3CH_2CH_2CH(CH_3)CHO$]: It will give Aldol condensation since the α-hydrogen atom is present.



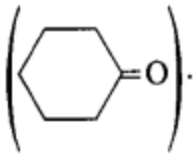
2–Methylpentanal — 3–Hydroxy–2, 4–dimethyl–2–propylheptanal

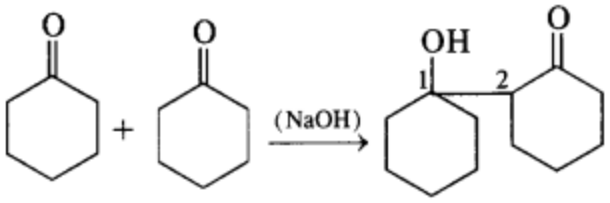
(iii) Benzaldehyde (C_6H_5CHO): It will give Cannizzaro's reaction since a-hydrogen is not present.

$$2\,C_6H_5CHO + NaOH\ (Conc.) \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Benzaldehyde — Benzyl alcohol — Sod. benzoate

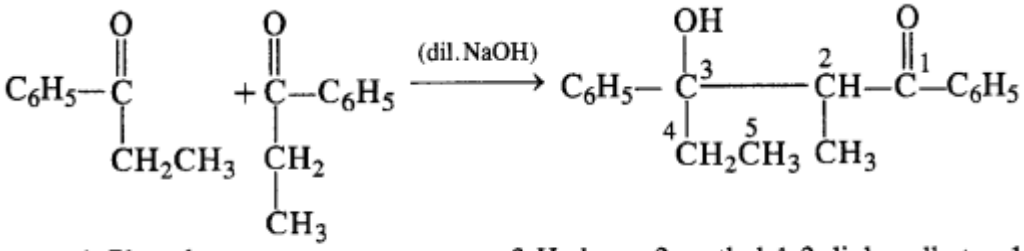
(iv) Benzophenone ($C_6H_5COC_6H_5$): It will not give any of the two reactions. Being ketone, does not take part in Cannizzaro's reaction. Without a-hydrogen, it fails to participate in Aldol condensation.

(v) **Cyclohexanone**  . It will give Aldol condensation since α-hydrogen atom is present



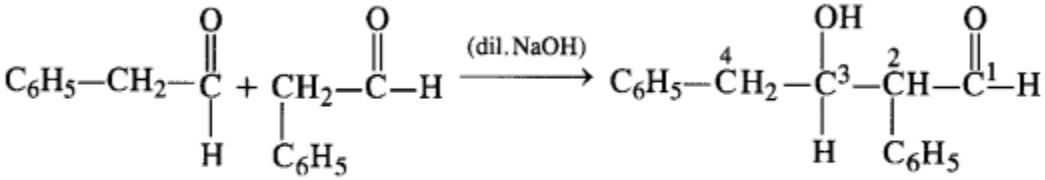
Cyclohexanone — 2-(1-Hydroxy-1-Cyclohexyl) cyclohexane-1-one (Aldol)

(vi) 1-Phenylpropanone ($C_6H_5COCH_2CH_3$): It will undergo Aldol condensation since the α-hydrogen atom is present.



1–Phenylpropanone — 3-Hydroxy-2-methyl-1,3-diphenylbutan-1-one

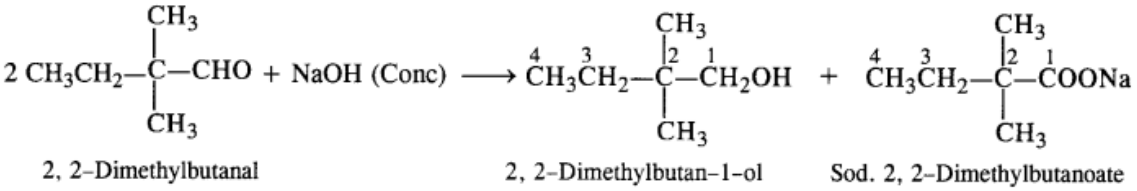
(vii) Phenylacetaldehyde ($C_6H_5CH_2CHO$): It will give Aldol condensation since the α-hydrogen atom is present.



Phenylacetaldehyde — 3–Hydroxy –2, 4–diphenylbutanal

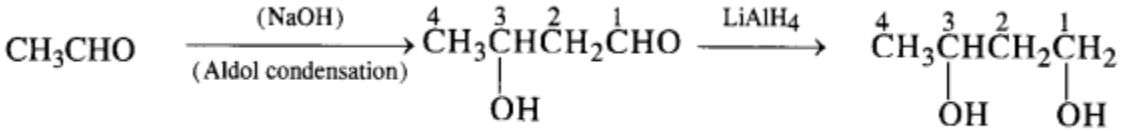
(viii) Butan-1-ol: It will not give any of the reactions.

(ix) **2, 2–Dimethylbutanal ($CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CHO$).** It will give Cannizzaro's reaction since no α-hydrogen atom is present.



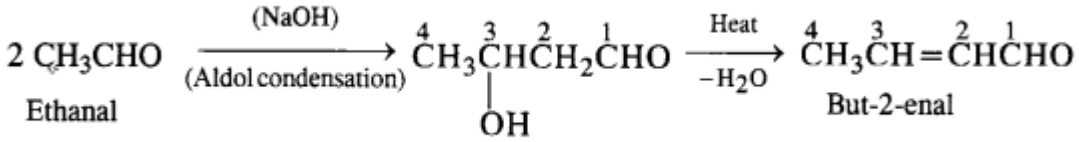
2, 2–Dimethylbutanal — 2, 2–Dimethylbutan–1–ol — Sod. 2, 2–Dimethylbutanoate

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



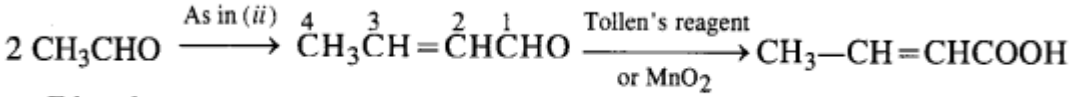
Ethanal — 3-Hydroxybutanal — Butane–1,3–diol

(ii) Ethanal to but-2-enal



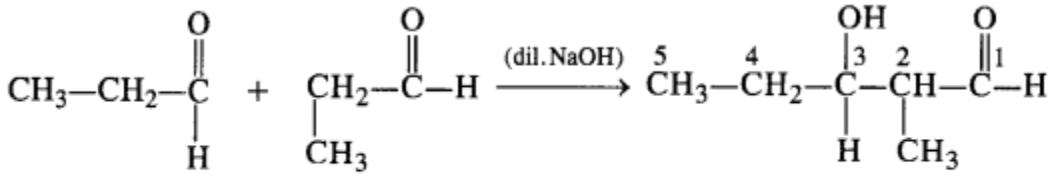
Ethanal — 3-Hydroxybutanal — But-2-enal

(iii) Ethanal into but-2-enoic acid



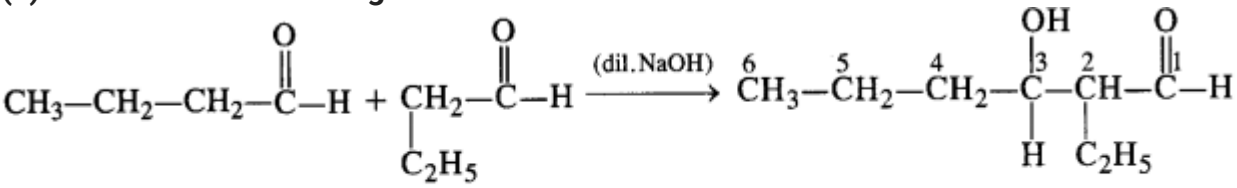
Ethanal — But-2-enal — But-2-enoic acid

Question 9.
Write the structural formulae and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde serves as a nucleophile and which as an electrophile.
Answer:
Both propanal and butanal have a-hydrogen atoms present. These can undergo self aldol condensation as well as cross aldol condensation to give four compounds as follows:
(i) Condensation involving propanal: It is a case of a self aldol condensation.



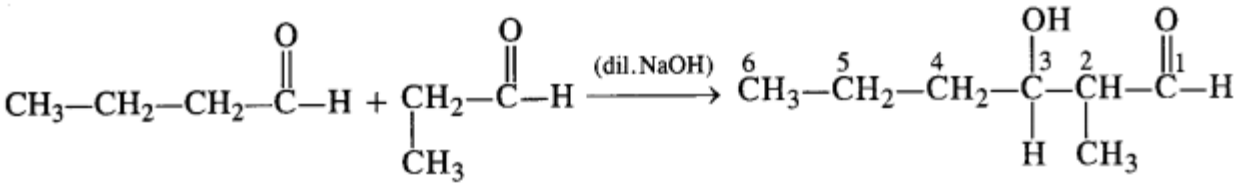
Propanal (Electrophile) Propanal (Nucleophile) 3-Hydroxy-2-methylpentanal

(ii) Condensation involving butanal: It is self aldol condensation.



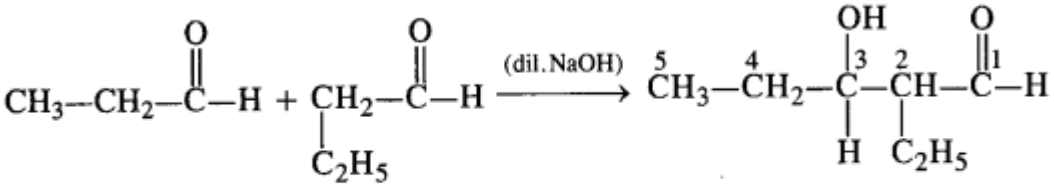
Butanal (Electrophile) Butanal (Nucleophile) 2-Ethyl-3-hydroxyhexanal

(iii) Condensation involving butanal (electrophile) and propanal (nucleophile): It is cross-aldol condensation.



Butanal (Electrophile) Propanal (Nucleophile) 3-Hydroxy-2-methylhexanal

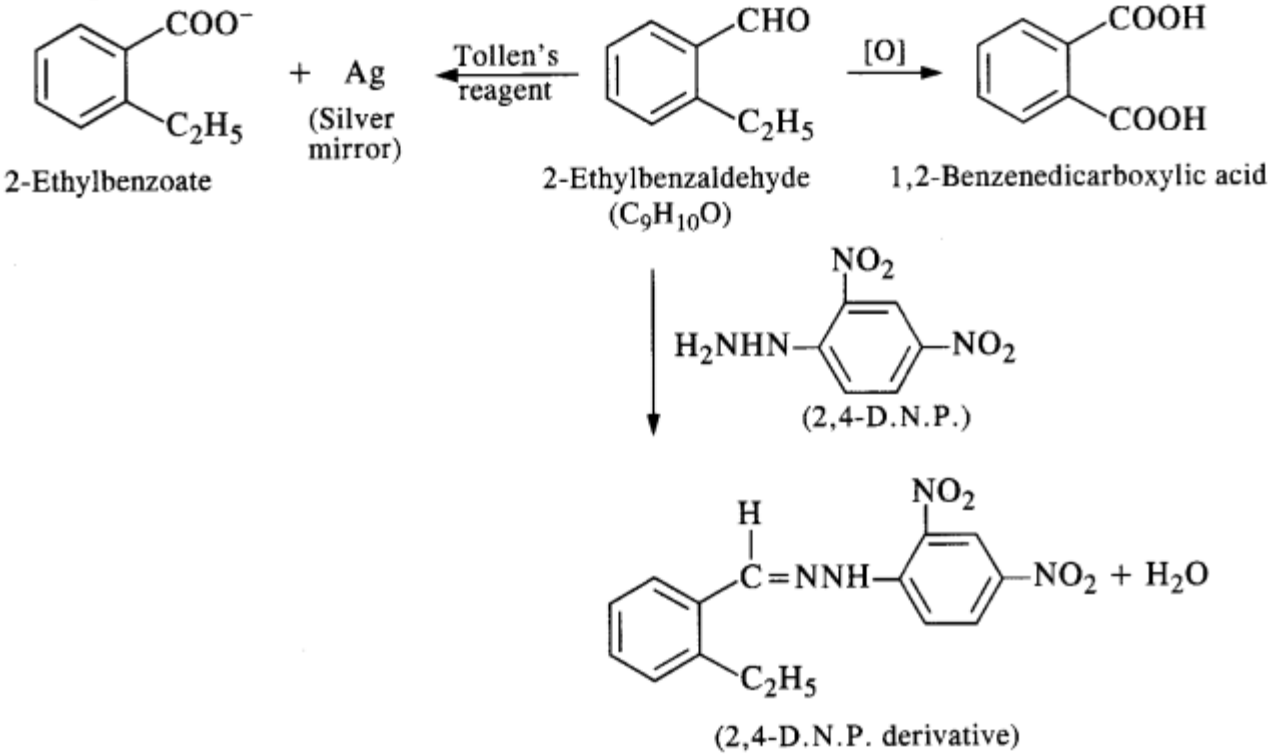
(iv) Condensation involving propanal (electrophile) and butanal (nucleophile): It is cross-aldol condensation.



Propanal (Electrophile) Butanal (Nucleophile) 2-Ethyl-3-hydroxypentanal

Question 10.
An organic compound with molecular formula CgHjoO forms 2, 4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro's reaction. On vigorous oxidation, it gives 1, 2 benzene dicarboxylic acid. Identify the compound. **(C.B.S.E. Outside Delhi 2012; Haryana Board 2013)**
Answer:
Since the compound forms 2, 4-DNP derivative on reacting with 2, 4-DNP, it is a carbonyl compound. As the compound reduces Tollen's reagent and undergoes Cannizzaro's reaction, it is an aldehyde and not a ketone. The data further reveals that the compound on vigorous oxidation gives 1, 2-benzene dicarboxylic acid. This clearly shows that in the compound which is of aromatic nature, CHO group is present at position-1 and C_2H_5 side chain at position-2. The given compound

is 2-ethyl benzaldehyde. The reactions involved are given below :



Question 11.

An organic compound [A] with molecular formula $C_8H_{16}O_2$ was hydrolysed with dilute sulphuric acid to give a carboxylic acid [B] and alcohol [C]. Oxidation of [C] with chromic acid produced [B]. The alcohol [C] on dehydration gave but-1-ene. Write equations for the reactions involved. **(C.B.S.E. 2008 Supp., C.B.S.E. 2009)**

Answer:

(i) The available data shows that the compound [A] upon hydrolysis gave a carboxylic acid [B] and alcohol [C]. It must be an ester.

(ii) Since the alcohol [C] upon oxidation with chromic acid gave back the carboxylic acid [B], both the acid and alcohol must have the same number of carbon atoms (four each).

(iii) The alcohol [C] upon dehydration gave an alkene.

The equations for the reactions are given:

$$\underset{\text{Butylbutanoate [A]}\ (C_8H_{16}O_2)}{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} \xrightarrow{H_2O/H^+} \underset{\text{Butanoic acid [B]}}{CH_3CH_2CH_2COOH} + \underset{\text{Butan-1-ol [C]}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\text{Butanoic acid [B]}}{CH_3CH_2CH_2COOH} \xleftarrow[\text{(oxidation)}]{H_2CrO_4} \underset{\text{Butan-1-ol [C]}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O]{\text{(Dehydration)}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

Question 12.

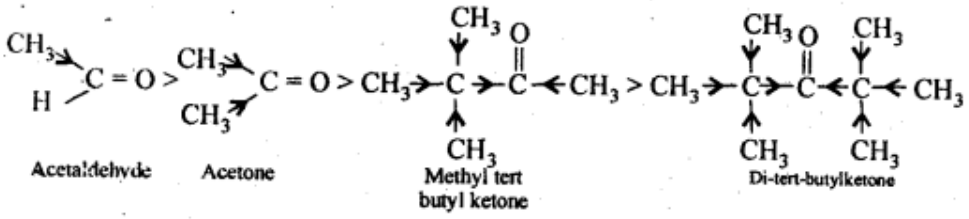
Arrange the following compounds in increasing order of their property as indicated:

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

(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CH\ COOH$, $CH_3CH_2CH_2COOH$ (acid strength).

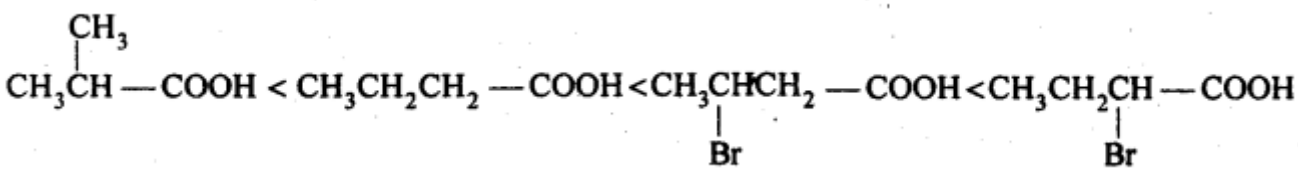
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic add, 4-Methoxybenzok acid (acid strength).

Answer:
(i) The reactivity of aldehydes and ketones towards HCN addition decreases as the +1 – effect of the alkyl groups increases. Secondly, it decreases with increase in steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon. Thus the decreasing order of reactivity towards HCN is,



+ I effect increases ⟶
Steric hindrance increases ⟶
Reactivity towards HCN addition decreases ⟶

(ii) We know that the + I-effect decreases while -I-effect increases the acidic strength of carboxylic acids. Since + I-effect of isopropyl group is more than that of propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$. Further since -I-effect decreases with distance, therefore $CH_3CH_2CHBrCOOH$ is a stronger acid than $CH_3CHBrCH_2COOH$. Thus, the overall acid strength increases in the order:

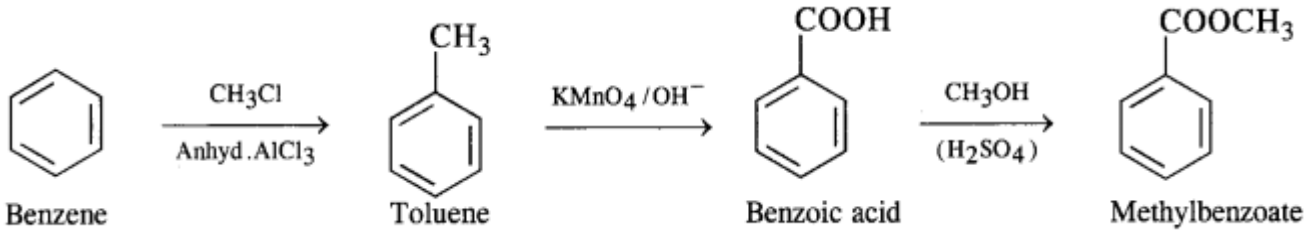


(iii) Since electron-donating groups decrease the acidic strength, therefore, 4-methoxy benzoic acid is a weaker acid than benzoic acid. Further, since electron-withdrawing groups increase the acidic strength, therefore, both 4-nitrobenzoic acid and 3,4-dinitrobenzoic acid are stronger acids than benzoic acid. Further due to the presence of an additional $-NO_2$ group at /w-position with respect to -COOH group, 3,4-dinitrobenzoic acid is a stronger acid than 4-nitrobenzoic acid. Thus, the overall acidic strength increases in the order:4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

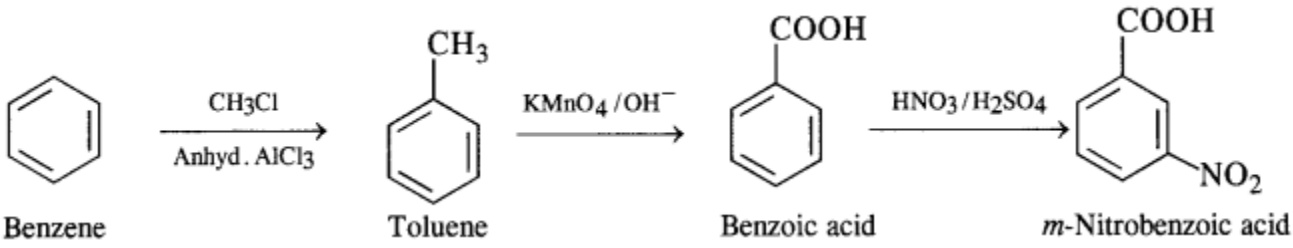
Question 13.
Give chemical tests to distinguish between the following pairs of compounds :
(i) Propanal and propanone **(C.B.S.E. Delhi 2011, 2012)**
(ii) Phenol and benzoic acid
(iii) Acetophenone and benzophenone
(iv) Benzoic acid and ethyl benzoate **(C.B.S.E. Outside Delhi 2009, 2011)**
(v) Pentan-2-one and pentane-3-one
(vi) Benzaldehyde and acetophenone **(C.B.S.E. Outside Delhi 2015)**
(vii) Ethanal and propanal **(C.B.S.E. Outside Delhi 2009, 2011, 2012)**
Answer:
(i) Propanal and propanone: Propanal will give a silver mirror upon heating with Tollen's reagent but propanone will not respond.
(ii) Phenol and benzoic acid: Benzoic acid will give brisk effervescence with sodium hydrogen carbonate ($NaHC0_3$) but phenol will not respond.
(iii) Acetophenone and benzophenone: Acetophenone is a methyl ketone. It will give a yellow

precipitate upon heating with I_2 and NaOH. Benzophenone will not respond.
(iv) Benzoic acid and ethyl benzoate: Benzoic acid will give brisk effervescence with sodium hydrogen carbonate ($NaHC0_3$) but ethyl benzoate (ester) will not respond.
(v) Pentan-2-one and pentan-3-one: Pentan-3-one is a methyl ketone and will give a yellow precipitate upon heating with I_2 and NaOH. Pentan-3-one will not respond.
(vi) Benzaldehyde and acetophenone: The distinction can also be made by iodoform test. Acetophenone will give yellow precipitate while benzaldehyde will not react.
(vii) Ethanal and propanal: Ethanal will respond to iodoform test and give yellow precipitate. Propanal will not react.

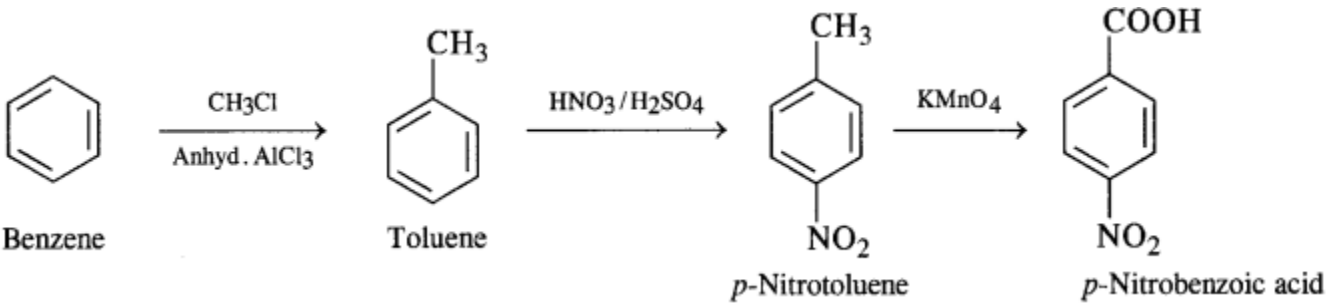
Question 14.
How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.
(i) Methylbenzoate
(ii) m-Nitrobenzoic acid
(iii) p-Nitrobenzoic acid
(iv) Phenylacetic acid
(v) p-nitrobenzaldehyde
Answer:
(i) Benzene to methylbenzoate



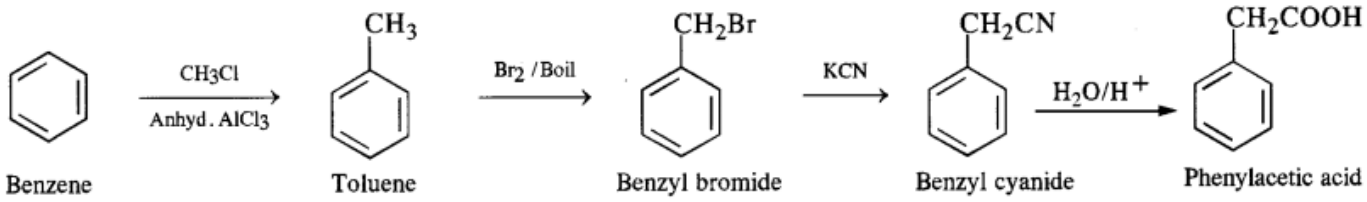
(ii) Benzene to m-nitrobenzoic acid



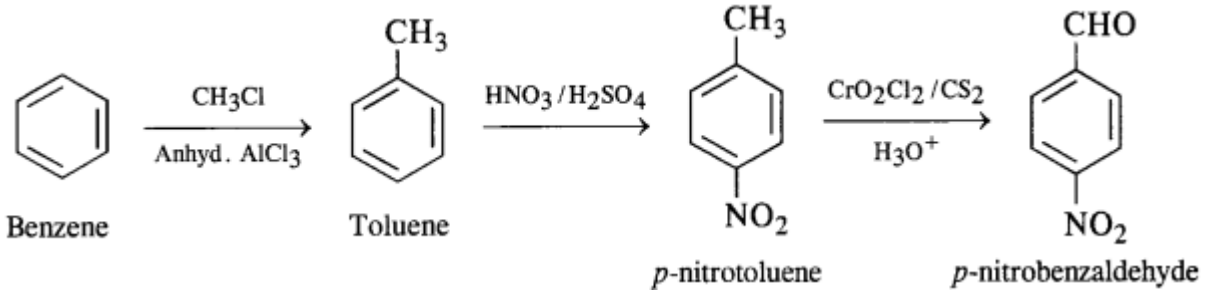
(iii) Benzene to p-nitrobenzoic acid



(vi) Benzene to phenylacetic acid

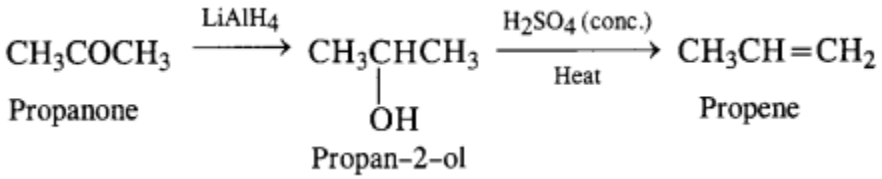


(v) Benzene to p-nitrobenzaldehyde

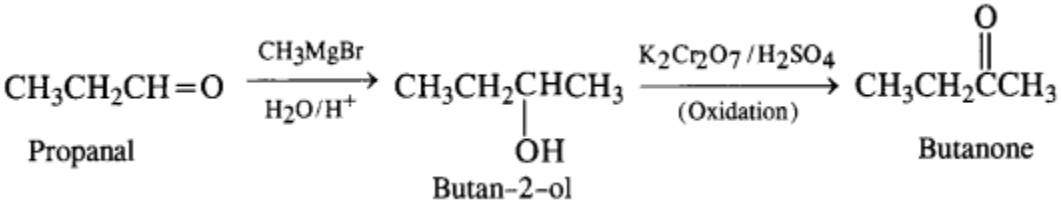


Question 15.
How will you bring about the following conversions in not more than two steps?
(i) Propanone to propene **(C.B.S.E. Delhi 2009, Uttarakhand Board 2009)**
(ii) Propanal to butanone
(iii) Ethanol to 3-hydroxybutanal **(C.B.S.E. Outside Delhi 2012)**
(iv) Benzaldehyde to benzophenone **(C.B.S.E. Outside Delhi 2012)**
(v) Benzaldehyde to 3-Phenylpropan-1-ol
(vi) Benzaldehyde to a-Hydroxyphenylacetic acid
(vii) Benzoic acid to benzaldehyde **(C.B.S.E. Delhi 2009, Outside Delhi 2017)**
(viii) Benzene to m-nitroacetophenone
(ix) Benzoic acid to /n-nitrobenzyl alcohol. **(C.B.S.E. Delhi 2012)**
Answer:

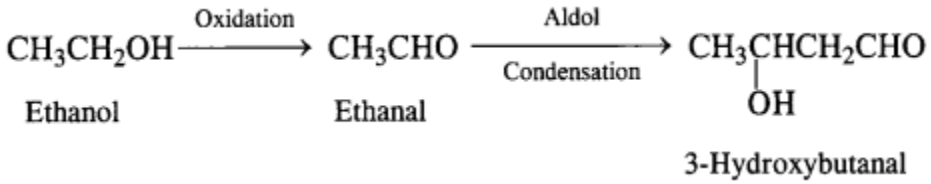
(i) Propanone to propene



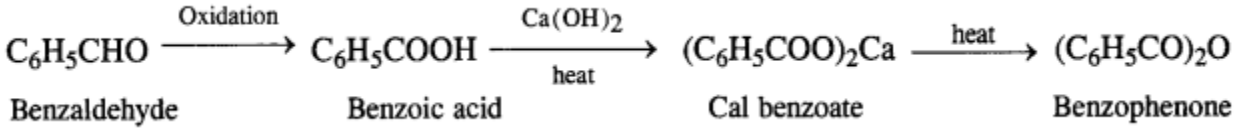
(ii) Propanal to butanone



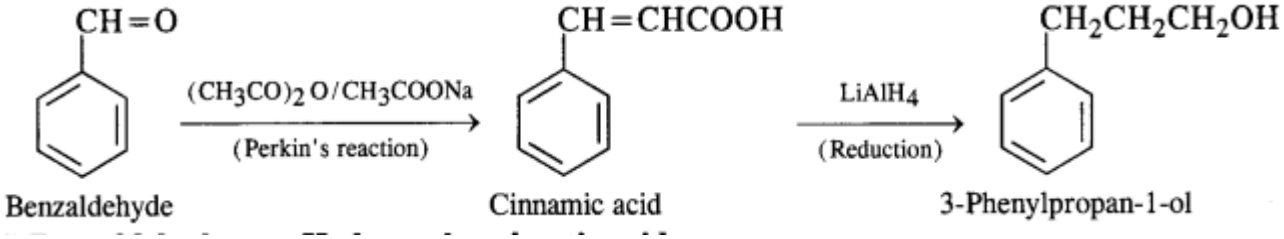
(iii) Ethanol to 3-hydroxybutanal



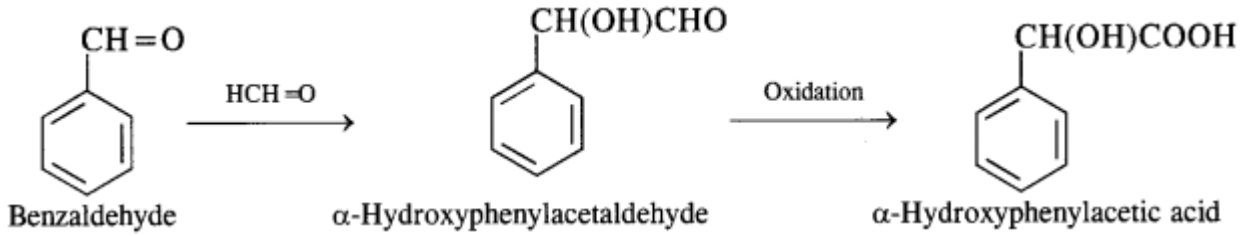
(iv) Benzaldehyde to benzophenone



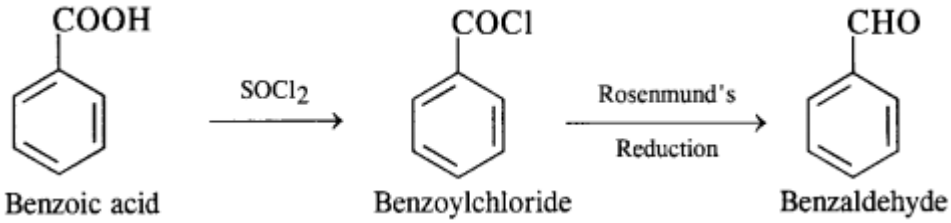
(v) Benzaldehyde to 3-phenylpropan-1-ol



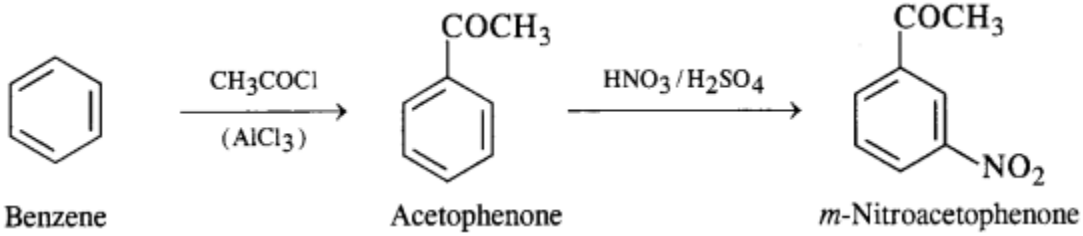
(vi) Benzaldehyde to a-Hydroxyphenylacetic acid



(vii) Benzoic acid to benzaldehyde



(viii) Benzene to m-nitroacetophenone



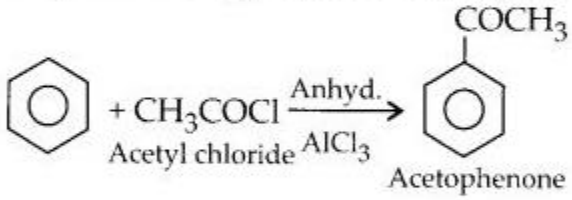
(ix) Benzoic acid to m-nitrobenzyl alcohol

Benzoic acid — *m*-Nitrobenzoic acid — *m*-Nitrobenzyl alcohol

Question 16:
Describe the following:
(i) Acylation
(ii) Cross-aldol condensation
(iii) Cannizzaro's reaction
(iv) Decarboxylation.
Answer:

(i) Acetylation : Acetylation is the process of introducing an $R\text{--}\overset{\overset{O}{\|}}{C}\text{—}$ group in compounds that contain a replaceable hydrogen atom. The best example of acetylation is Friedel-Crafts acylation reaction where *R*CO group is introduced on the benzene ring.

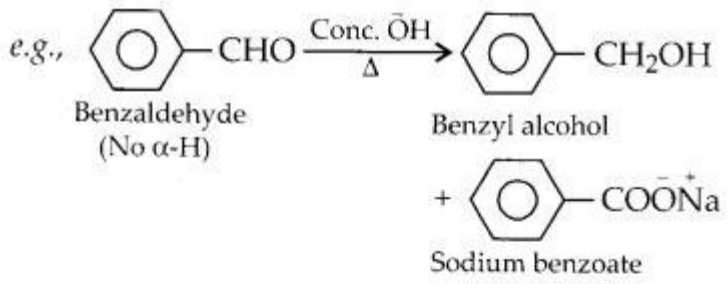
Reagents employed for the purpose of acylation are acyl chloride, acid anhydride etc. *e.g.,* Friedel-crafts acylation:



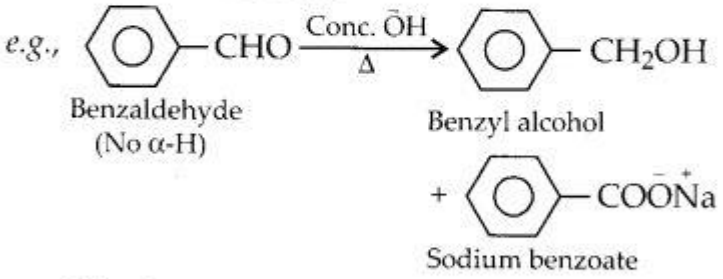
$$CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} CH_3COOC_2H_5 + HCl$$

Ethyl acetate

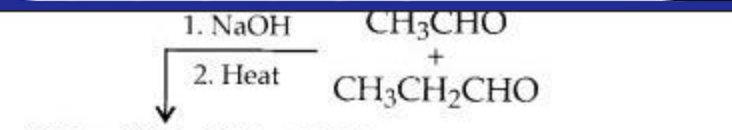
(ii) Cannizzaro reaction : Cannizzaro reaction is undergone by aldehydes or ketones that lack an α-hydrogen atom. Such carbonyl compounds in the presence of conc. NaOH and heat undergo disproportionation reaction to produce the corresponding carboxylate ion and alcohol.



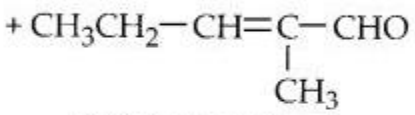
(ii) Cannizzaro reaction : Cannizzaro reaction is undergone by aldehydes or ketones that lack an α-hydrogen atom. Such carbonyl compounds in the presence of conc. NaOH and heat undergo disproportionation reaction to produce the corresponding carboxylate ion and alcohol.



(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.

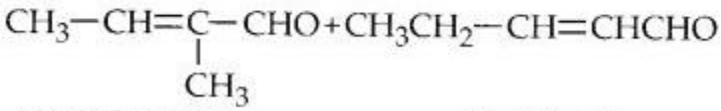


But-2-enal
From two molecules of ethanal



2-Methylpent-2-enal
From two molecules of propanal

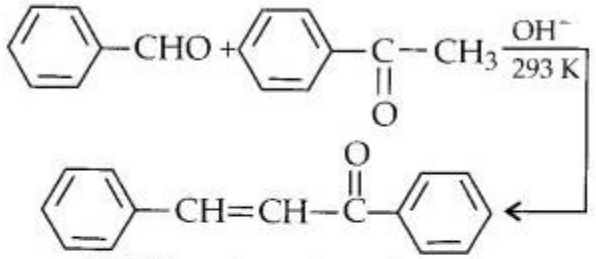
Simple or self aldol products



2-Methylbut-2-enal Pent-2-enal
From one molecule of ethanal and one molecule of propanal

Cross aldol products

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

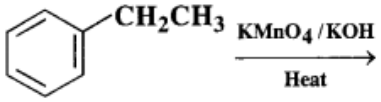


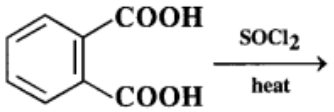
1,3-Diphenylprop-2-ene-1-one
(Benzalacetophenone) (Major product)

(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

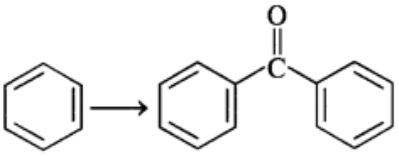
$$R\text{—}COONa \xrightarrow[\text{Heat}]{NaOH + CaO} R\text{—}H + Na_2CO_3$$

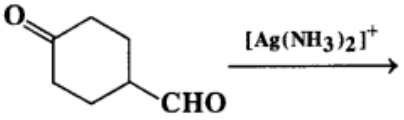
Question 17:
Complete each synthesis by giving missing starting material, reagent, or products.

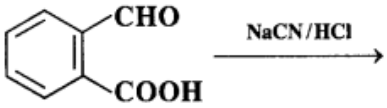
(i)  *(C.B.S.E. Outside Delhi 2008)*

(ii)  *(C.B.S.E. Outside Delhi 2008, 2011)*

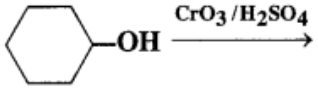
(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

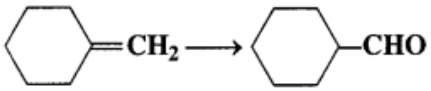
(iv)  *(C.B.S.E. Delhi 2009)*

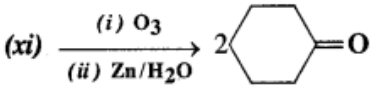
(v) 

(vi) 

(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil NaOH}}$ (viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$

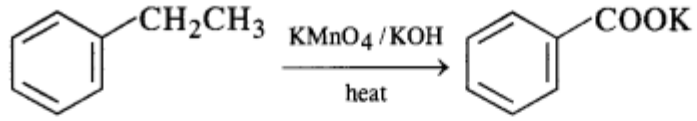
(ix) 

(x) 

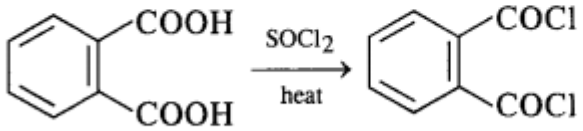
(xi) 

(C.B.S.E. Outside Delhi 2008)

Answer:

(i) 

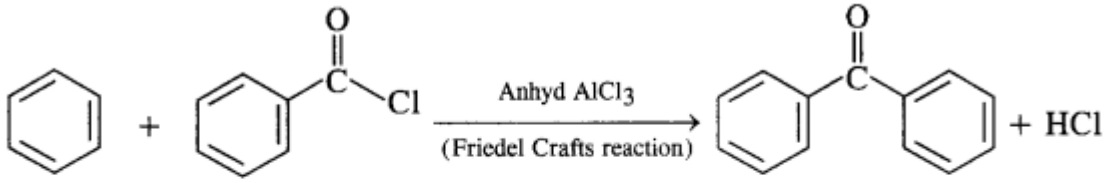
Ethyl benzene — Pot. benzoate

(ii) 

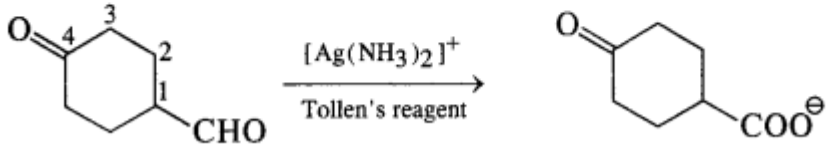
Phthalic acid — Phthaloyl chloride

(iii) $C_6H_5CH=\boxed{O + H_2}NCONHNH_2 \longrightarrow C_6H_5CH=NCONH_2 + H_2O$

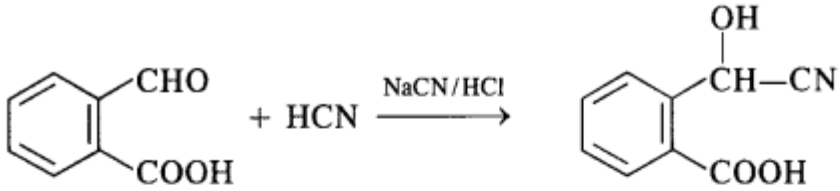
Benzaldehyde — Semicarbazide — Benzaldehyde semicarbazone

(iv) 

Benzene — Benzoyl chloride — Benzophenone

(v) 

4-Oxocyclohexanecarbaldehyde — 4-Oxocyclohexanecarboxylate anion

(vi) 

2-Formylbenzoic acid — 2-[1-hydroxycyanomethyl] benzoic acid

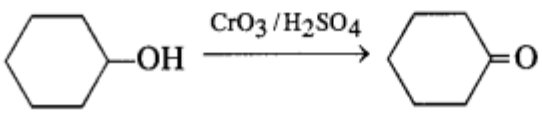
(vii) $C_6H_5CH=\boxed{O + H_2}C(CH_3)-CHO \xrightarrow[\text{Claisen Schmidt Condensation}]{\text{dil NaOH}} C_6H_5-\overset{3}{C}H=\overset{2}{C}(CH_3)-\overset{1}{C}HO$

Benzaldehyde — Propanal — 2-Methyl-3-phenylprop-2-enal

(viii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4} \overset{4}{C}H_3-\overset{OH}{\overset{|}{\overset{3}{C}}}H-\overset{2}{C}H_2-\overset{1}{C}OOC_2H_5 + H_2O$

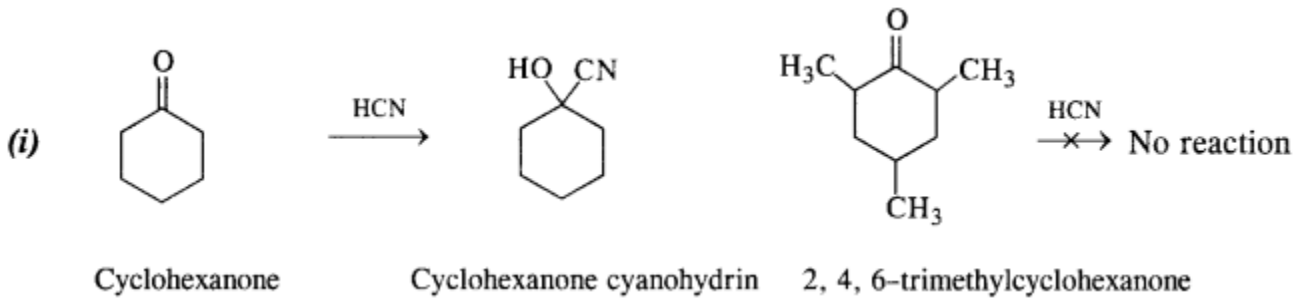
Ethyl-3-oxobutanoate — Ethyl-3-hydroxylbutanoate

(Only the ketonic group is reduced by $NaBH_4$. The ester group is not reduced.)

(ix) 

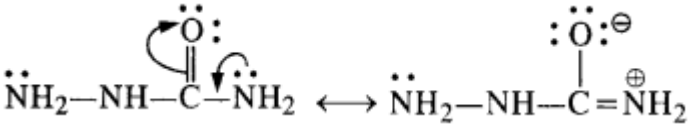
Cyclohexanol — Cyclohexanone

Question 18:
Give a plausible explanation for each of the following:
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.
(ii) There are two – NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazone.
(iii) During the preparation of esters from carboxylic acid and alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.
Answer:

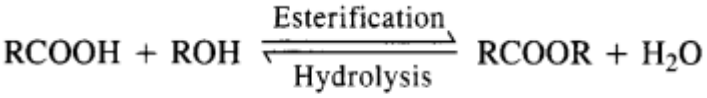


In cyclohexanone, the attack of CN" ion (nucleophile) can easily take place at the carbonyl carbon atom. However, in 2, 4, 6-trimethylcyclohexanone, the three CH_3 groups being electron releasing in nature (+ I effect) will considerably increase the electron density on the carbonyl carbon atom and the nucleophile attack does not seem to be feasible. Moreover, the two —CH_3 substituents at the ortho positions will also hinder the attack of nucleophile CN^- ion on the carbonyl group.

(ii) The structural formula of semi-carbazide is $NH_2NHCONH_2$. Although both the amino groups have lone electron pairs, one of these is in conjugation with the electron-withdrawing carbonyl group and acquires a positive charge. Therefore, it is not in a position to act as the nucleophile, and only one -NH_2 group is involved in the formation of semicarbazone.



(iii) The esterification carried in the presence of acid is of reversible nature and the reverse reaction is called ester hydrolysis.



In order that the reaction may proceed in the forward direction, ester or water formed in the reaction must be removed. Sulphuric acid added in esterification helps in removing molecules of H_20 as it is a dehydrating agent.

Question 19:
An organic compound contains 69-77% carbon, 11-63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Write the possible structure of the compound. **(C.B.S.E. Delhi 2008, 2009, Uttarakhand Board 2015)**

Answer:

Step I: Calculation of molecular formula of the compound

Percentage of oxygen = 100 – (% C + % H) = 100 – (69.77 + 11.63) = 18.6%

Element	Percentage	Atomic Mass	Gram atoms (moles)	Atomic ratio (Molar ratio)	Simplest whole no. ratio
C	69·77	12	$\frac{69\cdot77}{12} = 5\cdot88$	$\frac{5\cdot88}{1\cdot16} = 5\cdot06$	5
H	11·63	1	$\frac{11\cdot63}{1} = 11.63$	$\frac{11\cdot63}{1\cdot16} = 10\cdot0$	10
O	18·6	16	$\frac{18\cdot6}{16} = 1\cdot16$	$\frac{1\cdot16}{1\cdot18} = 1\cdot0$	1

$$\text{Empirical formula} = C_5H_{10}O$$

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

$$n = \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{86}{86} = 1$$

$$\therefore \quad \text{Molecular formula} = n \times \text{Empirical formula} = C_5H_{10}O.$$

Step II. Predicting the structure of the compound

- Since the compound forms an addition compound with $NaHS0_3$, it must be a carbonyl compound.
- As the compound does not reduce Tollen's reagent but gives a positive iodoform test, it must contain in it a methyl

ketonic $(-\overset{\overset{O}{\|}}{C}-CH_3)$ group.

Keeping in view these characteristics, the compound is $CH_3CH_2CH_2COCH_3$ (Pentan-2-one).

All the reactions in which pentan-2-one participates, are given for the benefit of the students.

***(i)* Action with sodium hydrogen sulphite ($NaHSO_3$)**

$$\underset{\text{Pentan-2-one}}{H_7C_3(CH_3)C{=}O} + NaHSO_3 \longrightarrow \underset{\text{Sod. bisulphite derivative of pentan-2-one}}{H_7C_3(CH_3)C(SO_3Na)(OH)}$$

***(ii)* Action with I_2 and NaOH (Iodoform reaction)**

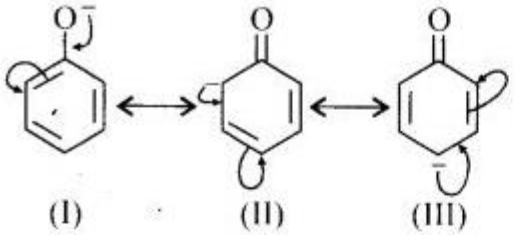
$$\underset{\text{Pentan-2-one}}{H_7C_3(CH_3)C{=}O} + 4NaOH + 3I_2 \xrightarrow{\text{heat}} \underset{\text{Iodoform (Yellow ppt)}}{CHI_3} + \underset{\text{Sod. butanoate}}{CH_3CH_2CH_2COONa} + 3NaI + 3H_2O$$

***(iii)* Vigorous oxidation**

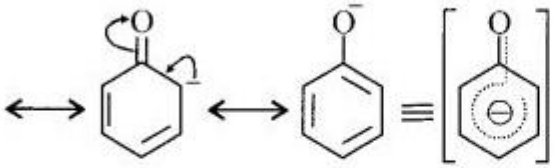
$$\underset{\text{Pentan-2-one}}{H_7C_3(CH_3)C{=}O} \xrightarrow[\text{oxidation}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Propanoic acid}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

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

(i) Phenoxide ion has the following resonating structures :

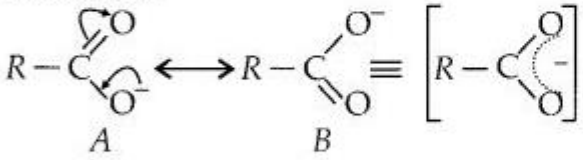


(I) (II) (III)



(IV) (V)

Carboxylate ion has the following resonance structures.



A B

(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.

(iii) The negative charge that rests on the electronegative O atom in carboxylate ion. We know that the presence of negative charge on an electronegative atom makes the ion more stable. For the same reason $RCOO^-$ is more stable than the phenoxide ion where the oxygen has no negative charge on it. For the above two reasons carboxylate ion is more stable and has higher acidity than phenol.