Aldehydes, Ketones and Carboxylic Acids

NCERT Intext Questions

Q. 1. Write the structures of the following compounds:

(*i*) α-Methoxypropionaldehyde

(*ii*) 3-Hydroxybutanal

(*iii*) 2-Hydroxycyclopentane carbaldehyde

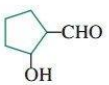
(*iv*) 4-oxopentanal

(*v*) Di-sec. butyl ketone

(*vi*) 4-Fluoroacetophenone

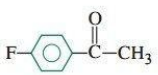
Ans. (*i*) $CH_3O-CH(-)-C(=O)-H$

(*ii*) $H_3C-CH(OH)-CH_2-C(=O)-H$

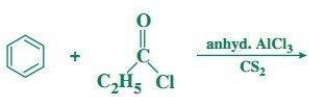
(*iii*) 

(*iv*) $CH_3-C(=O)-CH_2-CH_2-CHO$

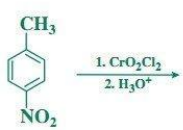
(*v*) $CH_3CH_2CH(CH_3)-C(=O)-CH(CH_3)-CH_2CH_3$

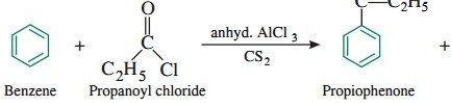
(*vi*) 

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

(*i*) 

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

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

Ans. (*i*) 

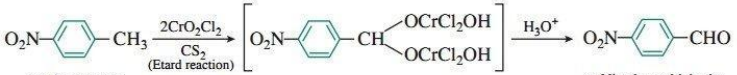
Benzene + Propanoyl chloride → Propiophenone + HCl

(*ii*) $(C_6H_5CH_2)_2Cd + 2CH_3-C(=O)-Cl \xrightarrow{\text{Dry ether}} 2\,C_6H_5CH_2-C(=O)-CH_3 + CdCl_2$

Dibenzyl cadmium; Acetyl chloride; 1-Phenylpropan-2-one

(*iii*) $H_3C-C\equiv C-H \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+},} [CH_3-C(OH)=CH_2] \xrightarrow{\text{Tautomerises}} CH_3-C(=O)-CH_3$

Propyne; Propanone

(*iv*) 

p-Nitrotoluene; *p*-Nitrobenzaldehyde

Q. 3. Arrange the following compounds in increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Q. 4. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(*i*) Ethanal, Propanal, Propanone, Butanone

(*ii*) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

[Hint: Consider steric effect and electronic effect.]

Ans. (*i*) The reactivity in nucleophilic addition reactions increases in the order:

Butanone < Propanone < Propanal < Ethanal

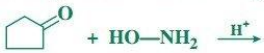
(*ii*) Acetophenone is a ketone. All the other three compounds are aldehydes. Hence, acetophenone is least reactive.

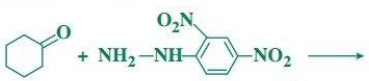
p-Tolualdehyde has an electron-donating methyl group at the para position of the benzene ring whereas *p*-nitrobenzaldehyde has an electron-withdrawing nitro group at the para position. Thus, *p*-tolualdehyde is less reactive and *p*-nitrobenzaldehyde is more reactive than benzaldehyde.

Therefore, the required order is as follows:

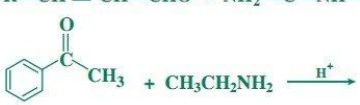
Acetophenone < *p*-Tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

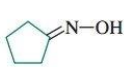
Q. 5. Predict the products of the following reactions:

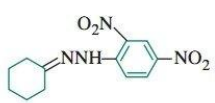
(*i*) 

(*ii*) 

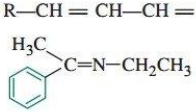
(*iii*) 

(*iv*) 

Ans. (*i*) 

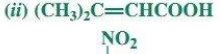
(*ii*) 

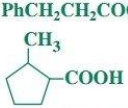
(*iii*) 

(*iv*) 

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

(*i*) $PhCH_2CH_2COOH$

(*ii*) 

(*iii*) 

(*iv*)

Ans. (*i*) 3-Phenylpropanoic acid

(*ii*) 3-Methylbut-2-enoic acid

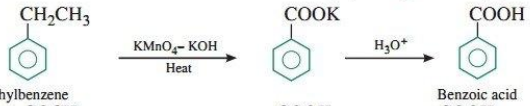
(*iii*) 2-Methylcyclopentanecarboxylic acid

(*iv*) 2, 4, 6-Trinitrobenzoic acid

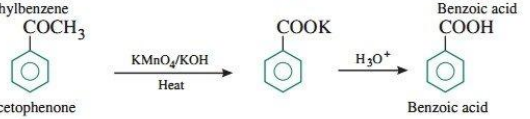
Q. 7. Show how each of the following compounds can be converted to benzoic acid:

(*i*) Ethylbenzene **(*ii*) Acetophenone**

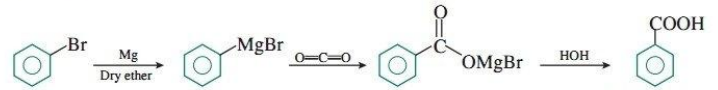
(*iii*) Bromobenzene **(*iv*) Phenylethene (Styrene)**

Ans. (*i*) 

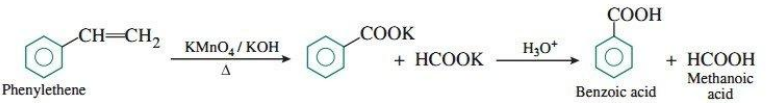
Ethylbenzene Benzoic acid

(*ii*) 

Acetophenone Benzoic acid

(*iii*) 

Bromobenzene Phenylmagnesium bromide Benzoic acid

(*iv*) 

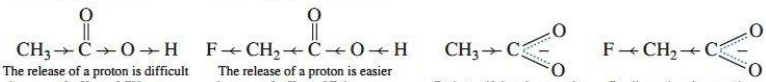
Phenylethene Benzoic acid

Q. 8. Which acid of each pair shown here would you expect to be stronger?

(*i*) CH_3CO_2H or CH_2FCO_2H **(*ii*) CH_2FCO_2H or CH_2ClCO_2H**

(*iii*) $CH_2FCH_2CH_2CO_2H$ or $CH_3—CHF—CH_2CO_2H$

(*iv*) $F_3C—C_6H_4—COOH$ or $H_3C—C_6H_4—COOH$

Ans. (*i*) 

The release of a proton is difficult because +I-effect of CH_3 group increases the electron density in the O—H bond.

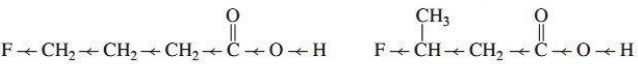
The release of a proton is easier because –I-effect of F decreases the electron density in the O—H bond.

By intensifying the negative charge , +I-effect destabilises the carboxylate ion.

By dispersing the negative charge, –I-effect stabilises the carboxylate ion.

Therefore, due to lesser electron density in the O—H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion, FCH_2COOH is a stronger acid than CH_3COOH.

(*ii*) The FCH_2COO^- ion is much more stable than $ClCH_2COO^-$ ion due to much stronger –I effect of F than Cl and thus FCH_2COOH is a stronger acid than $ClCH_2COOH$.

(*iii*) 

4-Fluorobutanoic acid 3-Fluorobutanoic acid

Inductive effect decreases with distance, therefore, –I effect of F is somewhat stronger in 3-fluorobutanoic acid than in 4-fluorobutanoic acid. Hence, CH_3CHFCH_2COOH is a stronger acid than $FCH_2CH_2CH_2COOH$.

(*iv*) 

CF_3 has a strong –I-effect, it stabilises the carboxylate ion by dispersing the –ve charge

CH_3 has a weak +I-effect, it destabilises the carboxylate ion by intensifying the –ve charge

Hence, due to greater stability of $F_3C—C_6H_4—COO^-$ (*p*) ion than $CH_3—C_6H_4COO^-$ (*p*) ion, $F_3C—C_6H_4—COOH$ (*p*) is a much stronger acid than $CH_3—C_6H_4—COOH$ (*p*).

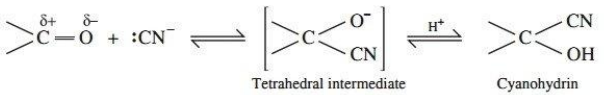
NCERT Exercises

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

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

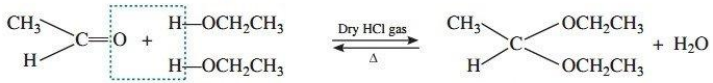
Ans. (*i*) gem-Hydroxynitriles, *i.e.*, compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. It is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



Tetrahedral intermediate Cyanohydrin

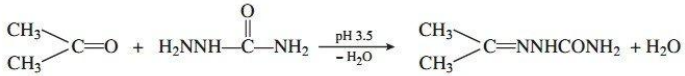
(*ii*) gem-Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.



Acetaldehyde Ethyl alcohol Acetaldehyde diethyl acetal

These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehydic group in organic synthesis.

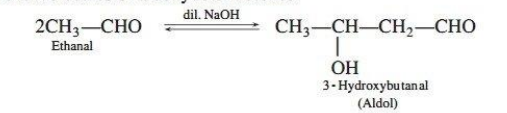
(*iii*) Semicarbazones are derivatives of aldehydes and ketones and are produced by the action of semicarbazide on them in weak acidic medium.



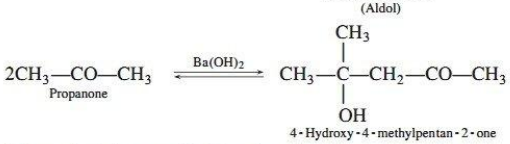
Acetone Semicarbazide Acetone semicarbazone

These are used for identification and characterisation of aldehydes and ketones.

(*iv*) Aldols are β-hydroxy aldehydes or ketones and are produced by the condensation two same or different molecules of aldehyde or ketones.

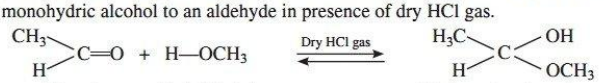


Ethanal 3-Hydroxybutanal (Aldol)



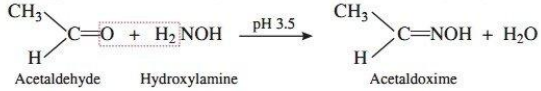
Propanone 4-Hydroxy-4-methylpentan-2-one

(*v*) gem-Alkoxyalcohols are called hemiacetals. These are produced by addition of one molecule of a monohydric alcohol to an aldehyde in presence of dry HCl gas.



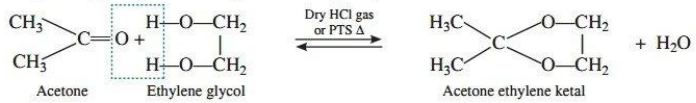
Ethanal Methyl alcohol 1-Hydroxy-1-methoxyethane (A hemiacetal)

(*vi*) Oximes are produced when aldehydes or ketones react with hydroxylamine in weak acidic medium.



Acetaldehyde Hydroxylamine Acetaldoxime

(*vii*) gem-Dialkoxyalkanes are called ketals. In ketals, the two alkoxy groups are present on the same carbon within the chain. These are produced when a ketone is heated with ethylene glycol in presence of dry HCl gas or *p*-toluenesulphonic acid (PTS).



Acetone Ethylene glycol Acetone ethylene ketal

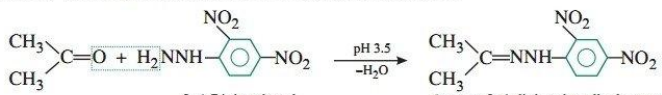
These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for protection of keto groups in organic synthesis.

(*viii*) Compounds containing $>C=N-$ group are called imines. These are produced when aldehydes and ketones react with ammonia derivatives.

Aldehyde/Ketone Ammonia derivative Imines

Z = H, Alkyl, aryl, $-NH_2$, $-OH$, $-C_6H_5NH$, $-NHCONH_2$, etc.

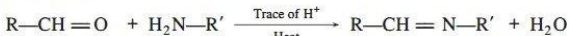
(*ix*) 2, 4-Dinitrophenylhydrazones (2, 4-DNP derivatives) are produced when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in weakly acidic medium.



2, 4-Dinitrophenyl hydrazine Acetone 2, 4-dinitrophenylhydrazone

2, 4-DNP derivatives are used for identification and characterisation of aldehydes and ketones.

(*x*) Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.



Aldehyde 1° Amine Schiff's base

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

(*i*) $CH_3CH(CH_3)CH_2CH_2CHO$ **(*ii*) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$**

(*iii*) $CH_3CH{=}CHCHO$ **[*CBSE 2019(56/5/2)*]**

(*iv*) $CH_3COCH_2COCH_3$ **(*v*) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$**

(*vi*) $(CH_3)_3CCH_2COOH$ **(*vii*) $OHCC_6H_4CHO$-*p***

Ans. (*i*) 4-Methylpentanal (*ii*) 6-Chloro-4-ethylhexan-3-one

(*iii*) But-2-en-1-al (*iv*) Pentane-2, 4-dione

(*v*) 3, 3, 5-Trimethylhexan-2-one (*vi*) 3, 3-Dimethylbutanoic acid

(*vii*) Benzene-1, 4-dicarbaldehyde

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

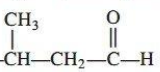
(*i*) 3-Methylbutanal **(*ii*) *p*-Nitropropiophenone**

(*iii*) *p*-Methylbenzaldehyde **(*iv*) 4-Methylpent-3-en-2-one**

(*v*) 4-Chloropentan-2-one **(*vi*) 3-Bromo-4-phenylpentanoic acid**

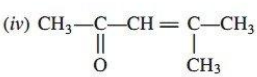
(*vii*) *p-p'*-Dihydroxybenzophenone **(*viii*) Hex-2-en-4-ynoic acid**

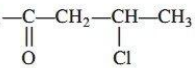
Ans. (*i*)

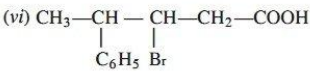


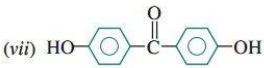
(*ii*)

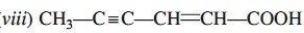
(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

(*vii*) 

(*viii*) 

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

(*i*) $CH_3CO(CH_2)_4CH_3$ (*ii*) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(*iii*) $CH_3(CH_2)_5CHO$ (*iv*) Ph—CH=CH—CHO

(*v*)  (*vi*) PhCOPh

Ans.

S.No.	IUPAC Name	Common Name
(*i*)	Heptan-2-one	Methyl *n*-pentyl ketone
(*ii*)	4-Bromo-2-methylhexanal	γ-Bromo-α-methylcaproaldehyde
(*iii*)	Heptanal	—
(*iv*)	3-Phenylprop-2-enal	β-Phenylacrolein
(*v*)	Cyclopentanecarbaldehyde	Cyclopentanecarbaldehyde
(*vi*)	Diphenylmethanone	Benzophenone

Q. 5. Draw structures of the following derivatives:

(*i*) **The 2, 4-dinitrophenylhydrazone of benzaldehyde**

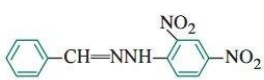
(*ii*) **Cyclopropanone oxime**

(*iii*) **Acetaldehydedimethylacetal**

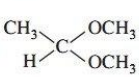
(*iv*) **The semicarbazone of cyclobutanone**

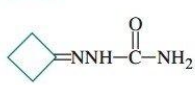
(*v*) **The ethylene ketal of hexan-3-one**

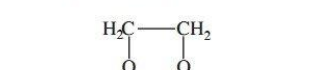
(*vi*) **The methyl hemiacetal of formaldehyde**

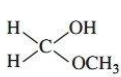
Ans. (*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

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

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

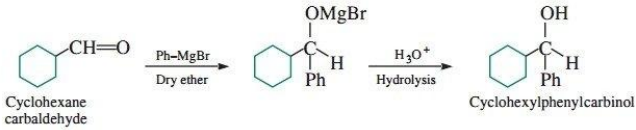
(*ii*) **Tollens' reagent**

(*iii*) **Semicarbazide and weak acid**

(*iv*) **Excess ethanol and acid**

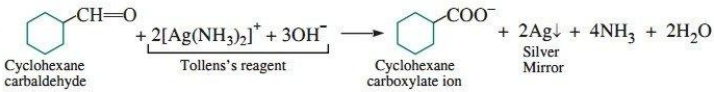
(*v*) **Zinc amalgam and dilute hydrochloric acid**

Ans. (*i*)



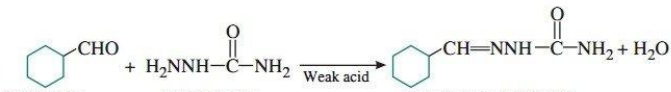
Cyclohexane carbaldehyde — Cyclohexylphenylcarbinol

(*ii*)



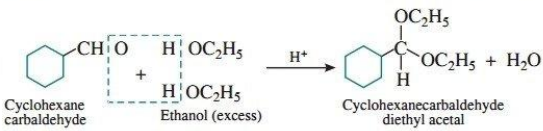
Cyclohexane carbaldehyde — Cyclohexane carboxylate ion

(*iii*)



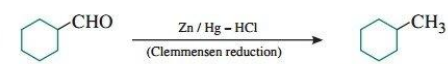
Cyclohexane carbaldehyde — Semicarbazide — Cyclohexanecarbaldehyde semicarbazone

(*iv*)



Cyclohexane carbaldehyde — Ethanol (excess) — Cyclohexanecarbaldehyde diethyl acetal

(*v*)



Cyclohexane carbaldehyde — Methylcyclohexane

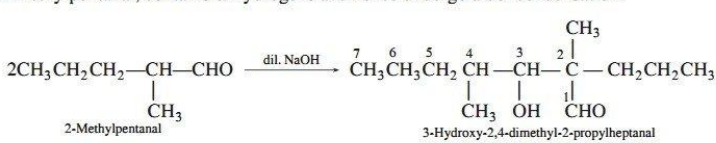
Q. 7. Which of the following compounds will undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(*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. (*i*) Methanal does not contain α-hydrogen and hence undergoes cannizzaro reaction.

Methanal — Methanol — Sodium methanoate

(*ii*) 2-Methylpentanal, contains α-hydrogens and hence undergo aldol condensation.



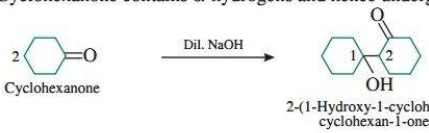
2-Methylpentanal — 3-Hydroxy-2,4-dimethyl-2-propylheptanal

(*iii*) Benzaldehyde does not contain α-hydrogen and hence undergoes cannizzaro reaction.

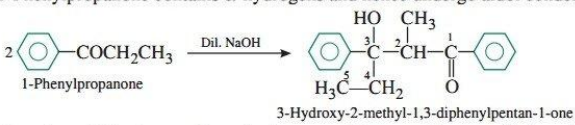
Benzaldehyde — Benzyl alcohol — Sodium benzoate

(*iv*) Benzophenone is a ketone having no α-hydrogen. It neither undergoes aldol condensation nor Cannizzaro reaction.

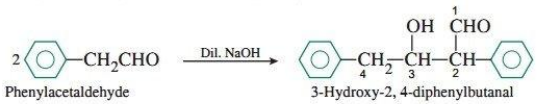
(*v*) Cyclohexanone contains α-hydrogens and hence undergo aldol condensation.



(*vi*) 1-Phenylpropanone contains α-hydrogens and hence undergo aldol condensation.

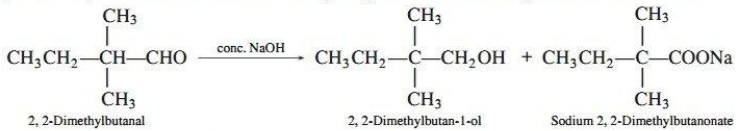


(*vii*) Phenylacetaldehyde contains α-hydrogen and hence undergoes aldol condensation.



(*viii*) Butan-1-ol is an alcohol, so it neither undergoes aldol condensation nor Cannizzaro reaction.

(*ix*) 2, 2-dimethylbutanal does not contain α-hydrogen and hence undergo Cannizzaro reaction.



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

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

Ans. (*i*) $2CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} CH_3CHOH-CH_2-CHO \xrightarrow[\text{(Reduction)}]{NaBH_4} CH_3-CHOH-CH_2CH_2OH$

Ethanal — 3-Hydroxybutanal — Butane-1.3-diol

(*ii*) $2CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} CH_3-CHOH-CH_2-CHO \xrightarrow[-H_2O]{H_3O^+/\text{Heat}} CH_3-CH=CH-CHO$

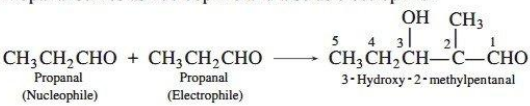
Ethanal — 3-Hydroxybutanal — But-2-enal

(*iii*) $2CH_3CHO \xrightarrow[(ii)\ H^+,\Delta]{(i)\ \text{dil. NaOH}} CH_3CH=CHCHO \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} CH_3CH=CHCO_2H$

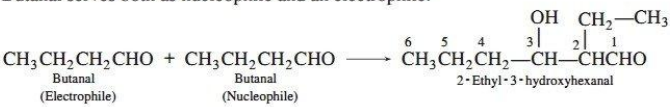
Ethanal — But-2-enal — But-2-enoic acid

Q. 9. Write structural formula 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.

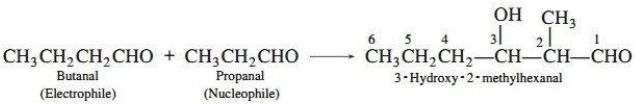
Ans. (*i*) Propanal serves as nucleophile and also as electrophile.



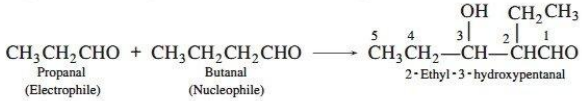
(*ii*) Butanal serves both as nucleophile and an electrophile.



(*iii*) Butanal as electrophile and propanal as nucleophile.



(*iv*) Propanal as electrophile and butanal as nucleophile.

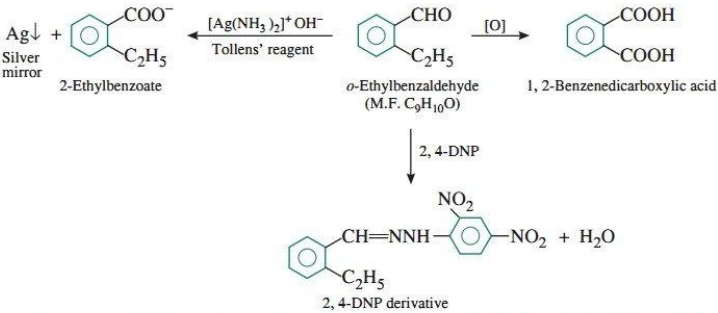


Q. 10. An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound. ***[HOTS]***

Ans. (*i*) The given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollens' reagent, it must be an aldehyde.

(*ii*) As it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.

(*iii*) On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. The only *o*-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is *o*-ethylbenzaldehyde. All the reactions can be explained on the basis of this structure.



Q. 11. An organic compound (*A*) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to 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.

[CBSE Delhi 2010; (AI) 2009] ***[HOTS]***

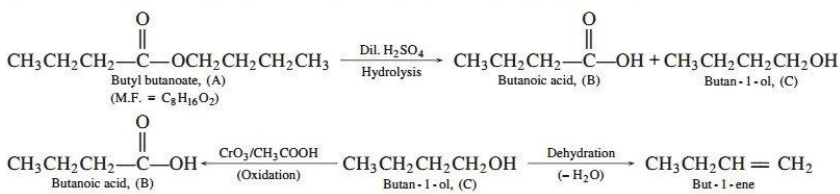
Ans. As the organic compound (*A*) with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid (*B*) and the alcohol (*C*) therefore (*A*) must be an ester and oxidation of (*C*) with chromic acid produces the acid (*B*), therefore, both the carboxylic acid (*B*) and alcohol (*C*) must contain the same number of carbon atoms.

Now ester (*A*) contains eight carbon atoms, therefore, both the carboxylic acid (B) and the alcohol (C) must contain four carbon atoms each.

As the alcohol (*C*) on dehydration gives but-1-ene, therefore, (*C*) must be a straight chain alcohol, *i.e.*, butan-1-ol.

If *C* is butan-1-ol, then the acid (*B*) which it gives on oxidation must be butanoic acid and the ester (*A*) must be butyl butanoate.

The relevant equations for all the reactions involved may be explained as follows:



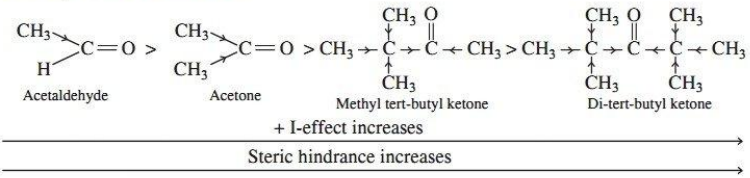
Q. 12. Arrange the following compounds in increasing order of their property as indicated:

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

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

(*iii*) Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid (acid strength).

Ans. (*i*) The reactivity towards HCN addition decreases as the +I-effect of the alkyl group/s increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon increases. Hence, the reactivity decreases in the order:

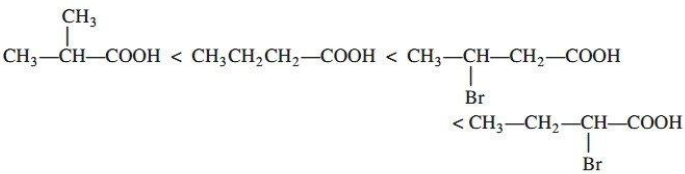


Thus, di-tert-butyl ketone < methyl tert-butyl ketone < Acetone < Acetaldehyde.

(*ii*) As we know + I-effect decreases while – I-effect increases the acid strength of carboxylic acids. As +I-effect of isopropyl group is more than that of *n*-propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Now –I-effect decreases with distance, therefore, $CH_3CH_2CH(Br)COOH$ is a stronger acid than $CH_3CH(Br)CH_2COOH$.

Therefore, the overall acid strength increases in the order:



(*iii*) As electron-donating groups decrease the acid strength, therefore 4-methoxybenzoic acid is a weaker acid than benzoic acid.

Now electron-withdrawing groups increase the acid strength, therefore, both 4-nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acids than benzoic acid. Further due to the presence of an additional NO_2 groups at *m*-position w.r.t. COOH group, 3, 4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid. Therefore, the overall acid strength increases in the following order:

4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4-dinitrobenzoic acid.

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

[*CBSE 2019(56/2/1)*]

(*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

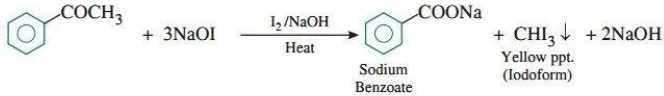
Ans. **(*i*) Propanal and propanone:**

Iodoform test: This test is given by propanone and not by propanal. Propanone on reacting with hot $NaOH/I_2$ gives a yellow precipitate of CHI_3 while propanal does not.

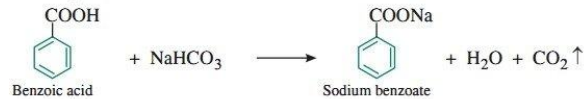
$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + \underset{\text{Sodium hypoiodite}}{3NaOI} \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + \underset{\text{Sodium acetate}}{CH_3COONa} + 2NaOH$$

(*ii*) **Acetophenone and benzophenone:** Acetophenone responds to iodoform test, but benzophenone does not.

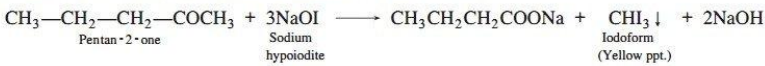


(*iii*) **Phenol and benzoic acid:** Benzoic acid reacts with $NaHCO_3$ giving CO_2 gas with effervescence, whereas phenol does not.

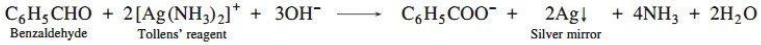


(*iv*) **Benzoic acid and ethyl benzoate:** Benzoic acid on reaction with sodium hydrogencarbonate gives out CO_2 gas with effervescence, while ethyl benzoate does not.

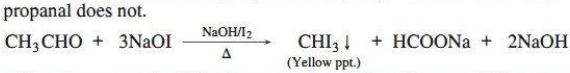
(*v*) **Pentan-2-one and Pentan-3-one:** Pentan-2-one when treated with NaOI (I_2/NaOH) gives yellow precipitate of iodoform but pentan-3-one does not give this test.



(*vi*) **Benzaldehyde and Acetophenone:** Benzaldehyde being an aldehyde gives silver mirror with Tollens' reagent but acetophenone being a ketone does not give this test.



(*vii*) **Ethanal (CH_3CHO) and propanal (CH_3CH_2CHO):** Ethanal responds to iodoform test, while propanal does not.



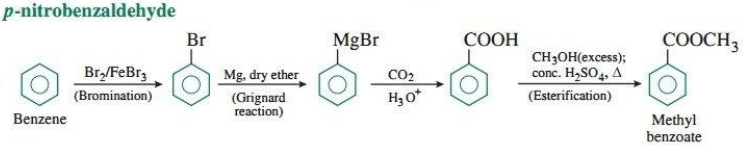
Q. 14. How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

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

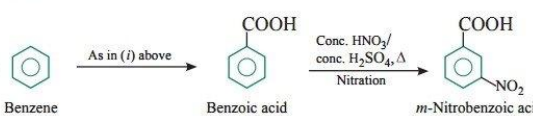
(*iii*) *p*-nitrobenzoic acid **(*iv*) Phenylacetic acid**

(*v*) *p*-nitrobenzaldehyde

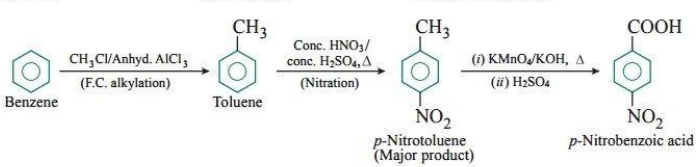
Ans. (*i*)

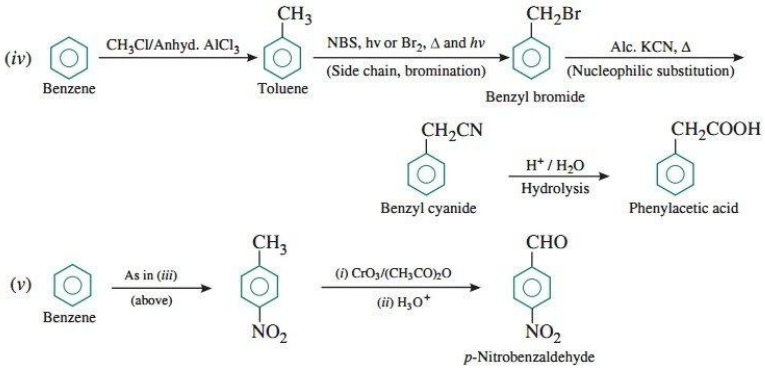


(*ii*)



(*iii*)





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

(*i*) Propanone to Propene **(*ii*) Benzoic acid to Benzaldehyde**

(*iii*) Ethanol to 3-Hydroxybutanal **(*iv*) Benzene to *m*-Nitroacetophenone**

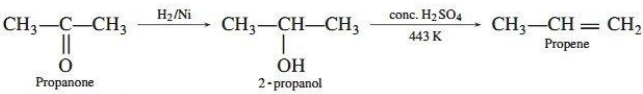
(*v*) Benzaldehyde to Benzophenone **(*vi*) Bromobenzene to 1-Phenylethanol**

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

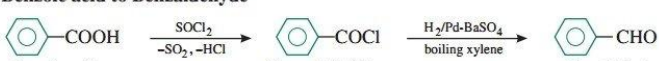
(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid

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

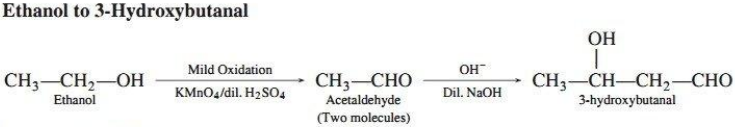
Ans. (*i*) Propanone to Propene



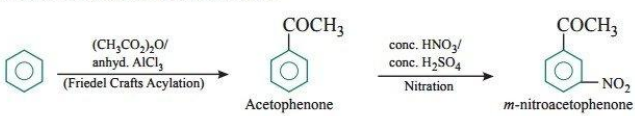
(*ii*) Benzoic acid to Benzaldehyde



(*iii*) Ethanol to 3-Hydroxybutanal

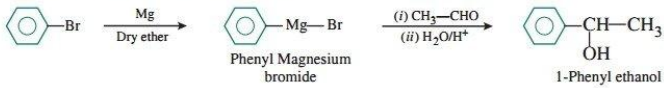


(*iv*) Benzene to *m*-Nitroacetophenone

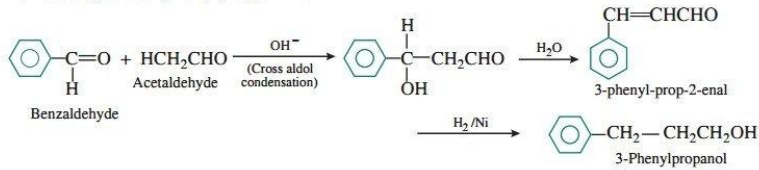


(*v*) Benzaldehyde to Benzophenone

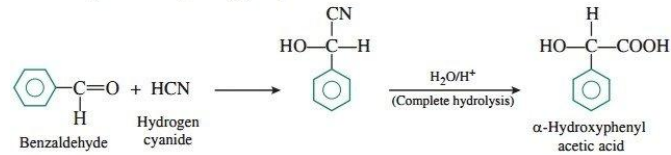
(*vi*) Bromobenzene to 1-phenylethanol:



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



(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid



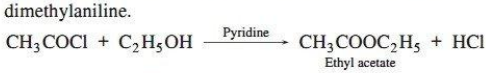
(*ix*) Benzoic acid to *m*-nitrobenzyl alcohol:

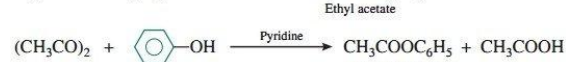
Q. 16. Describe the following:

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

(*iii*) Cross aldol condensation **(*iv*) Decarboxylation**

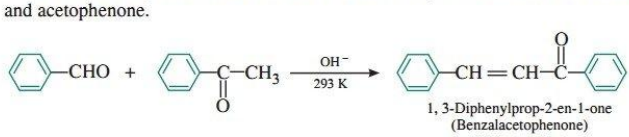
Ans. **(*i*) Acetylation:** The replacement of an active hydrogen of alcohols, phenols or amines with an acyl (RCO) group to form the corresponding esters or amides is called acetylation. This replacement is carried out by using acid chloride or an acid anhydride in the presence of a base like pyridine or dimethylaniline.





(*ii*) Cannizzaro reaction: Refer to Points to remember 17(*j*).

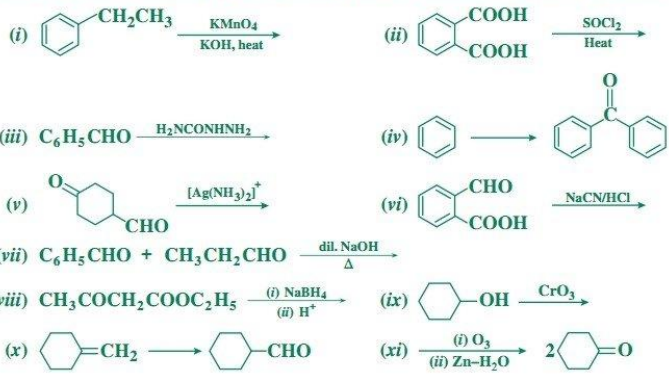
(*iii*) Cross aldol condensation: When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of benzaldehyde and acetophenone.



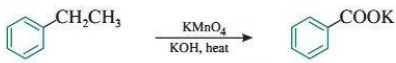
(iv) Decarboxylation: Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

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

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

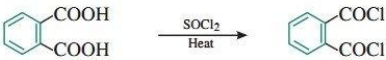


Ans. (i)



Ethylbenzene — Potassium benzoate

(ii)

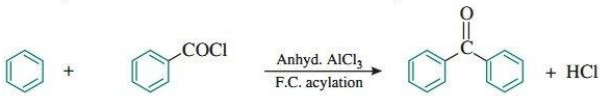


Phthalic acid — Phthaloyl chloride

(iii) $C_6H_5CHO + H_2NNHCONH_2 \longrightarrow C_6H_5CH{=}NNHCONH_2 + H_2O$

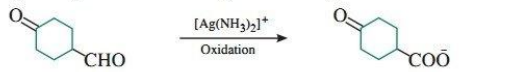
Benzaldehyde — Semicarbazide — Benzaldehyde semicarbazone

(iv)



Benzene — Benzoyl chloride — Benzophenone

(v) Only aldehydes are oxidised by Tollens' reagent.

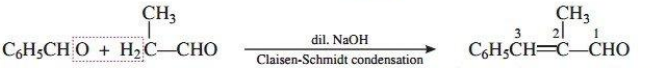


4-Oxocyclohexanecarbaldehyde — 4-Oxocyclohexanecarboxylate anion

(vi) Cyanohydrin formation occurs at the aldehyde group

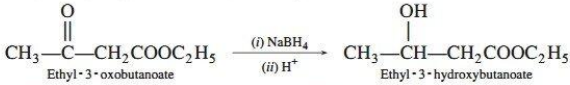
2-Formylbenzoic acid — 2-[1-Hydroxycyanomethyl] benzoic acid

(vii)

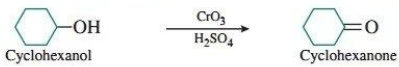


Benzaldehyde — Propanal — 2-Methyl-3-phenyl-prop-2-enal

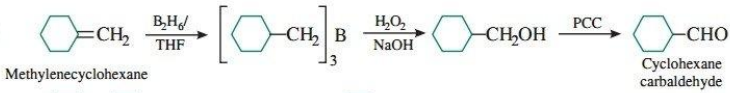
(*viii*) Only keto group is reduced by $NaBH_4$.



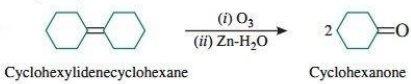
(*ix*)



(*x*)



(*xi*)



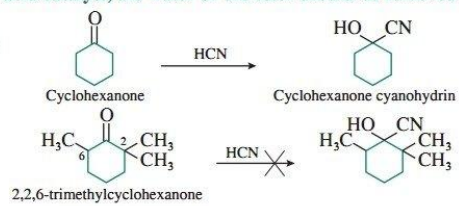
Q. 18. Give plausible explanation for each of the following:

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

(*ii*) There are two —NH_2 groups in semicarbazide, only one is involved in the formation of semicarbazone.

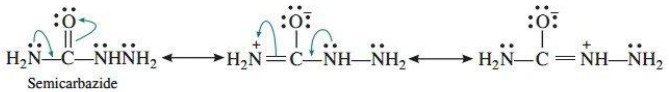
(*iii*) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans. (*i*)



Due to the presence of three methyl groups at α-position with respect to the C═O group, the nucleophilic attack by the CN^- ion does not occur due to steric hindrance. As there is no such steric hindrance in cyclohexanone, hence, nucleophilic attack by the CN^- ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield.

(*ii*)



Semicarbazide has two –NH_2 groups but one of them (*i.e.*, directly attached to C═O) is involved in resonance as shown above. Thus, electron density on this NH_2 group decreases hence it does not act as a nucleophile. In contrast, the lone pair of electrons on the other NH_2 group (*i.e.*, attached to —NH) is not involved in resonance and hence is available for nucleophilic attack on the C═O group of aldehydes and ketones.

(*iii*) The formation of esters from a carboxylic acid and an alcohol in presence of an acid catalyst is a reversible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

To shift the equilibrium in the forward direction, the water or the ester formed should be removed as fast as it is formed.

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

Ans.

Element	Percentage	Atomic mass	No. of moles	Simplest molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.81$	$\frac{5.81}{1.16} = 5$
H	11.63	1	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10$
O	(100 – 81.4) = 18.60	16	$\frac{18.60}{16} = 1.16$	$\frac{1.16}{1.16} = 1$

Empirical formula of the compound $A = C_5H_{10}O$

Molecular formula of the compound $A = n$ (Empirical formula)

$$n = \frac{\text{Molecular mass of compound A}}{\text{Empirical formula mass of compound A}}$$

Molecular mass of compound $A = 86$

Empirical formula mass of compound $A = 5 \times 12 + 1 \times 10 + 1 \times 16 = 60 + 10 + 16 = 86$

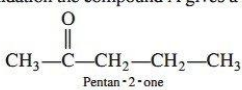
$$n = \frac{86}{86} = 1$$

Molecular formula of the compound A = 1 ($C_5H_{10}O$) = $C_5H_{10}O$

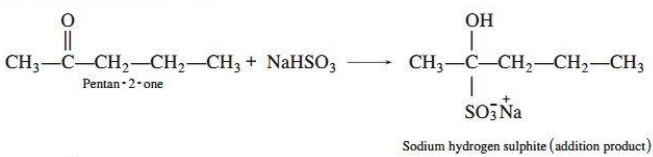
As the compound *A* forms addition compound with $NaHSO_3$ therefore it must be either an aldehyde or ketone.

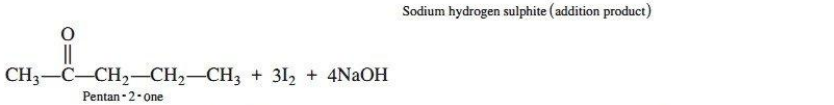
As it does not reduce Tollens' reagent and give positive iodoform test therefore it must be a methyl ketone.

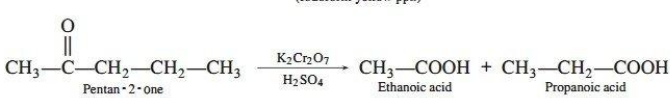
As on oxidation the compound A gives a mixture of ethanoic acid and propanoic acid, therefore compound A is



The chemical reactions are:

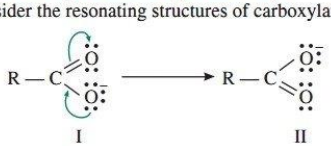


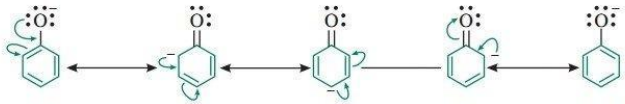




Q. 20. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is stronger acid than phenol. Why?

Ans. Consider the resonating structures of carboxylate ion and phenoxide ion.





III IV V VI VII

In the resonating structures IV, V, VI of phenoxide ion carry a negative charge on the less electronegative carbon atom. Therefore, their contribution towards the resonance stabilisation of phenoxide ion is very small and hence can be rejected.

In structures I and II of carboxylate ion the negative charge on the carboxylate ion is delocalised over two electronegative oxygen atoms while in structures III and VII of phenoxide ion, the negative charge on electronegative oxygen atom remains localised while the electrons of the benzene ring only are delocalised. As the delocalisation of benzene electrons contributes little towards the stability of phenoxide ion, therefore, carboxylate ion is much more resonance stabilised than phenoxide ion. Thus, the release of proton from carboxylic acid is much easier than from phenol. Hence, carboxylic acid is a stronger acid than phenol.

Multiple Choice Questions

Choose and write the correct option(s) in the following questions.

1. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution? [*NCERT Exemplar*]

(*a*) Butan-1-ol (*b*) Butan-2-ol (*c*) Both of these (*d*) None of these

2. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these condition? [*NCERT Exemplar*]

(*a*) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ (*b*) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(*c*) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + CO_2$ (*d*) $CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-H$

3. $CH_3-C\equiv CH \xrightarrow[1\%\,HgSO_4]{40\%\,H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Structure of 'A' and type of isomerism in the above reaction are respectively. [*NCERT Exemplar*]

(*a*) Prop–1–en–2–ol, metamerism (*b*) Prop–1–en–1–ol, tautomerism

(*c*) Prop–2–en–2–ol, geometrical isomerism (*d*) Prop–1–en–2–ol, tautomerism

4. Which of the following is most reactive in nucleophilic addition reactions ? [*CBSE 2023 (56/2/1)*]

(*a*) HCHO (*b*) CH_3CHO (*c*) CH_3COCH_3 (*d*) $CH_3COC_2H_5$

5. The formation of cyanohydrin from propanone is which type of reaction?

(*a*) Electrophilic substitution (*b*) Nucleophilic substitution

(*c*) Electrophilic addition (*d*) Nucleophilic addition

6. Compounds A and C in the following reaction are _____. [*NCERT Exemplar*]

$$CH_3CHO \xrightarrow[(ii)\,H_2O]{(i)\,CH_3MgBr} (A) \xrightarrow{H_2SO_4,\,\Delta} (B) \xrightarrow[\text{oxidation}]{\text{Hydroboration}} (C)$$

(*a*) identical (*b*) positional isomers

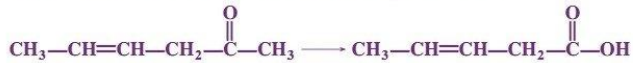
(*c*) functional isomers (*d*) optical isomers

7. The reagent which does not react with both, acetone and benzaldehyde is [*NCERT Exemplar*]

(*a*) Sodium hydrogensulphite (*b*) Phenyl hydrazine

(*c*) Fehling's solution (*d*) Grignard reagent

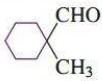
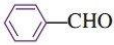
8. **Which is the most suitable reagent for the following conversion?** [*NCERT Exemplar*]



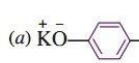
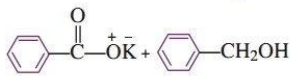
(*a*) Tollens' reagent (*b*) Benzoyl peroxide
(*c*) I_2 and NaOH solution (*d*) Sn and NaOH solution

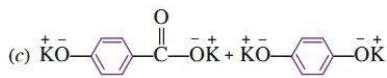
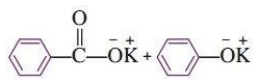
9. **Benzaldehyde after nitration gives**
(*a*) *o*-nitrobenzene (*b*) *p*-nitrobenzene
(*c*) 2, 4, 6-trinitrobenzene (*d*) *m*-nitrobenzene

10. **Cannizzaro's reaction is not given by _____.** [*NCERT Exemplar*]

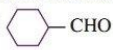
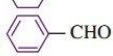
(*a*)  (*b*)  (*c*) HCHO (*d*) CH_3CHO

11. **Which product is formed when the compound**  **is treated with concentrated aqueous KOH solution?** [*NCERT Exemplar*]

(*a*)  (*b*) 

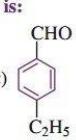
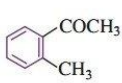
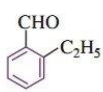
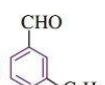
(*c*)  (*d*) 

12. **Which of the following does not give aldol condensation reaction?** [*CBSE 2023 (56/2/1)*]

(*a*) CH_3—CHO (*b*) 
(*c*) CH_3COCH_3 (*d*) 

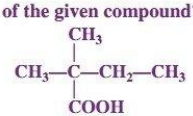
13. **An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests.**
(*i*) **Forms 2, 4-DNP derivative**
(*ii*) **Reduces Tollens' reagent**
(*iii*) **Undergoes Cannizzaro reaction**
(*iv*) **On vigorous oxidation, 1-2-benzenedicarboxylic acid is obtained.**

X is:

(*a*)  (*b*)  (*c*)  (*d*) 

14. **Iodoform test is not given by** [*CBSE 2020 (56/1/1)*]
(*a*) Ethanol (*b*) Ethanal
(*c*) Pentan-2-one (*d*) Pentan-3-one

15. **What is the correct IUPAC name of the given compound?** [*CBSE 2020 (56/1/1)*]



(*a*) 2, 2-Dimethylbutanoic acid (*b*) 2-Carboxyl-2-methylbutane
(*c*) 2-Ethyl-2-methylpropanoic acid (*d*) 3-Methylbutane carboxylic acid

16. **Which one of the following has lowest pK_a value?** [*CBSE 2023 (56/5/2)*]

(*a*) CH_3—COOH (*b*) O_2N—CH_2—COOH

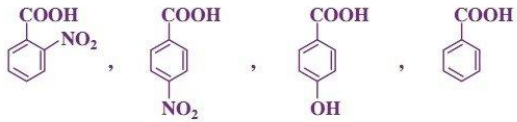
(*c*) Cl—CH_2—COOH (*d*) HCOOH

17. **Treatment of compound Ph—O—C(=O)—Ph with NaOH solution yields**

(*a*) Phenol (*b*) Sodium ethoxide

(*c*) Sodium benzoate (*d*) Benzophenone

18. **Arrange the following acids in order of the increasing acidity.**



(A) (B) (C) (D)

(*a*) B < C < A < D (*b*) A < B < C < D

(*c*) C < B < D < A (*d*) C < D < B < A

19. **Match the following Columns:**

Column–I	Column–II
(*i*) Oxalic acid	A. Benzene-1, 2-dicarboxylic acid
(*ii*) Benzoic acid	B. But-2-enoic acid
(*iii*) Phthalic acid	C. C_6H_5COOH
(*iv*) Crotonic acid	D. Ethanedioic acid

(*a*) (*i*) — D, (*ii*) — C, (*iii*) — A, (*iv*) — B

(*b*) (*i*) — A, (*ii*) — D, (*iii*) — B, (*iv*) — C

(*c*) (*i*) — B, (*ii*) — A, (*iii*) — C, (*iv*) — D

(*d*) (*i*) — C, (*ii*) — B, (*iii*) — A, (*iv*) — D

20. **Which of the following analogy is correct?**

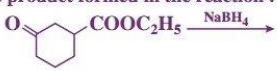
(*a*) 4-oxopentanal : $CH_3COCH_2CH_2CHO$ :: $FC_6H_5COCH_3$: 4-Fluoroacetophenone

(*b*) Benzaldehyde : Aldol condensation :: Acetic acid : Cannizaro reaction

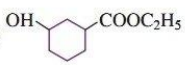
(*c*) $[Ag(NH_3)_2]^+$: Tollen's reagent :: CH_3I : Iodoform

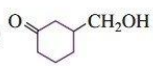
(*d*) $LiAlH_4$: reducing agent :: $NaBH_4$: oxidising agent

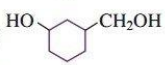
21. **The product formed in the reaction :**

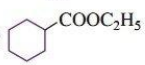


is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

Answers

1. (*b*)	**2.** (*b*)	**3.** (*d*)	**4.** (*a*)	**5.** (*d*)	**6.** (*b*)	**7.** (*c*)	**8.** (*c*)	**9.** (*d*)	**10.** (*d*)
11. (*b*)	**12.** (*d*)	**13.** (*c*)	**14.** (*d*)	**15.** (*a*)	**16.** (*b*)	**17.** (*c*)	**18.** (*d*)	**19.** (*a*)	**20.** (*a*)
21. (*a*)									

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***

(*b*) ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***

(*c*) ***Assertion (A) is correct, but Reason (R) is incorrect statement.***

(*d*) ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. **Assertion** (*A*) : Formaldehyde is a planar molecule.
Reason (*R*) : It contains sp^2 hybridised carbon atom.

2. **Assertion** (*A*) : The solubility of aldehydes and ketones in water decreases with increase in the size of alkyl group.
Reason (*R*) : Alkyl groups are electron-repelling groups.

3. **Assertion** (*A*) : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.
Reason (*R*) : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

4. **Assertion** (*A*) : Aldehydes and ketones, both react with Tollens' reagent to form silver mirror.
Reason (*R*) : Both, aldehydes and ketones contain a carbonyl group.

5. **Assertion** (*A*) : The α-hydrogen atom in carbonyl compounds is less acidic.
Reason (*R*) : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

6. **Assertion** (*A*) : Acetaldehyde undergoes aldol condensation with dil. NaOH.
Reason (*R*) : Aldehydes which do not contain α-hydrogen undergoes aldol condensation.

7. **Assertion** (*A*) : Carboxylic acids are more acidic than phenols.
Reason (*R*) : Phenols are ortho and para directing. ***[CBSE Sample Paper 2021]***

8. **Assertion** (*A*) : Reactivity of ketones is more than aldehydes.
Reason (*R*) : The carbonyl carbon of ketnoes is less electrophilic as compared to aldehydes. ***[CBSE 2020(56/3/1)]***

9. **Assertion** (*A*) : Benzoic acid does not undergo Friedel-crafts reaction.
Reason (*R*) : The carboxyl group is activating and undergo electrophilic substitution reaction. ***[CBSE 2020(56/4/2)]***

10. **Assertion** (*A*) : A carboxylate ion ($RCOO^-$) is stabilised by resonance to a greater extent as compared to the acid (RCOOH).
Reason (*R*) : The contributing structures of $RCOO^-$ are equivalent while those of RCOOH are not.

11. **Assertion** (*A*) : CH_3^- adds to >C = O group irrevesibly but CN^- ion adds reversibly.
Reason (*R*) : CH_3^- ion is much stronger nucleophile than CN^- ion.

12. **Assertion** (*A*) : Bromination of benzoic acid gives *m*-bromobenzoic acid. ***[CBSE 2023(56/5/2)]***
Reason (*R*) : Carboxyl group increases the electron density at the meta position.

Answers

1. (*a*) **2.** (*b*) **3.** (*b*) **4.** (*d*) **5.** (*d*) **6.** (*c*) **7.** (*b*) **8.** (*d*) **9.** (*c*) **10.** (*a*)
11. (*b*) **12.** (*c*)

Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

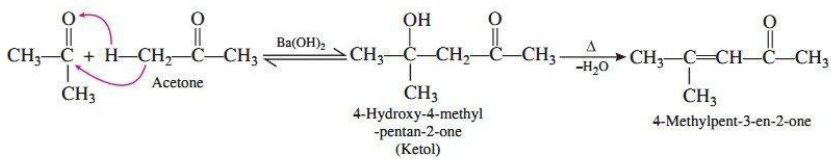
Aldehydes and ketones having atleast one α-hydrogen undergo a reaction in the presence of dilute alkali as a catalyst to form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (ketol), respectively. The aldol and ketol readily lose water to give α, β-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called aldol condensation. When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation.

1. **Give the IUPAC name of the compound formed when acetone undergoes self aldol condensation.**
2. **Identify the compounds that give 1, 3-diphenylprop-2-en-1-one after aldol condensation?**
3. **Give the reaction that gives of formation of products by self aldol condensation of acetone .**

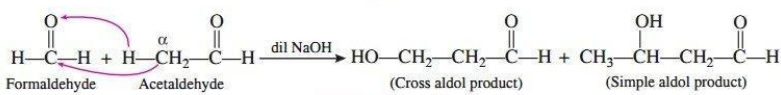
OR

Write the equation of cross aldol condensation between formaldehyde and acetaldehyde.

Answers

1. 4-methylpent-3-en-2-one
2. Benzaldehyde and acetophenone
3. 

OR

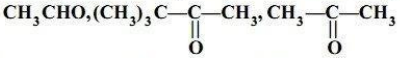


PASSAGE–2

The carbon – oxygen double bond is polarised in aldehydes and ketones due to higher electronegativity of oxygen relative to carbon. Therefore they undergo nucleophilic addition reaction with a number of nucleophiles such as HCN, $NaHSO_3$, alcohols, ammonia derivatives and Grignard reagents. Aldehydes are easily oxidised by mild oxidising agents as compared to ketones. The carbonyl group of carboxylic acid does not give reactions of aldehydes and ketones. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

Answer the following: **[*CBSE 2023(56/2/1)*]**

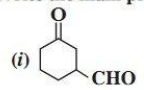
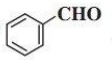
1. **Write the name of the product when an aldehyde reacts with excess alcohol in presence of dry HCl.**
2. **Why carboxylic acid is a stronger acid than phenol.**
3. **(*i*) Arrange the following compounds in increasing order of their reactivity towards CH_3MgBr:**



(*ii*) Write a chemical test to distinguish between propanal and propanone.

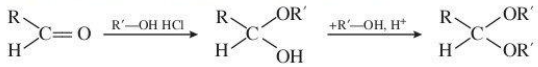
OR

Write the main product in the following:

(*i*)  $\xrightarrow{[Ag(NH_3)_2]^+}$ (*ii*)  $\xrightarrow{H_2NCONHNH_2}$

Answers

1. Gem-dialkoxy compound known as acetal is formed.



2. Carboxylic acid is stronger acid than phenol because

- Resonating structures of carboxylate ion are more stable than phenoxide ion.
- Negative charge is dispersing on two electronegative oxygens in carboxylate ion whereas it is on one oxygen atom in phenoxide ion.

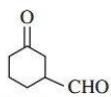
3. (*i*) Due to steric and electronic reasons in nucleophilic addition increasing order of reactivity towards CH_3MgBr reactions is

$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_3 \; < \; CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \; < \; CH_3-CHO$$

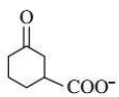
(*ii*) Propanal being an aldehyde gives silver mirror with Tollen's reagent but propanone being a ketone does not

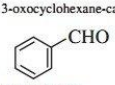
$$\underset{\text{Propanal}}{CH_3-CH_2-CHO} + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \longrightarrow \underset{\text{Tollens' reagent}}{} CH_3-CH_2-C\bar{O}O + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

OR

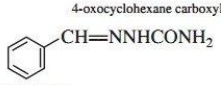
(*i*) 
3-oxocyclohexane-carbaldehyde

$\xrightarrow[\text{Oxidation}]{[Ag(NH_3)_2]^+}$


4-oxocyclohexane carboxylate ions

(*ii*) 
Benzaldehyde

$\xrightarrow{+H_2NNHCONH_2}$


Benzaldehyde semicarbazone

CONCEPTUAL QUESTIONS

Q. 1. Give IUPAC name of the following compound: [*CBSE (F) 2010*]

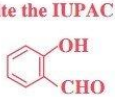
$(CH_3)_2C{=}CHCOCH_3$

Ans. 4-Methylpent-3-en-2-one

Q. 2. Write the structure of the following compound : 3-oxopentanal. [*CBSE (F) 2011*]

Ans. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$

Q. 3. Write the IUPAC name of the following compound: [*CBSE (F) 2014*]



Ans. 2-hydroxybenzaldehyde

Q. 4. Write the IUPAC name of the following compound: [*CBSE 2019 (56/3/2)*]

Ans. But-3-en-2-one

Q. 5. Give the name of the reagent that bring the following transformation: But-2-ene to ethanal.

Ans. O_3/H_2O—Zn dust

Q. 6. Arrange the following in increasing order of their boiling point:

CH_3CH_2OH, CH_3CHO, $CH_3—O—CH_3$ [*CBSE 2019 (56/3/2)*]

Ans. $CH_3—O—CH_3 < CH_3CHO < CH_3—CH_2—OH$

Q. 7. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions: ethanal, propanal, propanone, butanone. [*CBSE Delhi 2012*]

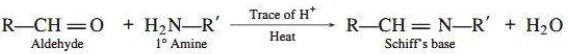
Ans. Butanone < Propanone < Propanal < Ethanal

Q. 8. What is Tollens' reagent? Write one usefulness of this reagent. [*CBSE (AI) 2010*]

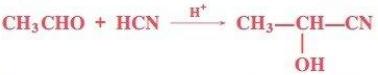
Ans. Ammonical silver nitrate ($AgNO_3 + NH_4OH$) solution is known as Tollens' reagent. It is used to detect the presence of —CHO group in an organic compound.

Q. 9. What do you mean by Schiff's base? Give an example.

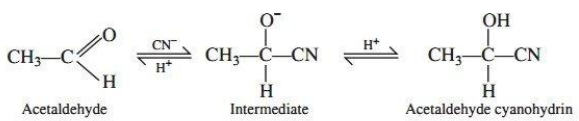
Ans. Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.



Q. 10. Propose the mechanism for the following reaction: [*HOTS*]



Ans. The reaction proceeds through the nucleophilic attack of CN^- ion as follows:



Q. 11. Name the aldehyde which does not give Fehling's solution test.

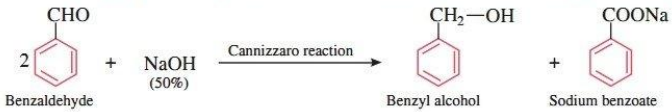
Ans. Benzaldehyde

Q. 12. Which of the following compounds would undergo Cannizzaro reaction: Benzaldehyde, Cyclohexanone, 2-Methylpentanal. [*CBSE Sample Paper 2020*]

Ans. Benzaldehyde

Q. 13. How will you prepare benzyl alcohol from benzaldehyde without using a reducing agent? [*HOTS*]

Ans.



Here, a concentrated solution of NaOH is used which is not a reducing agent.

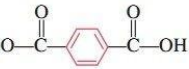
Q. 14. Write two important uses of formalin. [*CBSE Sample Paper 2011*]

Ans. Formalin is used in the

(*i*) preservation of biological specimens.

(*ii*) manufacture of bakelite.

Q. 15. Write the structural formula and IUPAC name of terephthalic acid.

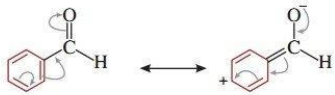
Ans.  ; IUPAC Name: Benzene-1, 4-dicarboxylic acid

Short Answer Questions–I

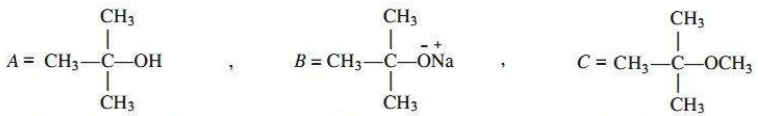
Each of the following questions are of 2 marks.

Q. 1. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Ans. The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.



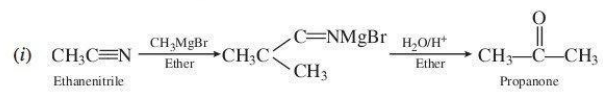
Q. 2. Complete the following reaction sequence: ***[NCERT Exemplar]***

Ans. 

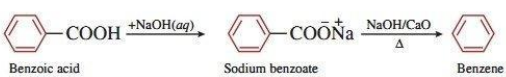
2-methylpropan-2-ol | Sodium *tert*-butoxide | 2-methoxy-2-methylpropane

Q. 3. Do the following conversions in not more than two steps: ***[CBSE 2023 (56/2/1)]***

(*i*) CH_3CN to $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (*ii*)  to

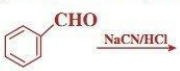
Ans. 

Ethanenitrile | Propanone



Benzoic acid | Sodium benzoate | Benzene

Q. 4. Complete the following reactions:

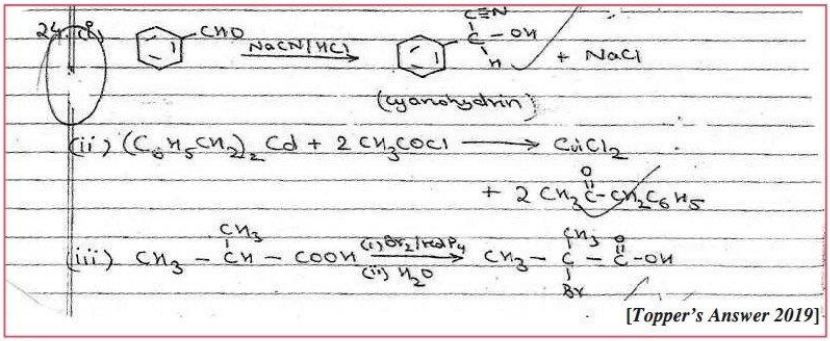
(*i*) 

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

(*iii*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2/Red\ P_4}$

[CBSE 2019 (56/1/1)]

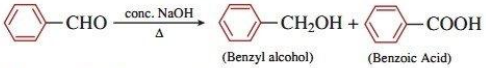
Ans.



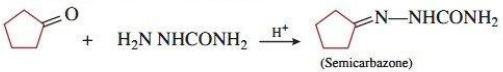
Q. 5. Write the products of the following reactions: **[*CBSE 2023 (56/4/2)*]**

(*i*) 

(*ii*) 

Ans. (*i*) 

This is called Cannizzaro reaction.

(*ii*) 

Q. 6. An organic compound '*A*' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane on treatment with Zn–Hg/HCl. '*A*' forms a dioxime with hydroxylamine and gives a positive Iodoform test and Tollens' test. Identify the compound *A* and deduce its structure. **[*HOTS*]**

Ans. As '*A*' gives positive iodoform test, so it has $CH_3-\overset{O}{\overset{\|}{C}}-$ group.

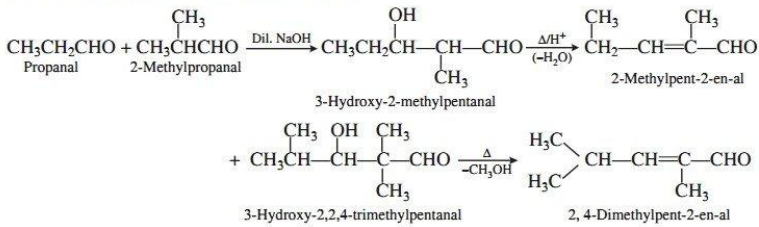
As '*A*' gives positive Tollens' test, so it must have —CHO group.

So '*A*' is $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CHO$

4-oxopentanal

Q. 7. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? Write the name of the reaction also. **[*NCERT Exemplar*] [*HOTS*]**

Ans. The reaction taking place is cross aldol condensation.



Q. 8. Give reasons to support the answer: [*CBSE Sample Paper 2022*]

(*i*) **Presence of Alpha hydrogen in aldehydes and ketones is essential for aldol condensation.**

(*ii*) **3–Hydroxypentan-2-one shows positive Tollen's test.**

Ans. (*i*) The alpha hydrogen atoms are acidic in nature due to presence of electron withdrawing carbonyl group. These can be easily removed by a base and the carbanion formed is resonance stabilized.

(*ii*) Tollen's reagent is a weak oxidizing agent not capable of breaking the C—C bond in ketones. Thus ketones cannot be oxidized using Tollen's reagent itself gets reduced to Ag.

Q. 9. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also. [*NCERT Exemplar*]

Ans. $C_6H_5\overset{\oplus}{C}O$ (Benzoylinium cation)

Friedel–Crafts acylation reaction

Q. 10. Do the following conversions in not more than two steps: [*CBSE (F) 2017*]

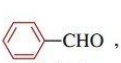
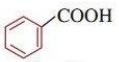
(*i*) **Propene to Acetone**

(*ii*) **Propanoic acid to 2-hydroxypropanoic acid**

Ans. (*i*) $\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[H^+]{H_2O} CH_3-\underset{|}{\overset{OH}{CH}}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$

(*ii*) $\underset{\text{Propanoic acid}}{CH_3-CH_2-COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{red P}} CH_3-\underset{|}{\overset{Cl}{CH}}-COOH \xrightarrow{NaOH(aq)} \underset{\text{2-Hydroxy propanoic acid}}{CH_3-\underset{|}{\overset{OH}{CH}}-COOH}$

Q. 11. An aromatic compound '*A*' on treatment with $CHCl_3$ and KOH gives two compounds, both of which give same product '*B*' when distilled with zinc dust. Oxidation of '*B*' gives '*C*' with molecular formula $C_7H_6O_2$. Sodium salt of '*C*' on heating with soda lime gives '*D*' which may also be obtained by distilling '*A*' with zinc dust. Identify '*A*', '*B*', '*C*' and '*D*'. [*CBSE 2019(56/5/2)*]

Ans. $A =$  , $B =$  , $C =$  , $D =$ 

Phenol Benzaldehyde Benzoic acid Benzene

Q. 12. Write the reagents used in the following reactions: [*CBSE Ajmer 2015*]

(*i*) $C_6H_5-CO-CH_3 \xrightarrow{?} C_6H_5-CH_2-CH_3$

(*ii*) $CH_3COOH \xrightarrow{?} CH_3-COCl$

Ans. (*i*) Zn—Hg, conc. HCl or H_2NNH_2 and KOH/ethylene glycol, Heat

(*ii*) PCl_5 or $SOCl_2$

Q. 13. Identify the compounds *A*, *B* and *C* in the following reaction: [*NCERT Exemplar*]

$$CH_3-Br \xrightarrow{Mg/Ether} (A) \xrightarrow[(ii)\ \text{Water}]{(i)\ CO_2} (B) \xrightarrow[\Delta]{CH_3OH/H^+} (C)$$

Ans. $A = \underset{\substack{\text{Methyl}\\ \text{magnesium bromide}}}{CH_3MgBr}$, $B = \underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$, $C = \underset{\substack{\text{Methyl}\\ \text{ethanoate}}}{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3}$

Q. 14. Arrange the following compounds in increasing order of their property as indicated:

(*i*) **CH_3COCH_3, $C_6H_5-CO-C_6H_5$, CH_3CHO (reactivity towards nucleophilic addition reaction)**

(*ii*) **$Cl-\underset{|}{\overset{Cl}{CH}}-COOH$, $Cl-CH_2-COOH$, CCl_3-COOH (acidic character)**

[*CBSE Bhubaneshwar 2015*]

Ans. (*i*) $C_6H_5COC_6H_5 < CH_3COCH_3 < CH_3CHO$ **1**

(*ii*) $Cl—CH_2—COOH < \underset{\underset{Cl}{|}}{Cl—CH—COOH} < CCl_3—COOH$ **1**

[*CBSE Marking Scheme Bhubaneshwar 2015*]

Q. 15. Give reasons:

(*i*) Oxidation of aldehydes is easier than ketones. **[*CBSE 2019 (51/5/2)*]**

OR

Oxidation of propanal is easier than propanone. **[*CBSE 2020 (56/4/3)*]**

(*ii*) CH_2═CH—COOH is more acidic than CH_3CH_2—COOH. **[*CBSE East 2016*]**

Ans. (*i*) As aldehydes contain H atom on the carbonyl group but ketones do not. Cleavage of C—H bond in aldehydes is easier than cleavage of C—C bond in ketones.

(*ii*) This is because in CH_2═CH—COOH, the carbonyl group attached to sp^2 hybridised carbon atom which is more electronegative and makes release of H^+ ion easy.

Q. 16. (*i*) Give reason: **[*CBSE 2019(56/2/1)*]**

(*a*) Benzoic acid is a stronger acid than acetic acid.

(*b*) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(*ii*) Give a simple chemical test to distinguish between propanal and propanone.

Ans. (*i*) (*a*) This is because of greater electronegativity of sp^2 hybridised carbonyl to which carboxyl carbon is attached in benzoic acid.

sp^2	sp^3
$C_6H_5—COOH$	$CH_3—COOH$
Benzoic acid	Acetic acid

(*b*) The methyl group due to its +ve I effect reduces the positive charge on carbonyl carbon atom. Moreover it also hinders the approach of the nucleophile. Since in ethanal there is one methyl group while in methanal there is no methyl group on carbonyl carbon atom therefore methanal is more reactive towards nucleophilic addition reaction than ethanal.

(*ii*) Propanal being an aldehyde gives silver mirror with Tollens' reagent while propanone being a ketone does not give this test.

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

Q. 17. Arrange the following in the decreasing order of their acidic character.

(*i*) C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH

(*ii*) CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

Ans. (*i*) $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$

(*ii*) $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

Q. 18. Arrange the following in order of property indicated for each set.

(*i*) CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ (increasing order of boiling points)

(*ii*) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ (increasing order of their acid strengths)

Ans. (*i*) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

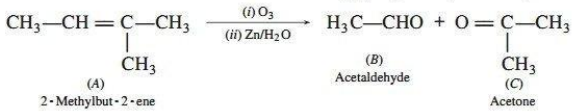
(*ii*) $(CH_3)_2CHCOOH < \underset{\underset{Br}{|}}{CH_3—CH—CH_2—COOH} < \underset{\underset{Br}{|}}{CH_3—CH_2—CH—COOH}$

Short Answer Questions–II

Each of the following questions are of 3 marks.

Q. 1. An alkene '*A*' molecular formula (C_5H_{10}) on ozonolysis gives a mixture of two compounds '*B*' and '*C*'. Compound '*B*' gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling's test but forms iodoforms. Identify the compounds '*A*', '*B*' and '*C*' giving suitable explanation and write the reactions of ozonolysis and iodoform formation from either '*B*' or '*C*'. [*CBSE Sample Paper 2020*] [*NCERT Exemplar*] [*HOTS*]

Ans. Compound '*B*' gives both Fehling's test and iodoform test and therefore it must be an aldehyde with —$COCH_3$ group. Moreover, compound '*C*' doesn't give Fehling's test but give positive iodoform test and therefore it must be a ketone with —$COCH_3$ group. Thus, the compound *A*, *B* and *C* are as follows:



$$CH_3—CHO + 3I_2 + 4NaOH \xrightarrow[\text{reaction}]{\text{Iodoform}} HCOONa + CHI_3\downarrow + 3NaI + 3H_2O$$

Other isomers of '*A*' will not give products corresponding to the given test.

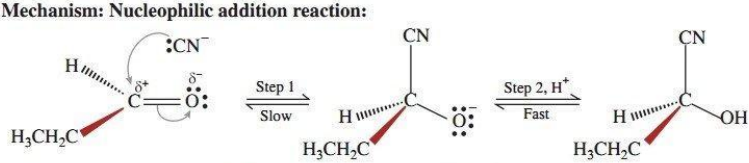
Q. 2. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why? [*NCERT Exemplar*] [*HOTS*]

Ans. CH_3CH_2CHO CH_3COCH_3

(I) (II)

(*i*) Compound I will react faster with HCN due to less steric hinderance and electronic reasons than II.

Mechanism: Nucleophilic addition reaction:



(*ii*) No, it is a reversible reaction. Hence, equilibrium is established.

(*iii*) Addition of acid inhibits the reaction because the formation of CN^- ions is prevented.

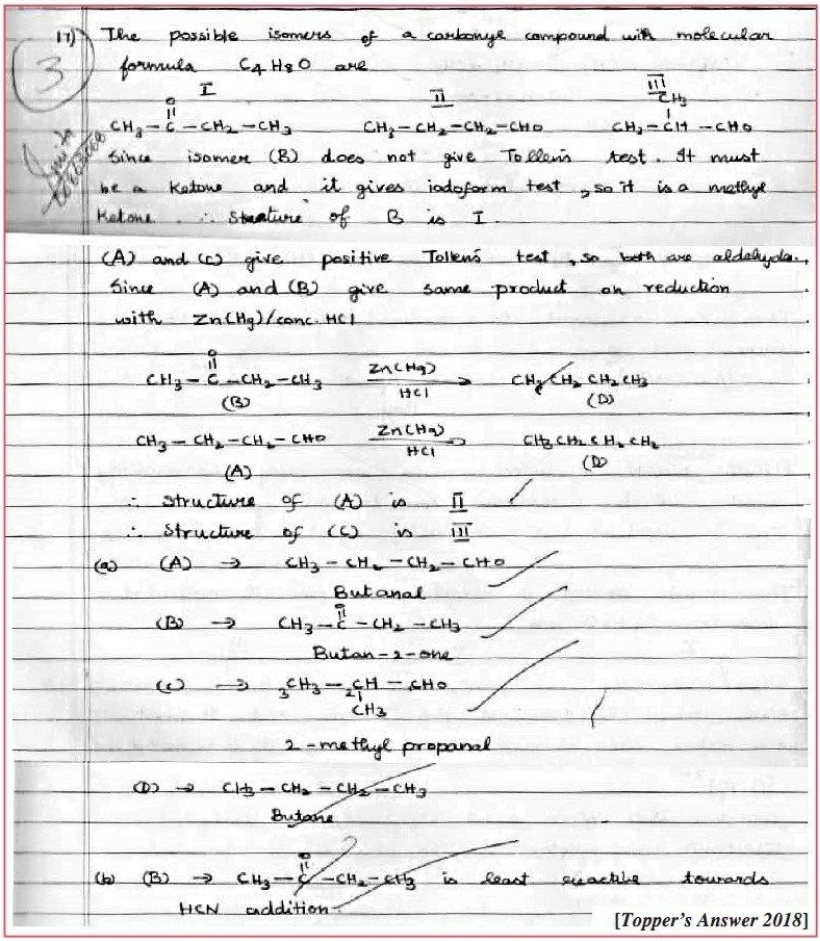
Q. 3. (*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollens' test whereas isomer (*B*) does not give Tollens' test but gives positive Iodoform test. Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give the same product (*D*).

(*i*) Write the structures of (*A*), (*B*), (*C*) and (*D*).

(*ii*) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN?

[*CBSE 2018*]

Ans.



(3)

ii) The possible isomers of a carbonyl compound with molecular formula C_4H_8O are

I $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ II $CH_3-CH_2-CH_2-CHO$ III $CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$

Since isomer (B) does not give Tollen's test. It must be a Ketone and it gives iodoform test, so it is a methyl Ketone. ∴ Structure of B is I.

(A) and (C) give positive Tollens test, so both are aldehydes. Since (A) and (B) give same product on reduction with $Zn(Hg)$/conc. HCl

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ (B) $\xrightarrow[HCl]{Zn(Hg)}$ $CH_3CH_2CH_2CH_3$ (D)

$CH_3-CH_2-CH_2-CHO$ (A) $\xrightarrow[HCl]{Zn(Hg)}$ $CH_3CH_2CH_2CH_3$ (D)

∴ Structure of (A) is II

∴ Structure of (C) is III

(a) (A) → $CH_3-CH_2-CH_2-CHO$ Butanal

(B) → $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ Butan-2-one

(C) → $CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$ 2-methyl propanal

(D) → $CH_3-CH_2-CH_2-CH_3$ Butane

(b) (B) → $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ is least reactive towards HCN addition

[*Topper's Answer 2018*]

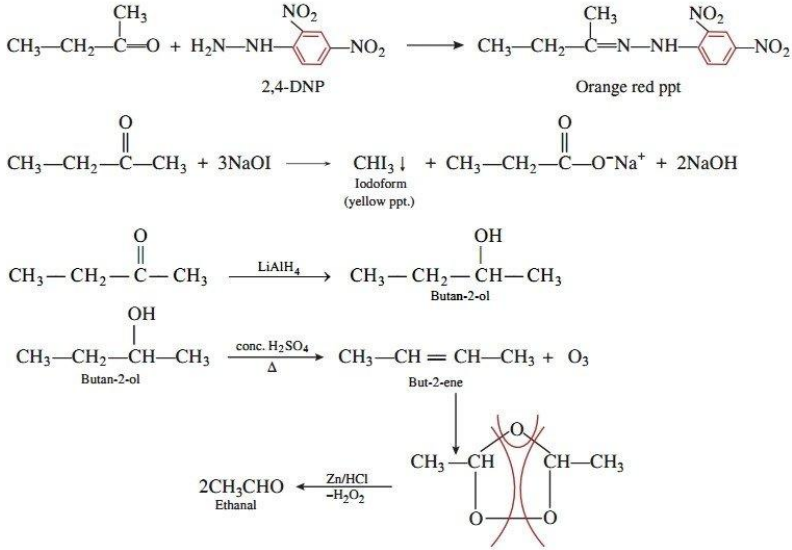
Q. 4. An organic compound (*A*) having molecular formula C_4H_8O gives orange red precipitate with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (*A*) on reduction with $NaBH_4$ gives compound (*B*) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (*C*). Compound (*C*) on Ozonolysis gives two molecules of ethanal.

Identify (*A*), (*B*) and (*C*) and write their structures. Write the reactions of compound (*A*) with (*i*) NaOH/I_2 and (*ii*) $NaBH_4$ and explain the reactions. [*HOTS*] [*CBSE 2020 (56/4/3)*]

Ans. *A* = Butan-2-one; $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ *B* = Butan-2-ol ; $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

C = But-2-ene ; $CH_3-CH=HC-CH_3$

Reactions involved:



Q. 5. An organic compound 'A', having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives 'B'. 'B' does not reduce Fehlings' solution but gives a yellow precipitate of the compound 'C' with I_2/NaOH. Deduce the structures of A, B and C. ***[CBSE 2023 (56/1/1)]***

Ans. $A = CH_3—\underset{\text{Propan-2-ol}}{CH(OH)—CH_3}$, $B = CH_3—\underset{\text{propanone}}{C(=O)—CH_3}$, $C = \underset{\text{Iodoform}}{CHI_3}$

Equation for the reaction involved:

$$\underset{\text{A}}{CH_3—CH(OH)—CH_3} \xrightarrow[573\ K]{Cu} \underset{\text{B}}{CH_3—C(=O)—CH_3} + H_2$$

$$\underset{\text{B}}{CH_3—C(=O)—CH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{C}}{CHI_3}\downarrow + CH_3COONa + 3NaI + 3H_2O$$

Q. 6. (*i*) Account for the following:

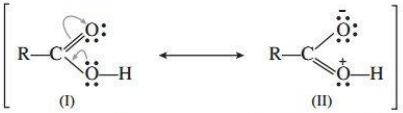
(*a*) $Cl—CH_2COOH$ is a stronger acid than CH_3COOH.

(*b*) Carboxylic acids do not give reactions of carbonyl group. ***[CBSE 2022]***

(*ii*) Out of $CH_3CH_2—CO—CH_2—CH_3$ and $CH_3CH_2—CH_2—CO—CH_3$, which gives iodoform test? ***[CBSE (A1) 2014]*** ***[CBSE 2022]***

Ans. (*i*) (*a*) Because of –I effect of Cl atom in $ClCH_2COOH$ and +I effect of CH_3 group in CH_3COOH the electron density in the O—H bond in $ClCH_2COOH$ is much lower than CH_3COOH. As a result O—H bond in $ClCH_2COOH$ is much weaker than in CH_3COOH therefore loses a proton more easily than CH_3COOH. Hence $ClCH_2COOH$ acid is stronger acid than CH_3COOH.

(*b*) Carboxylic acids are resonance hybrid of the following structures:



(I) (II)

Similarly, a carbonyl group of aldehydes and ketones may regarded as resonance hybrid of following structures.

(III) (IV)

Because of contribution of structure (IV), the carbonyl carbon in aldehydes and ketones is electrophilic. On the other hand, electrophilic character of carboxyl carbon is reduced due to contribution of structure (II). As carbonyl carbon of carboxyl group is less electropositive than carbonyl carbon in aldehydes and ketones, therefore, carboxylic acids do not give nucleophilic addition reactions of aldehydes and ketones.

(*ii*) $CH_3—CH_2—CH_2—COCH_3$

Q. 7. Arrange the following compounds in increasing order of their property as indicated:

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

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

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

[*CBSE (AI) 2012*]

Ans. (*i*) Methyl tert-butyl ketone < Acetone < Acetaldehyde

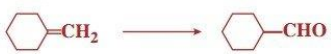
(*ii*) 4-Methoxy benzoic acid < Benzoic acid < 3,4-Dinitrobenzoic acid

(*iii*) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

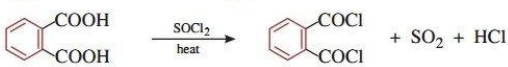
Q. 8. Complete each synthesis by giving missing reagents or products in the following:

(*i*) 

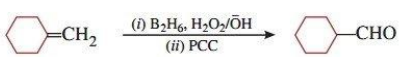
(*ii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(*iii*) 

[*CBSE (AI) 2011*]

Ans. (*i*) 

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

(*iii*) 

Q. 9. Write structures of compounds *A*, *B* and *C* in each of the following reactions:

(*i*) $C_6H_5Br \xrightarrow{Mg/dryether} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_2(g)} B \xrightarrow{PCl_5} C$

(*ii*) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

[*CBSE Delhi 2017*]

Ans. (*i*) $A = \underset{\text{Phenyl magnesium bromide}}{C_6H_5MgBr}$, $B = \underset{\text{Benzoic acid}}{C_6H_5COOH}$, $C = \underset{\text{Benzoyl chloride}}{C_6H_5COCl}$

(*ii*) $A = \underset{\text{Benzaldehyde}}{CH_3CHO}$, $B = CH_3—\underset{\text{3-Hydroxybutanal}}{\overset{\overset{OH}{|}}{CH}—CH_2—CHO}$, $C = \underset{\text{But-2-enal}}{CH_3—CH{=}CH—CHO}$

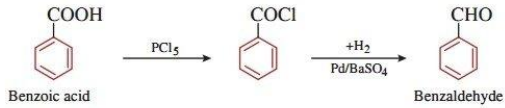
Q. 10. Do the following conversions in not more than two steps:

(*i*) Benzoic acid to Benzaldehyde

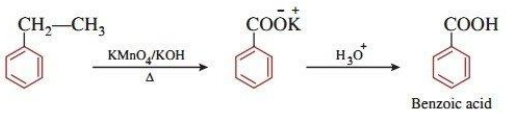
(*ii*) Ethyl benzene to Benzoic acid

(*iii*) Propanone to Propene **[*CBSE Delhi 2017*]**

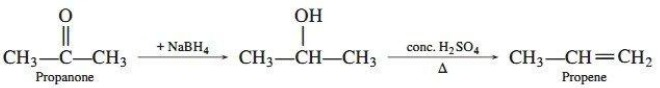
Ans. (*i*) Benzoic acid to Benzaldehyde



(*ii*) Ethyl benzene to Benzoic acid



(*iii*) Propanone to Propene



Q. 11. Predict the products of the following reactions:

(*i*) $CH_3—\underset{\underset{CH_3}{|}}{C}(=O) \xrightarrow[(ii)\ KOH/Glycol,\ \Delta]{(i)\ H_2N–NH_2} ?$

(*ii*) $C_6H_5—CO—CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(*iii*) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$ **[*CBSE Delhi 2015*]**

Ans. (*i*) $CH_3—CH_2—CH_3$ (Propane)

(*ii*) $C_6H_5COO^-Na^+$ (Sodium benzoate) and CHI_3 (Iodoform)

(*iii*) CH_4 (Methane)

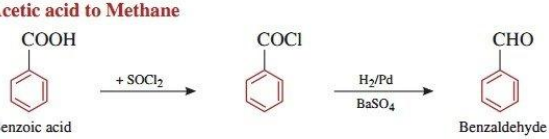
Q. 12. How do you convert the following?

(*i*) Benzoic acid to Benzaldehyde

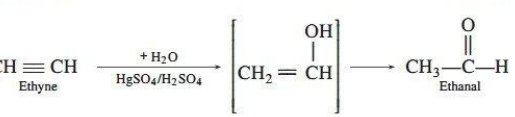
(*ii*) Ethyne to Ethanal

(*iii*) Acetic acid to Methane **[*CBSE (F) 2015*]**

Ans. (*i*)



(*ii*)



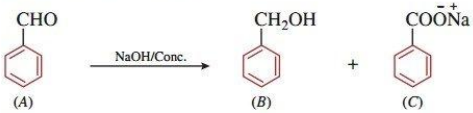
(*iii*)

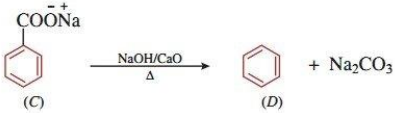
Q. 13. An organic compound (*A*) has characteristic odour. On treatment with NaOH, it forms compounds (*B*) and (*C*). Compound (*B*) has molecular formula C_7H_8O which on oxidation gives back (*A*). The compound (*C*) is a sodium salt of an acid. When (*C*) is treated with soda-lime, it yields an aromatic compound (*D*). Deduce the structures of (*A*), (*B*), (*C*) and (*D*). Write the sequence of reactions involved. ***[CBSE Sample Paper 2015]***

Ans. *A* =  ; *B* =  ; *C* =  ; *D* = 

Benzaldehyde; Benzyl alcohol; Sodium benzoate; Benzene

Reaction involved are:



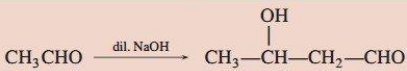


Q. 14. How would you bring about the following conversions? Write the complete equation in each case.

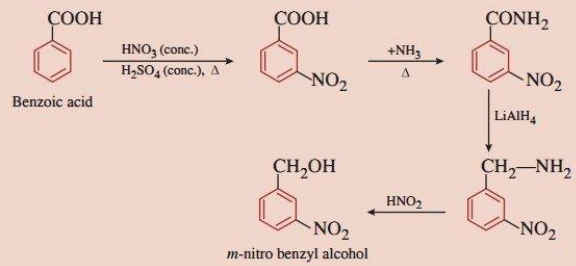
(*i*) Ethanal to 3-hydroxybutanal

(*ii*) Benzoic acid to *m*-nitrobenzyl alcohol

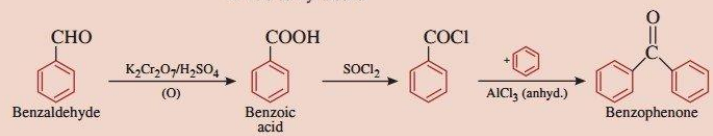
(*iii*) Benzaldehyde to benzophenone ***[CBSE (AI) 2011]***

Ans. (*i*) 

Ethanal; 3-Hydroxybutanal **1**

(*ii*) 

Benzoic acid; *m*-nitro benzyl alcohol **1**

(*iii*) 

Benzaldehyde; Benzoic acid; Benzophenone **1**

[CBSE Marking Scheme (AI) 2011]

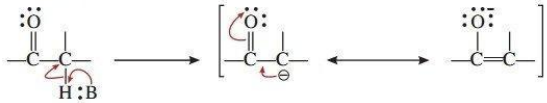
Q. 15. Give reasons:

(*i*) The α-hydrogen of aldehydes and ketones are acidic in nature. **[*CBSE 2020 (56/4/3)*]**

(*ii*) Propanone is less reactive than ethanal towards addition of HCN.

(*iii*) Benzoic acid does not give Friedel-Crafts reaction. **[*CBSE (F) 2016, CBSE 2022*]**

Ans. (*i*) The acidity of α-hydrogen atom of carbonyl carbon is due to the strong withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(*ii*) This is due to steric and electronic reasons. Sterically, the presence of two methyl groups in propanone hinders more the approach of nucleophile to carbonyl carbon than in ethanal having one methyl group. Electronically two methyl groups reduce the positivity of the carbonyl carbon more effectively in propanone than in ethanal.

(*iii*) Benzoic acid does not give Friedel Craft reaction because:

(*a*) the carboxyl group is strongly deactivating.

(*b*) the catalyst $AlCl_3$ which is a lewis acid gets bonded to the carboxyl group strongly.

Long Answer Questions

Each of the following questions are of 5 marks.

Q. 1. (*i*) Carry out the following conversions :

(*a*) Ethanal to But-2-en-1-al

(*b*) Propanoic acid to 2-chloropropanoic acid

(*ii*) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms iodoform. Identify the compounds 'A', 'B' and 'C'. **[*CBSE 2023 (56/1/1)*]**

Ans. (*i*) (*a*) $\underset{\text{Ethanal}}{2CH_3—CHO} \xrightleftharpoons{\text{dil NaOH}} CH_3—\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{CH}}—CH_2—CHO \xrightarrow[-H_2O]{\Delta} \underset{\text{But-2-en-1-al}}{CH_3—CH=CH—CHO}$

(*b*) $\underset{\text{Propanoic acid}}{CH_3—CH_2—COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{red P}} CH_3—\underset{\underset{Cl}{|}}{CH}—COOH$

(*ii*) $A = \underset{\text{2-Methylbut-2-ene}}{CH_3—\overset{\overset{CH_3}{|}}{C}=CH—CH_3}$, $B = \underset{\text{Ethanal}}{CH_3—\overset{\overset{O}{||}}{C}—H}$, $C = \underset{\text{Propanone}}{CH_3—\overset{\overset{O}{||}}{C}—CH_3}$

Equations for the reactions involved:

- $\underset{\text{(A)}}{CH_3—\overset{\overset{CH_3}{|}}{C}=CH—CH_3} \xrightarrow{+O_3} CH_3—\underset{\underset{\text{Ozonide}}{\text{(cyclic ozonide)}}}{\overset{\overset{CH_3}{|}}{C}(O)(O)CH—CH_3} \xrightarrow[Zn]{H_2O} \underset{\text{(B)}}{CH_3—\overset{\overset{O}{||}}{C}—H} + \underset{\text{(C)}}{CH_3—\overset{\overset{O}{||}}{C}—CH_3}$
- $\underset{\text{B}}{CH_3—CHO} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOONa + 3NaI + 3H_2O$

- $CH_3—\underset{C}{COCH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + CH_3COONa + 3NaI + 3H_2O$
- $\underset{(B)}{CH_3—CHO} + 2Cu^{2+} + 5\bar{O}H \longrightarrow CH_3COO^- + \underset{\text{Red brown ppt}}{Cu_2O} + 3H_2O$

Q. 2. **(*i*) A ketone *A* which undergoes haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. The compound *D* on hydrolysis in presence of zinc dust gives only acetaldehyde. Write the structures and IUPAC names of *A*, *B* and *C*. Write down the reactions involved.**

(*ii*) Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

(*a*) PhMgBr and then H_3O^+

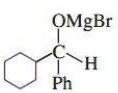
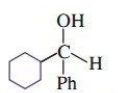
(*b*) Tollens' reagent. **[*CBSE Sample Paper 2017*]**

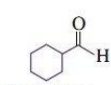
Ans. (*i*) $A = CH_3—\overset{O}{\overset{\|}{C}}—CH_2—CH_3$ (Butan-2-one), $B = CH_3—\underset{OH}{CH}—CH_2—CH_3$ (Butan-2-ol), $C = CH_3—CH=CH—CH_3$ (But-2-ene)

The reactions are as follows:

$$\underset{(A)}{CH_3—\overset{O}{\overset{\|}{C}}—CH_2—CH_3} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3—\underset{OH}{CH}—CH_2—CH_3} \xrightarrow{H_2SO_4\,(conc.)} \underset{(C)}{CH_3—CH=CH—CH_3}$$

$$(C) \xrightarrow{+O_3} (D) \xrightarrow{H_2O/Zn} \underset{\text{Acetaldehyde}}{2CH_3—\overset{O}{\overset{\|}{C}}—H}$$

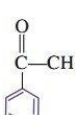
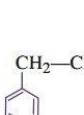
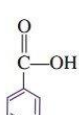
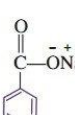
(*ii*) (*a*) Cyclohexane carbaldehyde $\xrightarrow[\text{Dry ether}]{\text{Ph-MgBr}}$  $\xrightarrow{H_3O^+}$  Cyclohexylphenyl carbinol

(*b*)  Cyclohexane carbaldehyde + $2[Ag(NH_3)_2]^+ + 3OH^-$ (Tollens' reagent) $\longrightarrow$  Cyclohexane carboxylate ion + $2Ag\downarrow$ (Silver mirror) $+ 4NH_3 + 2H_2O$

Q. 3. **Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions:** **[*CBSE Delhi 2016*]**

$$C_6H_6 \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3COCl} A \xrightarrow{Zn\text{-}Hg/\text{conc. } HCl} B \xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4\text{–}KOH,\ \Delta} C$$

$$A \xrightarrow{NaOI} D + E$$

Ans. $A =$  Acetophenone ; $B =$  Ethyl benzene ; $C =$  Benzoic acid ; D or $E = CHI_3$; E or $D =$  Sodium benzoate

Q. 4. (*i*) **Carry out the following conversions:** **[*CBSE 2019 (56/4/1)*]**

(*a*) ***p*-nitrotoluene to 2-bromobenzoic acid**

(*b*) **Propanoic acid to acetic acid**

(*ii*) **An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, *B* and *C*. Compound *B* gives positive Fehling test and also reacts with iodine and NaOH solution. Compound *C* does not give Fehling solution test but forms iodoform. Identify the compounds *A*, *B* and *C*.**

Ans. (*i*) (*a*)

(*b*) $CH_3CH_2COOH \xrightarrow[\text{Heat}]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$

$\xrightarrow{HNO_3,\ 273\ K} CH_3CH_2OH \xrightarrow{KMnO_4/H^+ \text{ or } OH^-} CH_3COOH$

(*ii*) *A* : 2-Methylbut-2-ene/$CH_3CH{=}C(CH_3)_2$

B: Ethanal/Acetaldehyde /CH_3CHO

C: Propanone/Acetone /CH_3COCH_3

Q. 5. (*i*) **Write the structures of *A*, *B*, *C* and *D* in the following reactions:**

$$C_6H_5COCl \xrightarrow{H_2/Pd-BaSO_4} A \xrightarrow{\text{conc. NaOH}} B + C$$

$$A \xrightarrow{CH_3MgBr/H_3O^+} D$$

(*ii*) **Distinguish between the following:**

(*a*) **C_6H_5—$COCH_3$ and C_6H_5—$COCH_2CH_3$**

(*b*) **Propanal and butan-2-one** **[*CBSE (F) 2014*]**

(*iii*) **Write the structure of 2-hydroxybenzaldehyde.** **[*CBSE Chennai 2015*]**

Ans. (*i*) *A* =  , *B* or *C* =  , *C* or *B* =  , *D* = 

Benzaldehyde; Sodium benzoate; Benzyl alcohol; 1-Phenyl ethanol

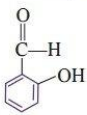
(*ii*) (*a*) $C_6H_5COCH_3$ being a methyl ketone gives iodoform test while $C_6H_5COCH_2CH_3$ does not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow C_6H_5COONa + \underset{\substack{\text{Iodoform}\\(\text{Yellow ppt.})}}{CHI_3\downarrow} + 2NaOH$$

(*b*) Propanal being an aldehyde reduces Tollens' reagent to silver mirror but propanone being a ketone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + \underset{\substack{\text{Silver}\\\text{mirror}}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\text{Tollens' reagent}} \text{No silver mirror}$$

(*iii*) 

Q. 6. (*i*) **Carry out the following conversions:**

(*a*) **Benzoic acid to aniline**

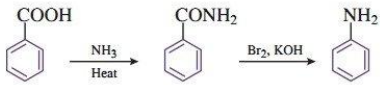
(*b*) **Bromomethane to ethanol**

(*ii*) **Write the structure of major product(s) in the following:**

(*a*) $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H \xrightarrow[(b)\ KOH,\ Glycol/heat]{(a)\ H_2N-NH_2}$

(*b*) $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO \xrightarrow{conc.\ NaOH}$

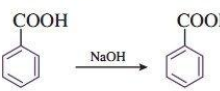
(*c*)  $\xrightarrow{NaOH}$ **[*CBSE 2019 (56/4/1)*]**

Ans. (*i*) (*a*) 

(*b*) $CH_3Br \xrightarrow{KCN\ (alc.)} CH_3CN \xrightarrow[H^+/OH^-]{H_2O} CH_3COOH \xrightarrow[H_3O^+]{LiAlH_4/Ether\ or\ B_2H_6} CH_3CH_2OH$

(*ii*) (*a*) $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H \xrightarrow[(b)\ KOH,\ Glycol/heat]{(a)\ H_2N-NH_2} CH_3CH_2CH_3$

(*b*) $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO \xrightarrow{conc.\ NaOH} (CH_3)_3CCH_2OH + (CH_3)_3CCOONa$

(*c*) 

Q. 7. (*i*) **Give a simple chemical test to distinguish between benzaldehyde and ethanal. [*CBSE (F) 2013*]**

(*ii*) **Bring out the following conversions:**

(*a*) **4-Nitrotoluene to 2-bromobenzoic acid**

(*b*) **Ethylcyanide to 1-phenyl propanone**

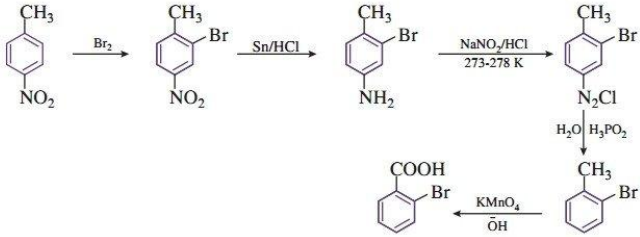
(*iii*) ***A* and *B* are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer *B* forms yellow precipitate of iodoform whereas isomer *A* does not form any precipitate. Write the formulae of *A* and *B*.**

Ans. (*i*) **Benzaldehyde and Ethanal**

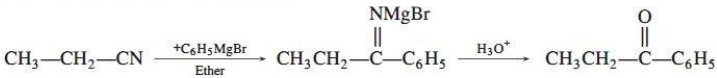
Ethanal reacts with NaOI (I_2/NaOH) to form yellow precipitate of iodoform while benzaldehyde does not give this test.

$$CH_3CHO + 3I_2 + 3NaOH \longrightarrow \overset{-\ +}{HCOONa} + \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3\downarrow} + 3NaI + 3H_2O$$

(*ii*) (*a*) **4-Nitrotoluene to 2-bromobenzoic acid**

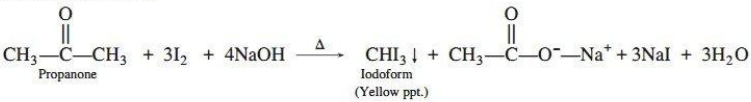


(*b*) **Ethylcyanide to 1-phenyl propanone**



(*iii*) $A = CH_3—CH_2—\overset{O}{\overset{\|}{C}}—H$ (Propanal) $\qquad B = CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ (Propanone)

Reaction involved:



Q. 8. (*i*) **Give a chemical test to distinguish between ethanal and ethanoic acid.**

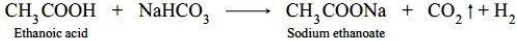
(*ii*) **Why is the α-hydrogens of aldehydes and ketones are acidic in nature?**

(*iii*) **An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B'on heating with soda lime gives methane.**

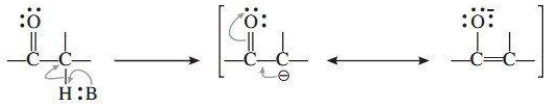
(*a*) **Identify 'A', 'B' and 'C'.**

(*b*) **Out of 'B' and 'C', which will have higher boiling point? Give reason.** **[*CBSE 2023(56/5/2)*]**

Ans. (*i*) Ethanoic acid being an acid reacts with $NaHCO_3$ solution to give birsk effervescence due to evolution of CO_2 while ethanal does not.

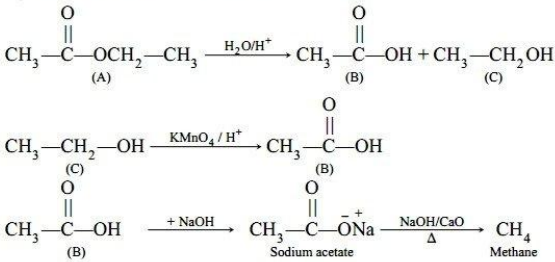


(*ii*) The acidity of α-hydrogen atom of carbonyl carbon is due to the strong withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(*iii*) (*a*) $A = CH_3—\overset{O}{\overset{\|}{C}}—O—CH_2—CH_3$, Ethyl ethanoate $\qquad B = CH_3—\overset{O}{\overset{\|}{C}}—OH$, Ethanoic acid $\qquad C = CH_3—CH_2—OH$, Ethanol

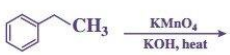
Equations for the reactions involved:

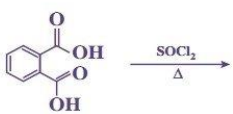


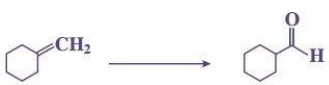
2. This is due to boiling point of ethanoic acid (B) is higher than Ethanol (C).
   — Ethanoic acid form stronger hydrogen bonds than ethanol because the —O—H bond in ethanoic acid is more strongly polarised due to the adjacent electron-withdrawing.
   — The negatively polarised oxygen atom of the carbonyl group can also form hydrogen bonds with the positively polarised H-atom of the O—H bond of the other molecule.

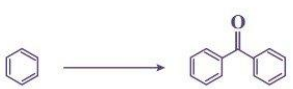
Q. 9. Complete each synthesis by giving missing starting material, reagent or products:

(*i*) 

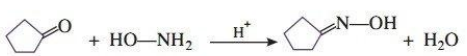
(*ii*) 

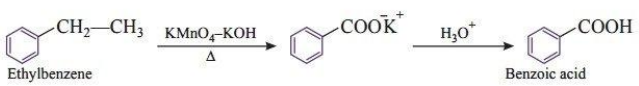
(*iii*) 

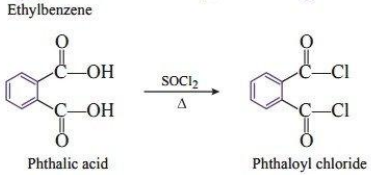
(*iv*) 

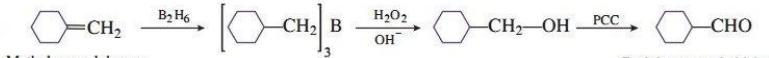
(*v*) 

[*CBSE Sample Paper 2017*]

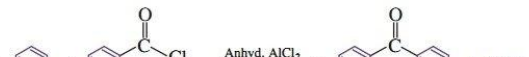
Ans. (*i*) 

(*ii*) 

(*iii*) 

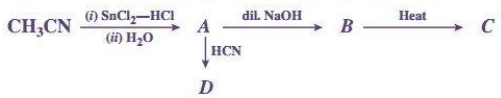
(*iv*) 

Methylenecyclohexane — Cyclohexanecarbaldehyde

(*v*) 

Benzene + Benzoyl chloride → Benzophenone

Q. 10. **(*i*) Write the structures of *A*, *B*, *C* and *D* in the following reactions:**



(*ii*) Distinguish between:

(*a*) C_6H_5—CH=CH—$COCH_3$ and C_6H_5—CH=CH—$COCH_2CH_3$

(*b*) CH_3CH_2COOH and HCOOH

(*iii*) Arrange the following in the increasing order of their boiling points:

CH_3CH_2OH, CH_3COCH_3, CH_3COOH **[*CBSE North 2016*]**

Ans. (*i*) *A* = $CH_3—\overset{\overset{O}{\|}}{C}—H$ Ethanal

B = $CH_3—\overset{OH}{\underset{|}{CH}}—CH_2—\overset{\overset{O}{\|}}{C}—H$ 3-Hydroxybutanal

C = $CH_3—CH=CH—\overset{\overset{O}{\|}}{C}—H$ But-2-enal

D = $CH_3—\overset{OH}{\underset{|}{CH}}—CN$ 2-Hydroxy propanenitrile

(*ii*) (*a*) C_6H_5CH=CH—$COCH_3$ on warming with NaOI (I_2/NaOH) gives yellow precipitate of iodoform while C_6H_5CH=CH—CO—CH_2—CH_3 does not.

$$C_6H_5CH=CHCOCH_3 + 3NaOI \longrightarrow \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3\downarrow} + C_6H_5CH=CH—\bar{C}OONa^+ + 2NaOH$$

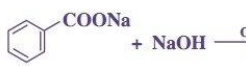
(*b*) Formic acid reduces Tollens' reagent to metallic silver while propionic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2 + 2H_2O + 4NH_3$$

(*iii*) $CH_3—CO—CH_3 < CH_3—CH_2—OH < CH_3—COOH$

Q. 11. **(*i*) Write the product(s) in the following reactions:**

(*a*) 

(*b*) 

(*c*) $CH_3—CH=CH—CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL-H} ?$

(*ii*) Give simple chemical tests to distinguish between the following pairs of compounds:

(*a*) Butanal and Butan-2-one

(*b*) Benzoic acid and Phenol **[*CBSE (AI) 2017*]**

Ans. (*i*) (*a*) 

Cyclohexane cyanohydrin

(*b*) 

Benzene

(*c*) $CH_3—CH = CH—CHO$

But-2-en-1-al

(*ii*) (*a*) Butanal being an aldehyde reduces Tollens' reagent to give silver mirror but butan-2-one being a ketone does not.

$$\underset{\text{Butanal}}{CH_3—CH_2—CH_2—CHO} + 2\underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \underset{\text{Butanoate ion}}{CH_3—CH_2—CH_2—COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(*b*) Benzoic acid decomposes $NaHCO_3$ to produce brisk effervescence due to evolution of CO_2 while phenol does not.

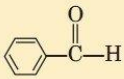
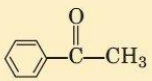
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COO^-Na^+} + CO_2\uparrow + H_2O$$

Questions for Practice

Choose and write the correct answer for each of the following.

1. **Which of the following compounds is most reactive towards nucleophilic addition reactions?** [*NCERT Exemplar*]

(*a*) $CH_3—C(=O)—H$ (*b*) $CH_3—C(=O)—CH_3$

(*c*)  (*d*) 

2. **The acid formed when propyl magnesium bromide is treated with CO_2 is**

(*a*) C_3H_7COOH (*b*) C_2H_5COOH

(*c*) both (*a*) and (*b*) (*d*) None of these

3. **Carbonyl group undergoes**

(*a*) Electrophilic addition reaction

(*b*) Nucleophilic addition reactions

(*c*) Both (*a*) and (*b*)

(*d*) None of these

4. **Toluene can be oxidised to benzoic acid by**

(*a*) $KMnO_4$(alk.) (*b*) $K_2Cr_2O_7$

(*c*) Both (*a*) and (*b*) (*d*) None of these

5. **Complete the following analogy:**

$$C_6H_5COCH_3 \xrightarrow{NaOI} A + B$$

(*a*) A : $C_6H_5I_3$ :: B : CH_3COOH

(*b*) A : C_6H_5COONa :: B : CHI_3

(*c*) A : CO_2 :: B : CH_3COONa

(*d*) A : C_6H_5COONa :: B : CH_3I

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement.

6. **Assertion (*A*) :** Acetic acid does not undergo haloform reaction.
   Reason (*R*) : Acetic acid has no alpha hydrogen.

7. **Assertion (*A*) :** 2, 2-Dimethylpropanal undergoes Cannizzaro reaction with conc. NaOH.
   Reason (*R*) : Cannizzaro reaction is a disproportionation reaction.

8. **Assertion (*A*) :** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
   Reason (*R*) : Carboxyl group increases the electron-density at *meta*-position.

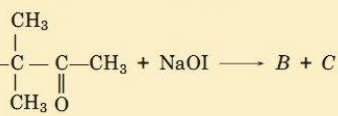
9. **Assertion (*A*) :** Aromatic acids do not undergo Friedel-Crafts reaction.
   Reason (*R*) : —COOH group is a *m*-directing group.

10. **Assertion (*A*) :** $(CH_3)_3C$ COOH does not undergo HVZ reaction.
    Reason (*R*) : $(CH_3)_3C$ COOH does not have any α-hydrogen.

Answer the following questions:

11. Complete the following reactions by identifying *A*, *B* and *C*.

(*i*) $A + H_2(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CH—CHO$

(*ii*)

$+ NaOI \longrightarrow B + C$

12. Give reasons for the following:

(*i*) Benzaldehyde reduces Tollens' reagent but not the Fehling's or Benedict's solution.

(*ii*) $(CH_3)_2CH—CHO$ undergoes aldol condensation whereas $(CH_3)_3C—CHO$ does not.

[*CBSE (F) 2017*]

13. Write reasons for the following statements:

(*i*) Benzoic acid does not undergo Friedel-Crafts reaction.

(*ii*) Oxidation of aldehydes is easier than that of ketones. **[*CBSE 2022 (54/4/2)*]**

14. Write the equations involved in the following reactions:

(*i*) Wolff-Kishner reduction

(*ii*) Etard reaction **[*CBSE Delhi 2017*]**

15. Write the reagents required in the following reactions:

(*i*) $CH_2{=}CH{-}CH_2OH \xrightarrow{?} CH_2{=}CH{-}CHO$

(*ii*) $CH_3{-}COOH \xrightarrow{?} CH_3{-}CONH_2$ **[*CBSE Allahabad 2015*]**

16. An organic compound '*A*' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It does not reduce Tollens' or Fehling's reagent and does not decolourise bromine water also. On oxidation with chromic acid (H_2CrO_4), it gives a carboxylic acid (*B*) with molecular formula $C_7H_6O_2$. Deduce the structures of *A* and *B*.

17. Do the following conversions in not more than two steps:

(*i*) Toluene to Benzoic acid

(*ii*) Benzaldehyde to 1-Phenylethanol **[*CBSE 2023 (56/4/2)*]**

18. Write the products formed when $(CH_3)_3C{-}CHO$ reacts with the following:

(*i*) Zinc amalgam and dilute hydrochloric acid

(*ii*) Concentrated sodium hydroxide solution **[*CBSE 2020 (56/3/2)*]**

(*iii*) Semicarbazide and a weak acid **[*CBSE 2019 (56/5/2)*]**

19. Write the chemical equations for the following conversions (not more than 2 steps):

(*i*) Ethyl benzene to benzene

(*ii*) Acetaldehyde to butane-1, 3-diol

(*iii*) Acetone to propene

20. An alkene 'A' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.

[*CBSE Sample Paper 2022*]

21. An organic compound '*A*' (C_3H_4) on hydration in presence of $H_2SO_4/HgSO_4$ gives compound '*B*' (C_3H_6O). Compound '*B*' gives white crystalline product (*D*) with sodium hydrogensulphite. It gives negative Tollens' test and positive iodoform's test. On drastic oxidation '*B*' gives compound '*C*' ($C_2H_4O_2$) along with formic acid. Identify compounds '*A*', '*B*' and '*C*' and explain all the reactions.

22. (*i*) Distinguish with a suitable chemical test:

(*a*) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$

(*b*) Ethanal and Ethanoic acid

(*ii*) Write the structure of oxime of acetone.

(*iii*) Identify A to D.

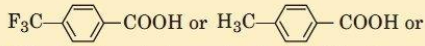
$$CH_3COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr/CH_3/MgBr} C$$

$$B \xrightarrow{LiAlH_4} D$$

[*CBSE 2023 (56/1/1)*]

23. (*i*) Draw structure of the 2, 4-dinitrophenylhydrazone of benzaldehyde.

(*ii*) Which acid of the following pair is a stronger acid?



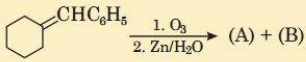
(*iii*) Write the chemical equation involved in Rosenmund's reduction.

(*iv*) Why are α-hydrogen atoms of aldehydes and ketones acidic in nature?

(*v*) Write a chemical test to distinguish between Benzaldehyde and Benzoic acid.

[*CBSE 2023 (56/4/2)*]

24. Identify the unknown organic compounds (A) to (E) in the following series of chemical reactions.

(*i*) 

(*ii*) $(A) + (B) \xrightarrow{\text{dil. NaOH}} (C) + H_2O$

(*iii*) $(C) \xrightarrow[2.\ Zn/H_2O]{1.\ O_3} (A) + (D)$

(*iv*) $(D) \xrightarrow[\Delta]{H_2/Ni} (E)$

Answers

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*c*) **5.** (*b*) **6.** (*c*) **7.** (*b*) **8.** (*c*) **9.** (*b*) **10.** (*b*)