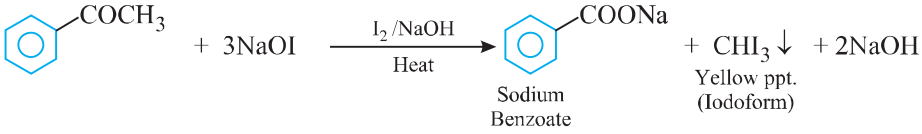
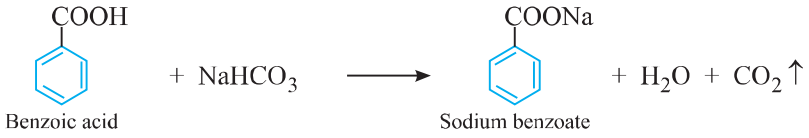
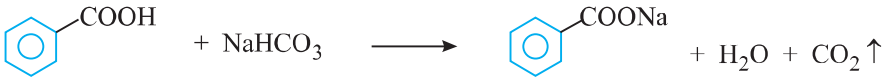
(*ii*) Acetophenone and benzophenone: Acetophenone responds to iodoform test, but benzophenone does not.



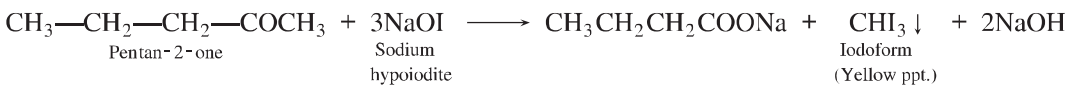
(*iii*) Phenol and benzoic acid: Benzoic acid reacts with $NaHCO_3$ giving CO_2 gas with effervescence, whereas phenol does not.



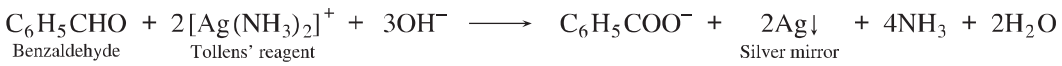
(*iv*) Benzoic acid and ethyl benzoate: Benzoic acid on reaction with sodium hydrogencarbonate gives out CO_2 gas with effervescence, while ethyl benzoate does not.



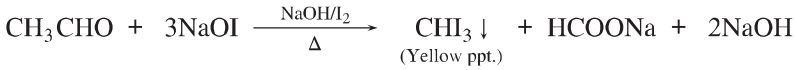
(*v*) Pentan-2-one and Pentan-3-one: Pentan-2-one when treated with NaOI (I_2/NaOH) gives yellow precipitate of iodoform but pentan-3-one does not give this test.



(*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.



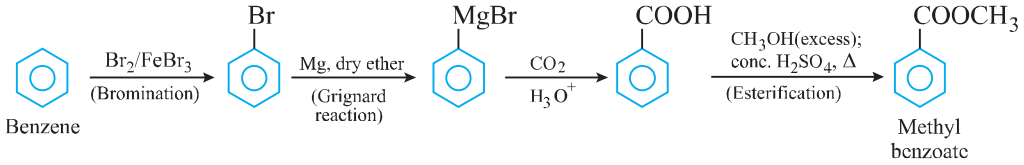
Q. 14. How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

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

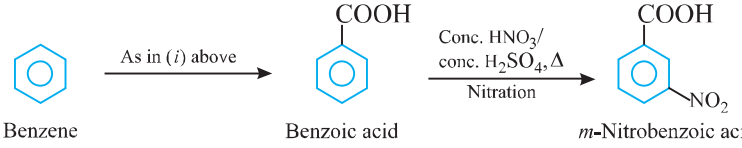
(*iii*) *p*-nitrobenzoic acid **(*iv*) Phenylacetic acid**

(*v*) *p*-nitrobenzaldehyde

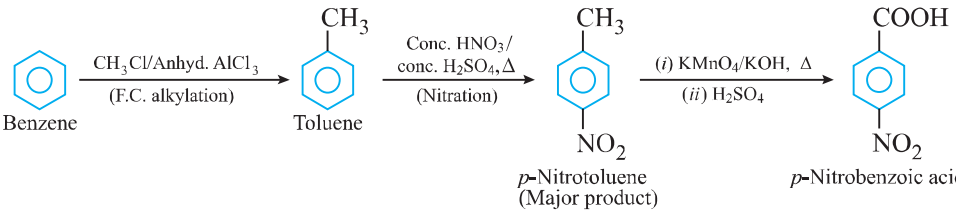
Ans. (*i*)

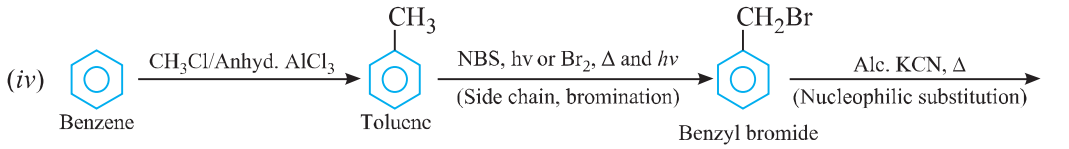


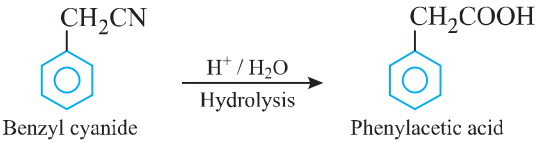
(*ii*)

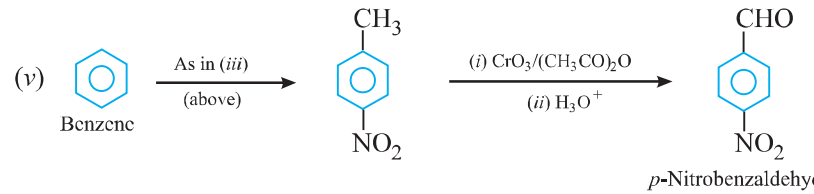


(*iii*)









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**

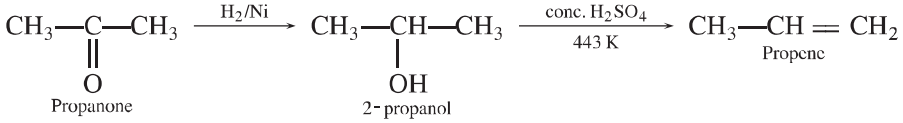
(*v*) Benzaldehyde to Benzophenone **(*vi*) Bromobenzene to 1-Phenylethanol**

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

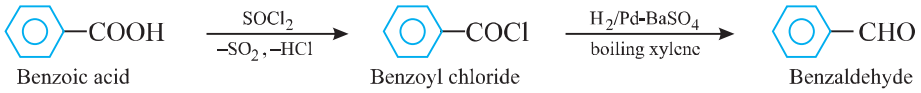
(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid

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

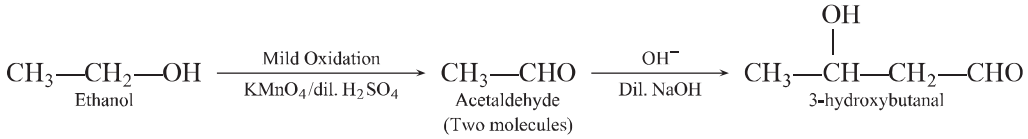
Ans. (*i*) Propanone to Propene



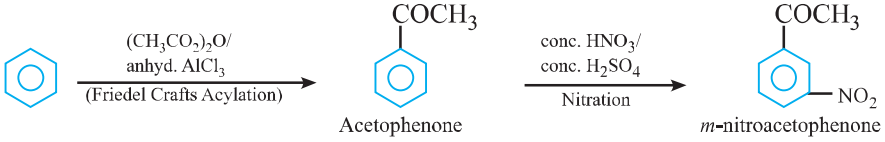
(*ii*) Benzoic acid to Benzaldehyde



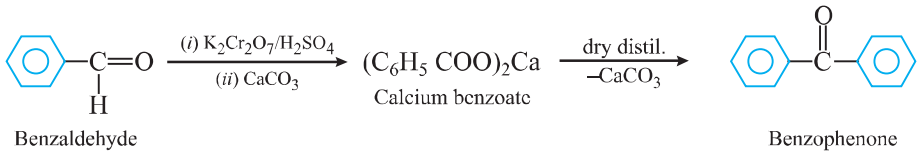
(*iii*) Ethanol to 3-Hydroxybutanal



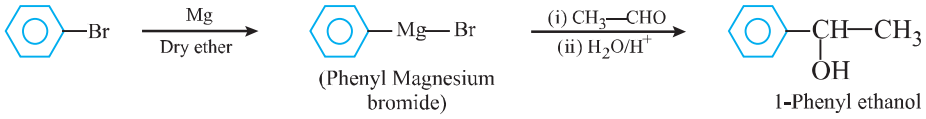
(*iv*) Benzene to *m*-Nitroacetophenone



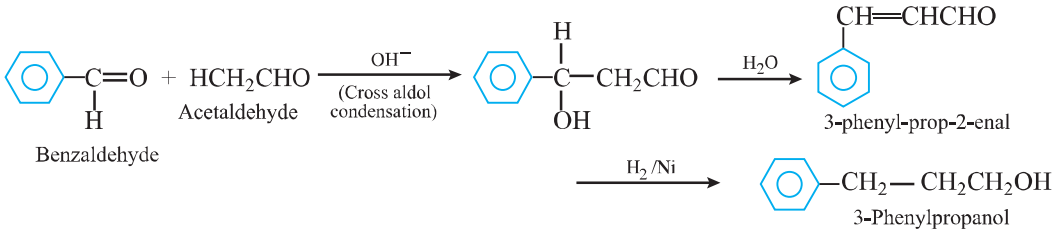
(*v*) Benzaldehyde to Benzophenone



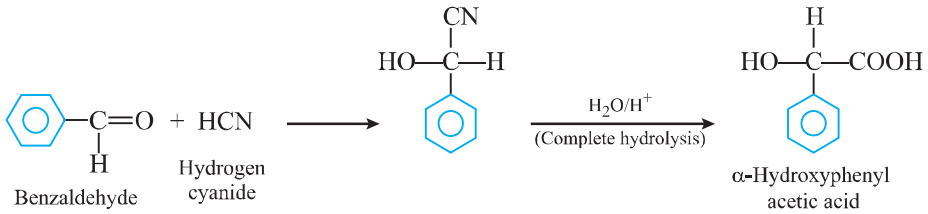
(*vi*) Bromobenzene to 1-phenylethanol:



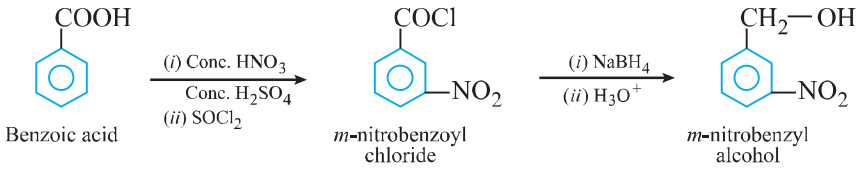
(*vii*) Benzaldehyde to 3-phenylpropan-1-ol:



(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid



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



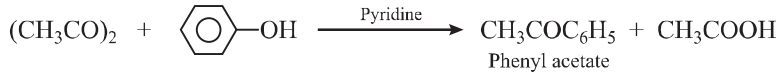
Q. 16. Describe the following:

(*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.

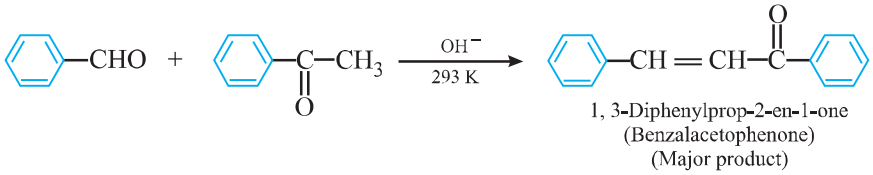
$$CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



$$CH_3COCl + C_2H_5NH_2 \longrightarrow \underset{\text{N-Ethylacetamide}}{CH_3CONHC_2H_5} + HCl$$

(*ii*) Cannizzaro reaction: Refer to Basic Concepts Point 17(*j*).

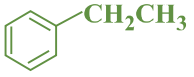
(*iii*) Cross aldol condensation: When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of benzaldehyde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

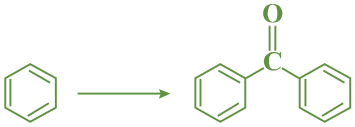


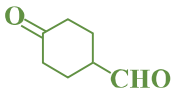
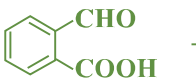
***(iv)* Decarboxylation:** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

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

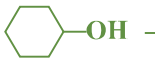
Q. 17. Complete each synthesis by giving missing starting material, reagent or products.

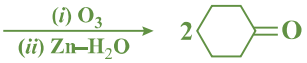
(*i*)  (*ii*) 

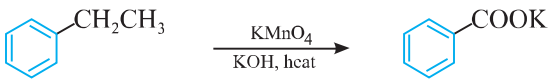
(*iii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$ (*iv*) 

(*v*)  (*vi*) 

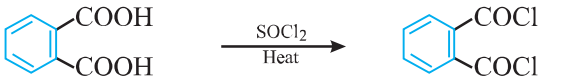
(*vii*) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow[\Delta]{\text{dil. NaOH}}$

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

(*x*)  (*xi*) 

Ans. (*i*) 

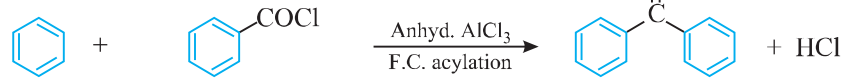
Ethylbenzene — Potassium benzoate

(*ii*) 

Phthalic acid — Phthaloyl chloride

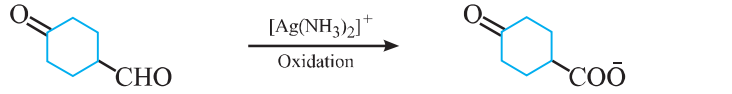
(*iii*) $C_6H_5CHO + H_2NNHCONH_2 \longrightarrow C_6H_5CH=NNHCONH_2 + H_2O$

Benzaldehyde — Semicarbazide — Benzaldehyde semicarbazone

(*iv*) 

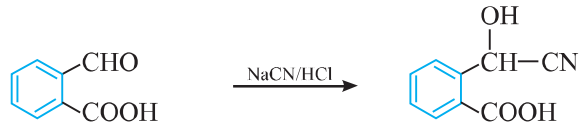
Benzene — Benzoyl chloride — Benzophenone

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

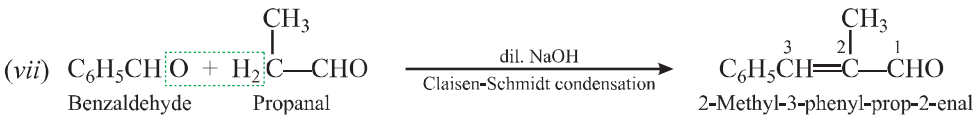


4-Oxocyclohexanecarbaldehyde — 4-Oxocyclohexanecarboxylate anion

(*vi*) Cyanohydrin formation occurs at the aldehyde group

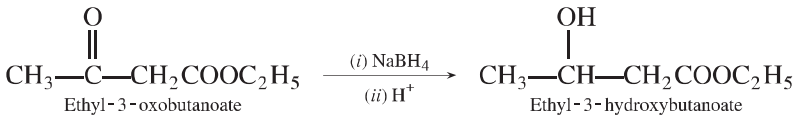


2-Formylbenzoic acid — 2-[1-Hydroxycyanomethyl] benzoic acid

(*vii*) 

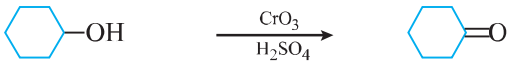
Benzaldehyde — Propanal — 2-Methyl-3-phenyl-prop-2-enal

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



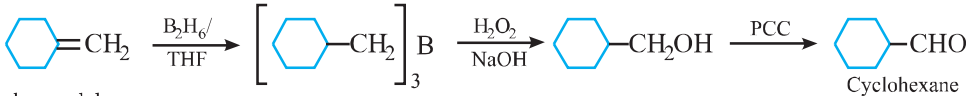
Ethyl-3-oxobutanoate — Ethyl-3-hydroxybutanoate

(*ix*)



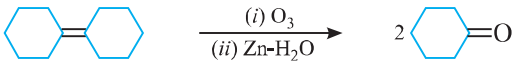
Cyclohexanol — Cyclohexanone

(*x*)



Methylenecyclohexane — Cyclohexane carbaldehyde

(*xi*)



Cyclohexylidenecyclohexane — Cyclohexanone

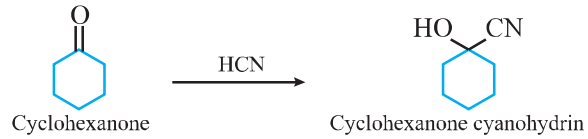
Q. 18. Give plausible explanation for each of the following:

(*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*)

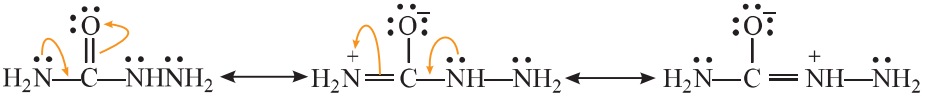


Cyclohexanone — Cyclohexanone cyanohydrin

2,2,6-trimethylcyclohexanone

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.

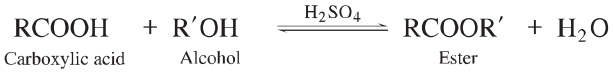
(*ii*)



Semicarbazide

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.



Carboxylic acid — Alcohol — Ester

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.

[CBSE Delhi 2009; (AI) 2009] ***[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 $A = 5 \times 12 + 1 \times 10 + 1 \times 16 = 60 + 10 + 16 = 86$

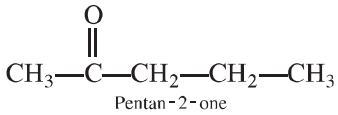
$$n = \frac{86}{86} = 1$$

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.

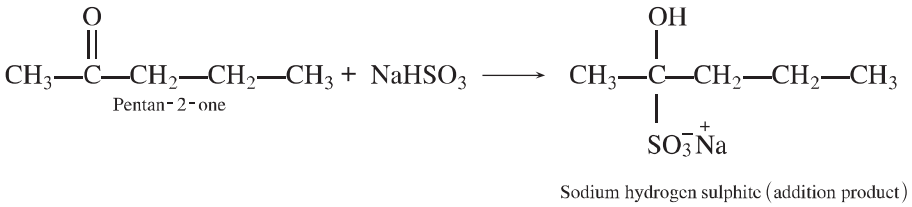
As it does not reduce Tollens' reagent and give positive iodoform test therefore it must be a methyl ketone.

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

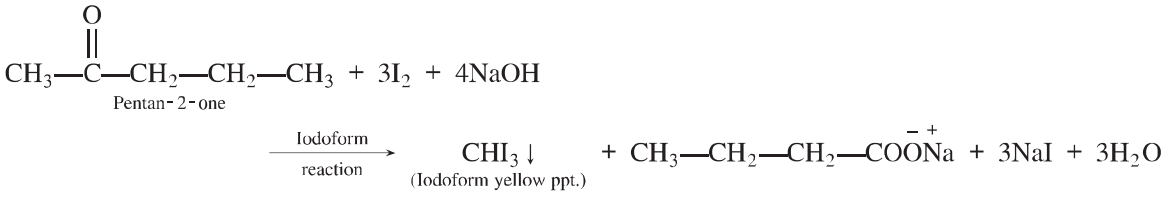


Pentan-2-one

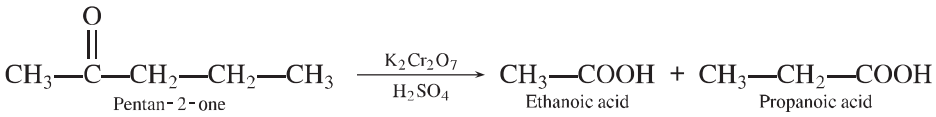
The chemical reactions are:



Pentan-2-one — Sodium hydrogen sulphite (addition product)



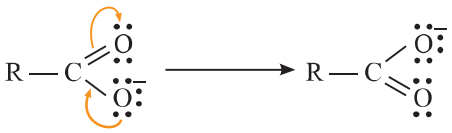
Pentan-2-one — (Iodoform yellow ppt.)



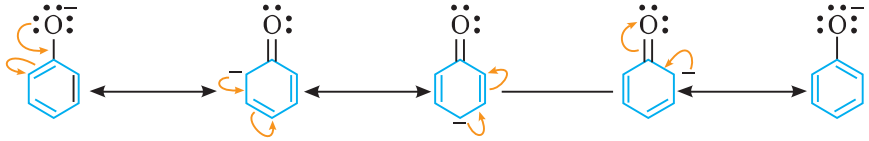
Pentan-2-one — Ethanoic acid — Propanoic acid

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.



I — II



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 [1 mark]

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*) $CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-H$

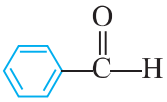
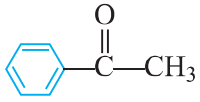
3. $CH_3-C\equiv CH \xrightarrow[1\%\,HgSO_4]{40\%\,H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

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 compounds is most reactive towards nucleophilic addition reactions? *[NCERT Exemplar]*

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

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

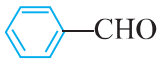
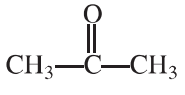
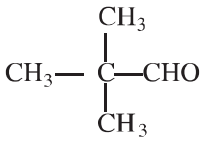
(*c*) Fehling's solution (*d*) Grignard reagent

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

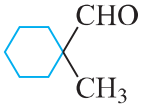
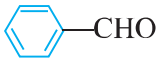
(*a*) Tollens' reagent (*b*) Benzoyl peroxide

(*c*) I_2 and NaOH solution (*d*) Sn and NaOH solution

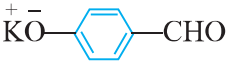
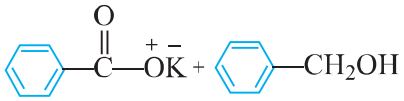
9. Which of the following compounds do not undergo aldol condensation?

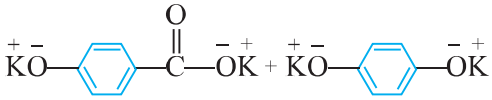
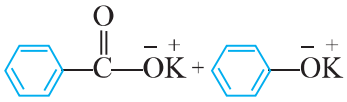
(*a*) $CH_3—CHO$ (*b*)  (*c*)  (*d*) 

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 reactions will not result in the formation of carbon-carbon bond?

(*a*) Friedel-Crafts acylation (*b*) Wurtz reaction

(*c*) Cannizzaro reaction (*d*) Reimer-Tiemann reaction

13. An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests.

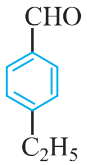
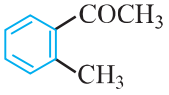
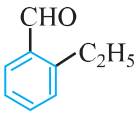
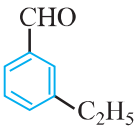
(*i*) Forms 2, 4-DNP derivative

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

(*a*) C_3H_7COOH (*b*) C_2H_5COOH (*c*) both (*d*) None of these

15. Treatment of compound  with NaOH solution yields [*NCERT Exemplar*]

(*a*) Phenol (*b*) Sodium phenoxide (*c*) Sodium benzoate (*d*) Benzophenone

16. Which of the following compounds will give brisk effervescence of CO_2 on treatment with $NaHCO_3$?

(*a*) Phenol (*b*) Acetic acid (*c*) both (*d*) None of these

17. The correct order of increasing acidic strength is _____. [*NCERT Exemplar*]

(*a*) Phenol < Ethanol < Chloroacetic acid < Acetic acid

(*b*) Ethanol < Phenol < Chloroacetic acid < Acetic acid

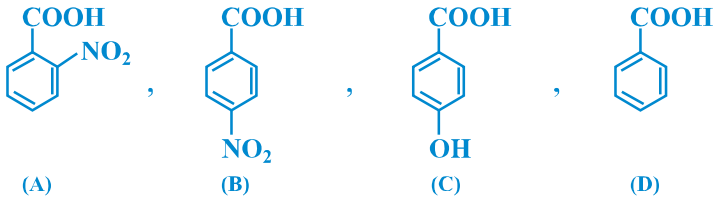
(*c*) Ethanol < Phenol < Acetic acid < Chloroacetic acid

(*d*) Chloroacetic acid < Acetic acid < Phenol < Ethanol

18. The weakest acid among the following is:

(*a*) $CHCl_2COOH$ (*b*) CH_3COOH (*c*) $CH_2ClCOOH$ (*d*) CCl_3COOH

19. 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

20. Which one of the following reagents is used for the conversion of ethanoic acid to ethanoic anhydride?

(*a*) P_2O_5, Δ (*b*) $SOCl_2$, Δ (*c*) PCl_3, Δ (*d*) both (*a*) and (*b*)

Answers

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

8. 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.

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

Answers

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

Passage-based/Case-based Questions

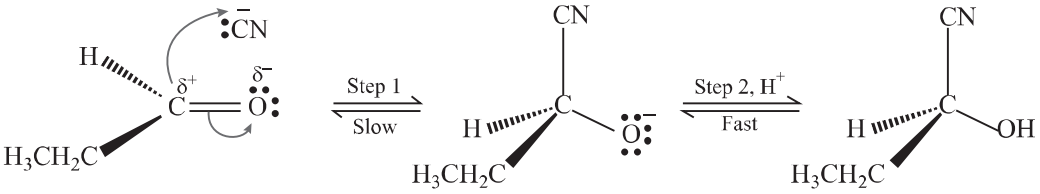
Read the given passages and answer the questions that follow.

PASSAGE–1

Aldehydes and ketones are highly reactive compounds. Since both these classes of organic compounds have the same functional group, *i.e.*, polarized carbonyl group, they show a number of common reactions. However, the presence of a H-atom on the carbonyl group of aldehydes make them much more reactive than ketones. At the same time, this H-atom is responsible for many reactions in which aldehydes differ from ketones. The carbonyl group $(>C{=}O)$ undergoes nucleophilic addition reactions due to electronegativity difference between carbon and oxygen atoms. Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. Further aldehydes and ketones having atleast one α-H atom in the presence of dilute alkali as a catalyst form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (ketol). This reaction is known as aldol condensation. Aldehydes which do not have an α-hydrogen undergo disproportionation reaction in the presence of concentrated alkali giving a mixture of alcohol and salt of carboxylic acid. This reaction is called Cannizzaro reaction. Cannizzaro reaction involves a hydride ion shift from the carbonyl carbon that is attacked by the base to another carbonyl carbon. Since, there is no hydrogen attached to the carbonyl carbon in a ketone therefore it does not undergo Cannizzaro reaction.

1. Propose the mechanism for the following reaction:

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

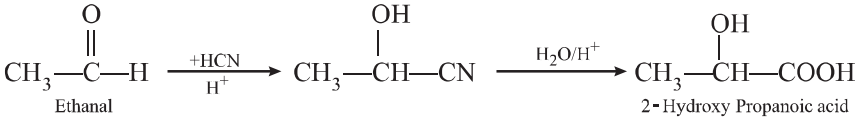


2. Propanone is less reactive than ethanal towards nucleophilic addition reactions. Why?

Ans. The methyl group due to its +I effect reduces the magnitude of positive charge on carbonyl carbon atom. Moreover, it also hinders the approach of the nucleophile. Since in propanone, there are two methyl groups while in acetaldehyde there is one methyl group, therefore, propanone is less reactive than acetaldehyde towards nucleophilic addition reactions.

3. How will you convert ethanal to 2-hydroxy propanoic acid?

Ans.

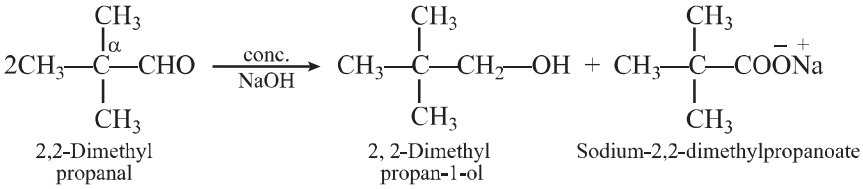


4. Which of the following compounds will undergo Cannizzaro reaction?

(*i*) $(CH_3)_3—C—CHO$ (*ii*) $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CHO$

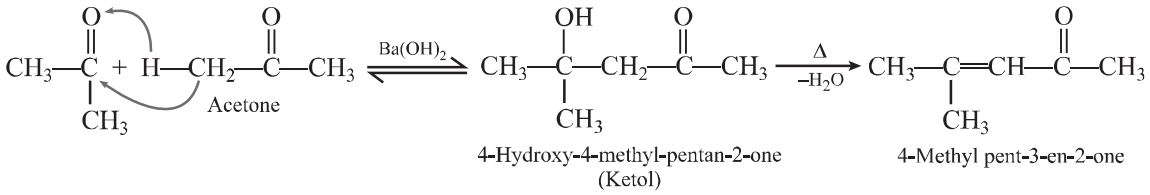
Write the structures of expected product of the Cannizzaro reaction.

Ans. (*i*) will undergo Cannizzaro reaction as it does not contain α-hydrogen.



5. What happens when acetone undergoes aldol condensation? Write the reaction and name of the products.

Ans.



PASSAGE–2

Carboxylic acids are the most acidic amongst all the organic compounds studied so far. However,carboxylic acids are much weaker acids than the mineral acids.

Carboxylic acids are more acidic than alcohols and phenols due to the less electrophilic nature of carboxyl carbon which puts a partial positive charge on the hydroxyl O-atom. The value of K_a is a measure of the acidic strength of an acid. Greater the value of K_a, greater is the tendency of the acid to ionize and hence stronger is the acid. The acidic strength of saturated aliphatic carboxylic acids depends mainly upon the inductive effect of the substituent and its position with respect to —COOH group. Electron-donating substituents tend to decrease whereas electron-withdrawing substituents tend to increase the acidic strength. The acidic strength of aromatic carboxylic acids, on the other hand depends upon both the inductive and the resonance effect of the substituents.

1. What is meant by 'acidity constant' K_a? How is it expressed?

Ans. Acidity constant K_a is a measure of the strength of the acid. It is expressed as,

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

2. What makes ethanoic acid a stronger acid than ethanol?

Ans. Ethanoate ion obtained by loss of a proton from ethanoic acid is stabilized by resonance but ethoxide ion obtained by loss of a proton from ethanol does not.

3. Why is pK_a of chloroacetic acid lower than pK_a of acetic acid?

Ans. Due to –I effect of Cl atom and +I effect of CH_3 group the electron density in the O—H bond in chloroacetic acid is much weaker than in acetic acid and hence loses a proton more easily than acetic acid.

4. Arrange the following in the decreasing order of their acidic character:

CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

Ans. $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

5. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

Ans.
- 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.

Very Short Answer Questions [1 mark]

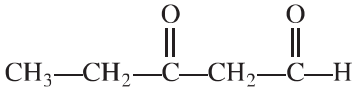
Q. 1. Give IUPAC name of the following compound: *[CBSE (F) 2010]*

$(CH_3)_2C{=}CHCOCH_3$

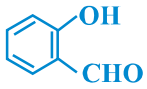
Ans. 4-Methyl-pent-3-en-2-one

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

Ans.



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.

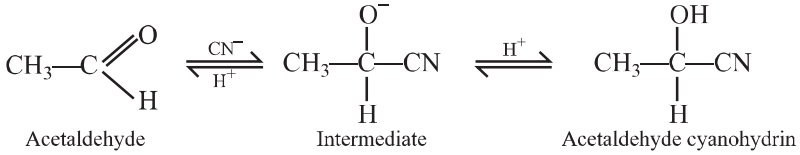
Ans. Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.

$$\underset{\text{Aldehyde}}{R—CH=O} + \underset{1^\circ\text{ Amine}}{H_2N—R'} \xrightarrow[\text{Heat}]{\text{Trace of } H^+} \underset{\text{Schiff's base}}{R—CH=N—R'} + H_2O$$

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

$$CH_3CHO + HCN \xrightarrow{H^+} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CN$$

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



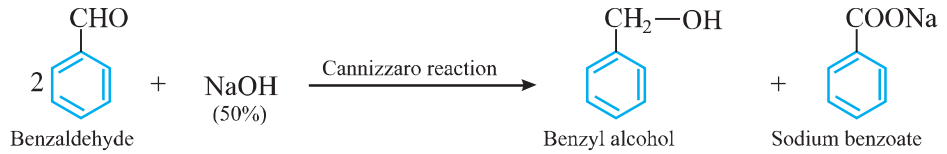
Acetaldehyde Intermediate Acetaldehyde cyanohydrin

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

Ans. Benzaldehyde

Q. 12. How will you prepare benzyl alcohol from benzaldehyde without using a reducing agent? ***[HOTS]***

Ans.



Benzaldehyde — Benzyl alcohol — Sodium benzoate

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

Q. 13. Write two important uses of formalin. ***[CBSE Sample Paper 2011]***

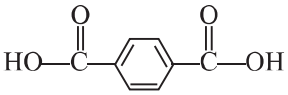
Ans. Formalin is used in the

(*i*) preservation of biological specimens.

(*ii*) manufacture of bakelite.

Q. 14. Write the structural formula and IUPAC name of terephthalic acid.

Ans.

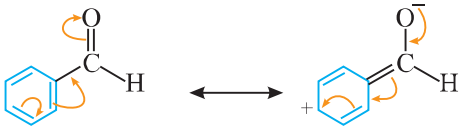


Benzene-1, 4-dicarboxylic acid

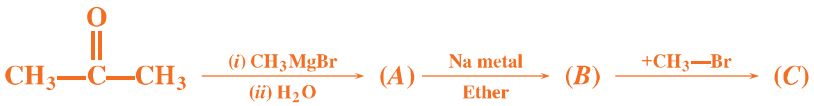
Short Answer Questions–I [2 marks]

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

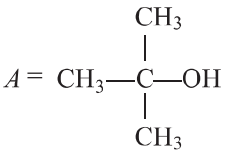
Ans. The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.



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

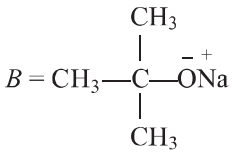


Ans.

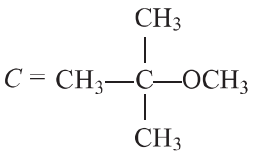


2-methyl propan-2-ol

,



Sodium tert. butoxide



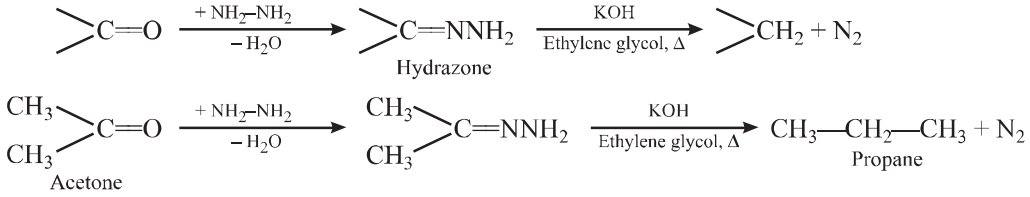
2-methoxy-2-methylpropane

Q. 3. Write the equations involved in the following reactions:

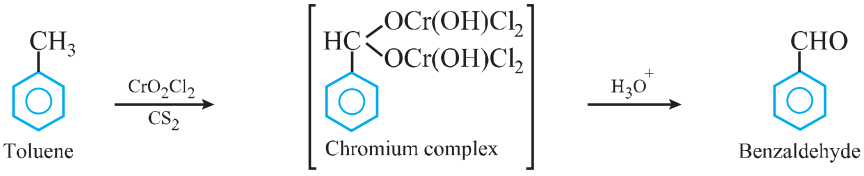
(*i*) Wolff-Kishner reduction

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

Ans. (*i*) **Wolff–Kishner reduction:**



(*ii*) **Etard reaction:**



Q. 4. Write structures of main compounds *A* and *B* in each of the following reactions. **[*CBSE 2019(56/2/3)*]**

(*i*) $CH_3CH_2OH \xrightarrow{PCC} A \xrightarrow{CH_3OH/dry\ HCl(g)} B$

(*ii*) $C_6H_5COCH_3 \xrightarrow{NaOI} A + B$

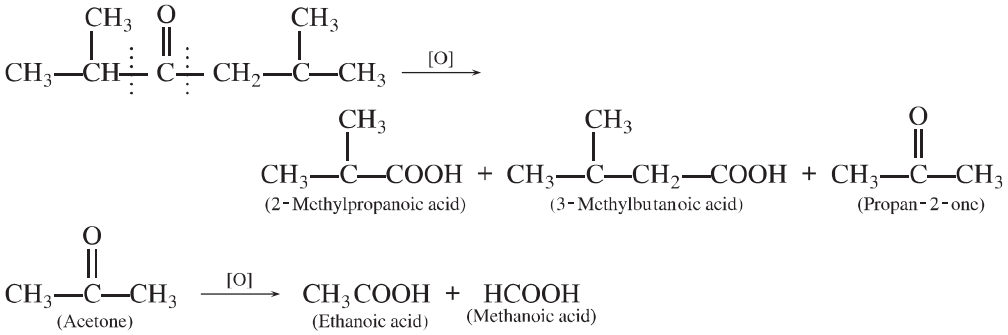
Ans. (*i*) $A = CH_3—\overset{\overset{O}{\|}}{C}—H$ (Acetaldehyde)

$B = CH_3—\underset{\underset{OH}{|}}{\overset{\overset{OCH_3}{|}}{C}}—H$ (Hemiacetal)

(*ii*) *A* and *B* = CHI_3 (Iodoform), $C_6H_5—\overset{\overset{O}{\|}}{C}—O^-Na^+$ (Sodium benzoate)

Q. 5. Oxidation of ketones involves carbon–carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one. **[*NCERT Exemplar*]**

Ans.



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 $CH_3—\overset{\overset{O}{\|}}{C}—$ group.

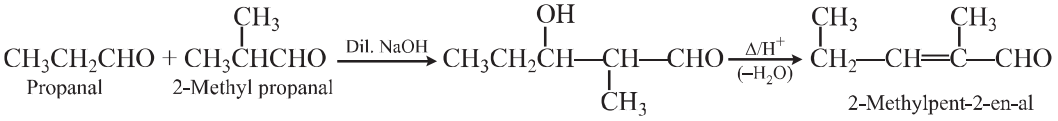
As '*A*' gives positive Tollens' test, so it must have —CHO group.

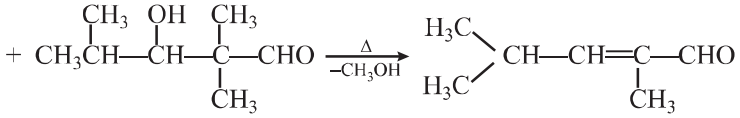
So '*A*' is $CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_2CHO$

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. Name the reagents used in the following reactions: ***[CBSE Delhi 2015]***

(*i*) $CH_3—CO—CH_3 \xrightarrow{?} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$

(*ii*) $C_6H_5—CH_2—CH_3 \xrightarrow{?} C_6H_5—COO^-K^+$

Ans. (*i*) Sodium borohydride ($NaBH_4$) or Lithium aluminium hydride ($LiAlH_4$)

(*ii*) Alkaline potassium permanganate ($KMnO_4$—KOH)

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

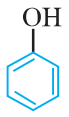
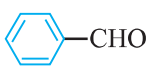
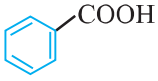
Ans. (*i*) $CH_3—CH=CH_2 \xrightarrow[H^+]{H_2O} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3—\overset{\overset{O}{||}}{C}—CH_3$

Propene — Acetone

(*ii*) $CH_3—CH_2—COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/red\ P} CH_3—\underset{\underset{Cl}{|}}{CH}—COOH \xrightarrow{NaOH(aq)} CH_3—\underset{\underset{OH}{|}}{CH}—COOH$

Propanoic acid — 2-Hydroxy propanoic acid

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*]**

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

Ans. $A =$ CH_3MgBr (Methyl magnesium bromide), $B = CH_3—\overset{\overset{O}{\|}}{C}—OH$ (Ethanoic acid), $C = CH_3—\overset{\overset{O}{\|}}{C}—O—CH_3$ (Methyl ethanoate)

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

[*CBSE Bhubaneshwar 2015*]

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

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

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.

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

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

Short Answer Questions–II [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'. ***[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:

$$\underset{\text{(A)}\\\text{2-Methylbut-2-ene}}{CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} \underset{\text{(B)}\\\text{Acetaldehyde}}{H_3C-CHO} + \underset{\text{(C)}\\\text{Acetone}}{O=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3}$$

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

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

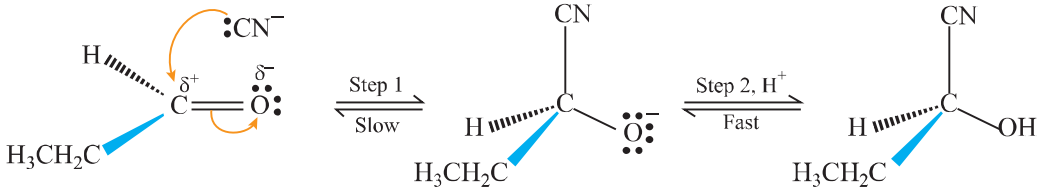
Q. 2. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If 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 $\quad$ CH_3COCH_3

(I) $\quad$ (II)

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

Mechanism: Nucleophilic addition reaction:



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

(*c*) 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. (*i*) $A = CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—H$, Butanal; $B = CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$, Butanone,

$C = CH_3—\underset{\underset{CH_3}{|}}{CH}—\overset{\overset{O}{\|}}{C}—H$, 2-Methylpropanal; $D = CH_3—CH_2—CH_2—CH_3$, Butane

(*ii*) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$, Butanone (*B*)

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; $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

B = Butan-2-ol ; $CH_3—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3$

C = But-2-ene ; $CH_3—CH=HC—CH_3$

Reactions involved:

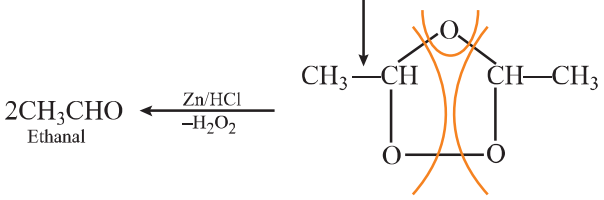
$CH_3—CH_2—\underset{\underset{CH_3}{|}}{C}=O + H_2N—NH—C_6H_3(NO_2)—NO_2 \longrightarrow CH_3—CH_2—\underset{\underset{CH_3}{|}}{C}=N—NH—C_6H_3(NO_2)—NO_2$

2,4-DNP — Orange red ppt

$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 + 3NaOI \longrightarrow \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + CH_3—CH_2—\overset{\overset{O}{\|}}{C}—O^-Na^+ + 2NaOH$

$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{LiAlH_4} \underset{\text{Butan-2-ol}}{CH_3—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3}$

$CH_3—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} \underset{\text{But-2-ene}}{CH_3—CH=CH—CH_3} + O_3$



$\xrightarrow[-H_2O_2]{Zn/HCl} \underset{\text{Ethanal}}{2CH_3CHO}$

Q. 5. An unknown aldehyde 'A' on reacting with alkali gives a β-hydroxy aldehyde, which loses water to form an unsaturated aldehyde, But-2-enal. Another aldehyde 'B' undergoes disproportionation reaction in the presence of conc. alkali to form products C and D. C is an arylalcohol with the formula, C_7H_8O.

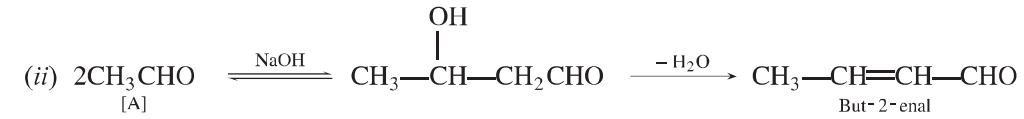
(*i*) Identify A and B.

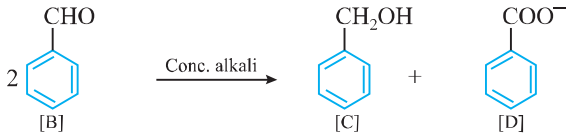
(*ii*) Write the sequence of reactions involved.

(*iii*) Name the product, when 'B' reacts with zinc amalgam and hydrochloric acid. **[*HOTS*]**

Ans. (*i*) A is CH_3CHO (ethanal) and B is C_6H_5CHO (benzaldehyde).

(*ii*)





(*iii*) Toluene.

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

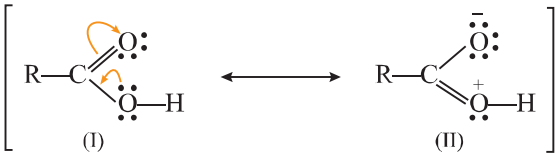
(*a*) $Cl—CH_2COOH$ is a stronger acid than CH_3COOH.

(*b*) Carboxylic acids do not give reactions of carbonyl group.

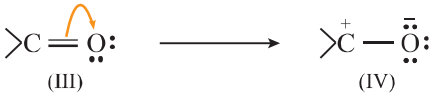
(*ii*) Out of $CH_3CH_2—CO—CH_2—CH_3$ and $CH_3CH_2—CH_2—CO—CH_3$, which gives iodoform test? **[*CBSE (AI) 2014*]**

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:



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



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

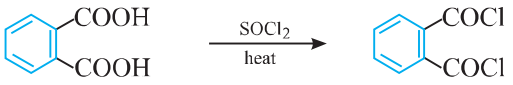
(*iii*) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

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

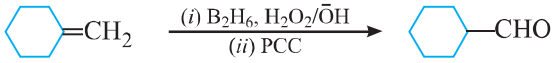
(*i*) 

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

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

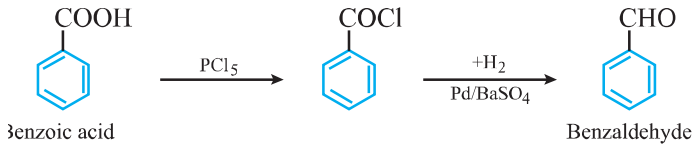
Q. 10. Do the following conversions in not more than two steps: [*CBSE Delhi 2017*]

(*i*) **Benzoic acid to Benzaldehyde**

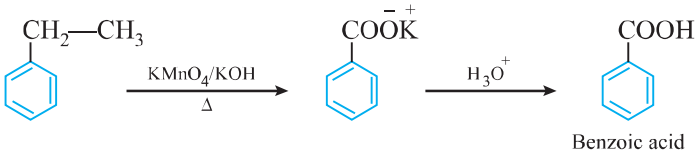
(*ii*) **Ethyl benzene to Benzoic acid**

(*iii*) **Propanone to Propene**

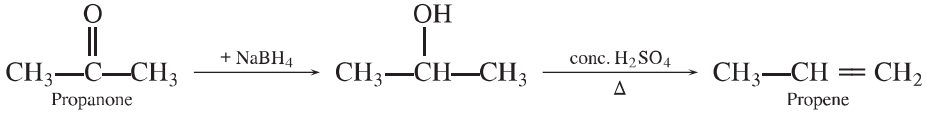
Ans. (*i*) **Benzoic acid to Benzaldehyde**



(*ii*) **Ethyl benzene to Benzoic acid**



(*iii*) **Propanone to Propene**



Q. 11. Predict the products of the following reactions: **[*CBSE Delhi 2015*]**

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

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

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

Ans. (*i*) $CH_3—CH_2—CH_3$ (Propane)

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

(*iii*) CH_4 (Methane)

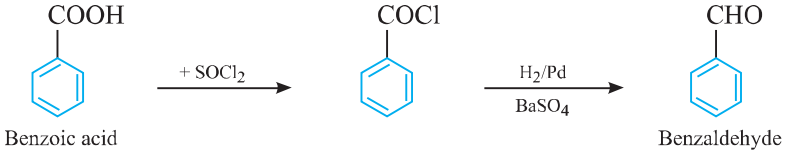
Q. 12. How do you convert the following?

(*i*) Benzoic acid to Benzaldehyde

(*ii*) Ethyne to Ethanal

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

Ans. (*i*)



Benzoic acid — Benzaldehyde

(*ii*) $CH \equiv CH \xrightarrow[HgSO_4/H_2SO_4]{+H_2O} \left[CH_2=\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}H\right] \longrightarrow CH_3—\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}—H$

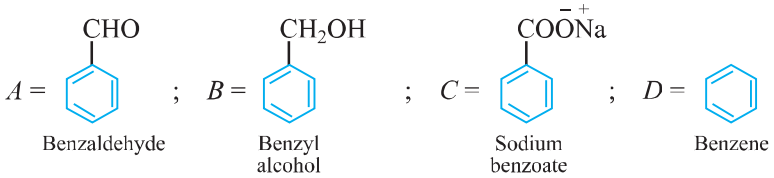
Ethyne — Ethanal

(*iii*) $CH_3COOH \xrightarrow{+NaOH} CH_3\overset{-}{C}OO\overset{+}{N}a \xrightarrow[\Delta]{NaOH/CaO} CH_4$

Acetic acid — Methane

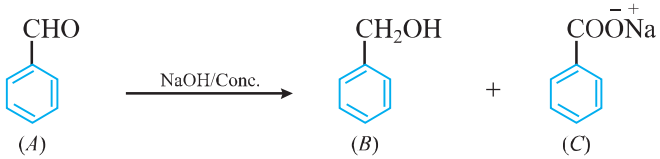
Q. 13. An organic compound (*A*) has characteristic odour. On treatment with NaOH, it forms compounds (*B*) and (*C*). Compound (*B*) has molecular formula C_7H_8O which on oxidation gives back (*A*). The compound (*C*) is a sodium salt of an acid. When (*C*) is treated with soda-lime, it yields an aromatic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

Ans.

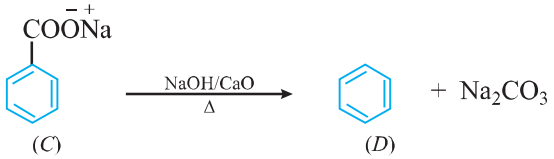


Benzaldehyde — Benzyl alcohol — Sodium benzoate — Benzene

Reaction involved are:



(*A*) (*B*) (*C*)



(*C*) (*D*)

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*) CH_3CHO (Ethanal) $\xrightarrow{\text{dil. NaOH}}$ $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—CHO$ (3-Hydroxybutanal)

(*ii*) Benzoic acid $\xrightarrow[H_2SO_4\text{ (conc.), }\Delta]{HNO_3\text{ (conc.)}}$ *m*-Nitro benzoic acid $\xrightarrow{+NH_3,\ \Delta}$ *m*-Nitro benzamide $\xrightarrow{LiAlH_4}$ *m*-Nitro benzyl amine $\xrightarrow{HNO_2}$ *m*-Nitro benzyl alcohol

(*iii*) Benzaldehyde $\xrightarrow[(O)]{K_2Cr_2O_7/H_2SO_4}$ Benzoic acid $\xrightarrow{SOCl_2}$ Benzoyl chloride $\xrightarrow[AlCl_3\text{ (anhyd.)}]{+\text{ Benzene}}$ Benzophenone

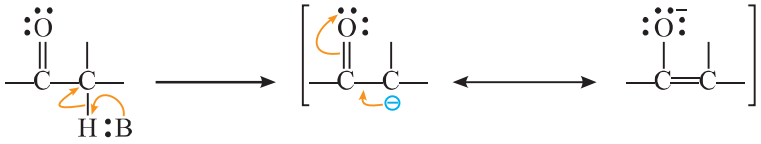
Q. 15. Give reasons:

(*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*]**

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 [5 marks]

Q. 1. Give names of the reagents that bring about the following transformations:

(*i*) Hexan-1-ol to hexanal

(*ii*) *p*-Fluorotoluene to *p*-fluorobenzaldehyde

(*iii*) Ethanenitrile to ethanol

(*iv*) Allyl alcohol to propenal

(*v*) Ethanoic acid to ethanol

Ans. (*i*) $[C_5H_5NH]^+[CrO_3Cl]^-$ (PCC)

(*ii*) CrO_3 in the presence of acetic anhydride/1. CrO_2Cl_2 2. H_3O^+

(*iii*) Diisobutyl aluminium hydride (DIBAL-H)

(*iv*) PCC

(*v*) $LiAlH_4$

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.

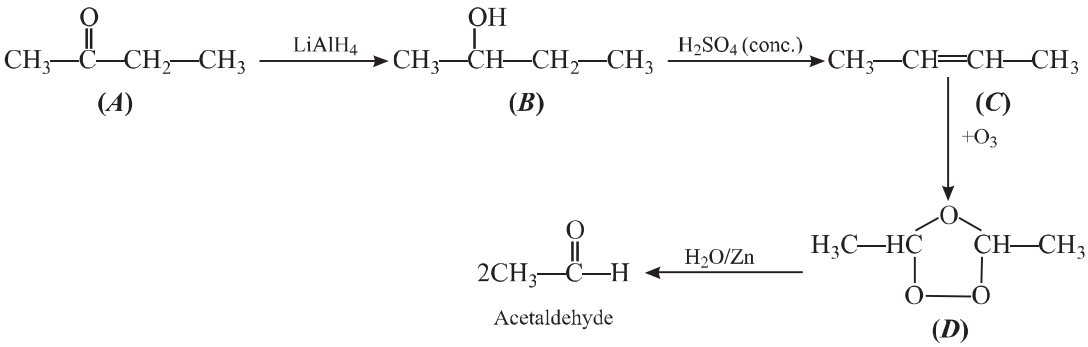
(*a*) PhMgBr and then H_3O^+

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

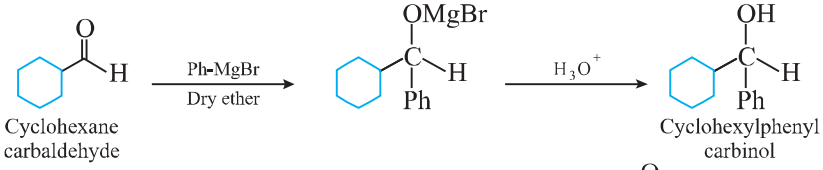
Ans. (*i*) $A = CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$, $B = CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—CH_3$, $C = CH_3—CH=CH—CH_3$

Butan-2-one; Butan-2-ol; But-2-ene

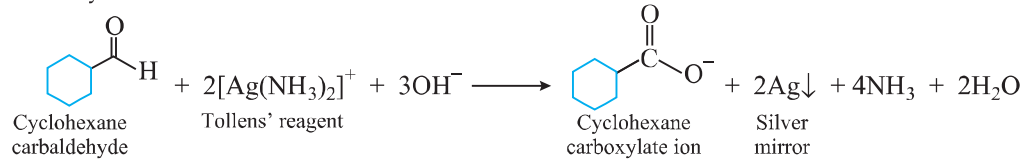
The reactions are as follows:



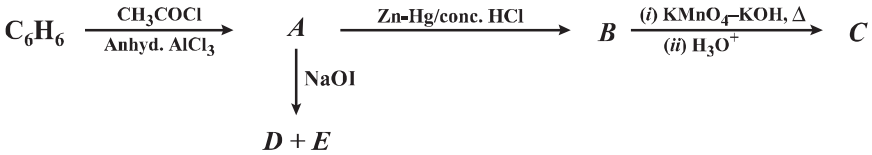
(*ii*) (*a*)

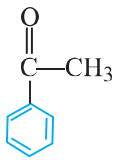
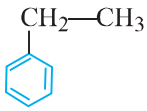
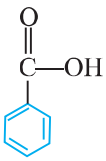
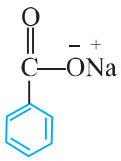


(*b*)



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



Ans. $A =$  ; $B =$  ; $C =$  ; D or $E = CHI_3$; E or $D =$ 

Acetophenone; Ethyl benzene; Benzoic acid; Iodoform; Sodium benzoate

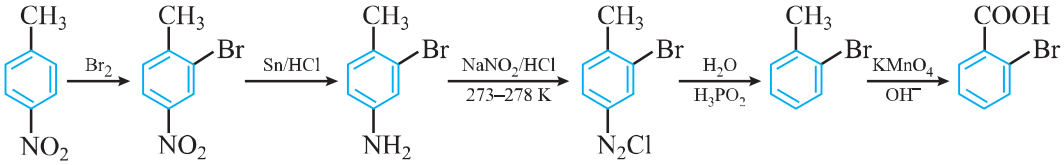
Q. 4. **(*i*) Carry out the following conversions:** **[*CBSE 2019 (56/4/1)*]**

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

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

(*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:**

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

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

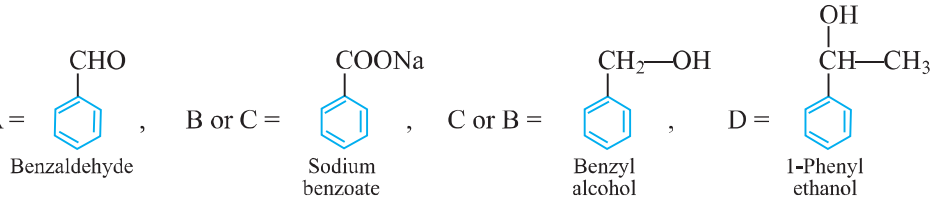
(*ii*) Distinguish between the following:

(*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*)



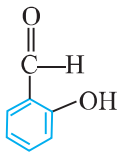
(*ii*) (*a*) $C_6H_5COCH_3$ being a methyl ketone gives iodoform test while $C_6H_5COCH_2CH_3$ does not.

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

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

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

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

(*iii*) 

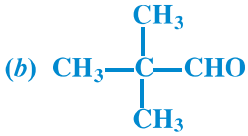
Q. 6. **(*i*) Carry out the following conversions:**

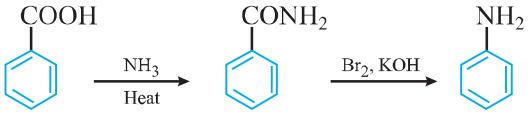
(*a*) Benzoic acid to aniline

(*b*) Bromomethane to ethanol

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

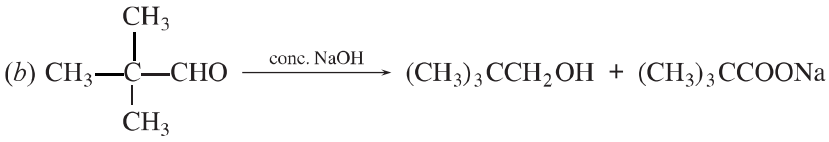
(*a*) $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H \xrightarrow[(b)\ KOH,\ Glycol/heat]{(a)\ H_2N-NH_2}$

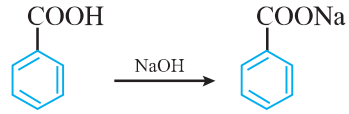
(*b*)  **[*CBSE 2019 (56/4/1)*]**

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*) 

(*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

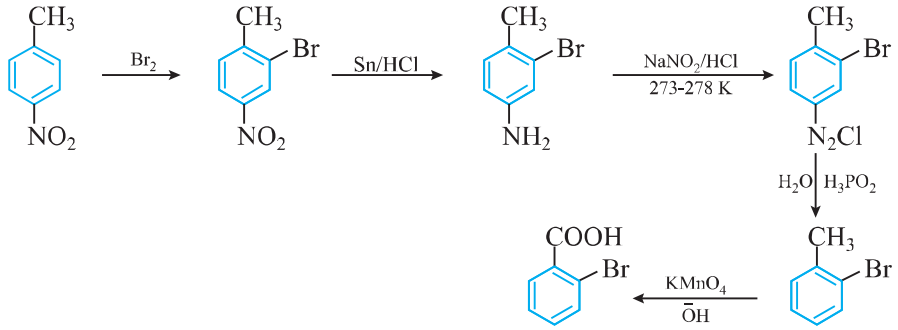
(*iii*) A and B are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

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

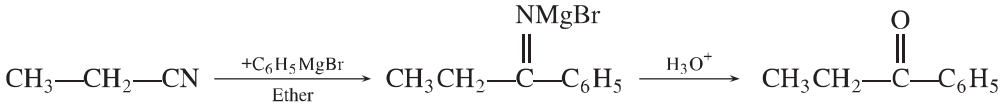
Ethanal reacts with NaOI (I_2/NaOH) to form yellow precipitate of iodoform while benzaldehyde does not give this test.

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

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



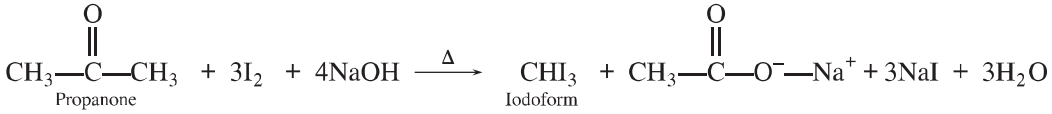
(*b*) Ethylcyanide to 1-phenyl propanone



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

B = $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ Propanone

Reaction involved:



Q. 8. An organic compound 'A' on treatment with ethyl alcohol gives carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. B on heating with $Ca(OH)_2$ gives 'E' with molecular formula C_3H_6O. 'E' does not give Tollens' test or reduce Fehling solution but forms 2, 4-dinitrophenyl hydrazone. Identify A, B, C, D, E. [*HOTS*]

Ans. A = $(CH_3—\overset{O}{\overset{\|}{C}})_2O$ Acetic anhydride

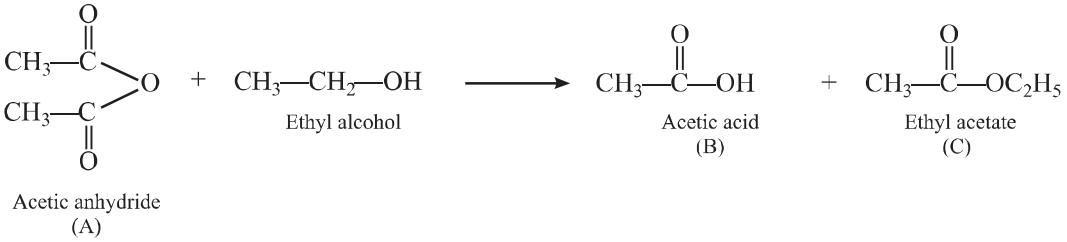
B = $CH_3—\overset{O}{\overset{\|}{C}}—OH$ Acetic acid

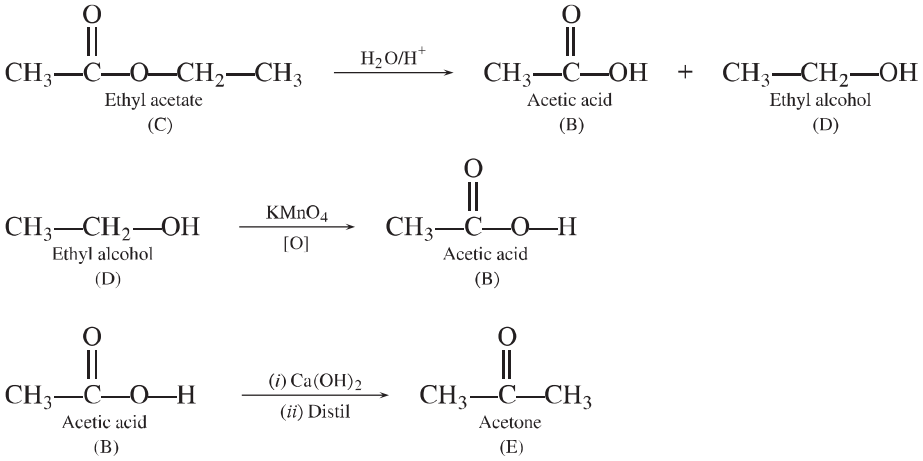
C = $CH_3—\overset{O}{\overset{\|}{C}}—O—CH_2—CH_3$ Ethyl acetate

D = $CH_3—CH_2—OH$ Ethyl alcohol

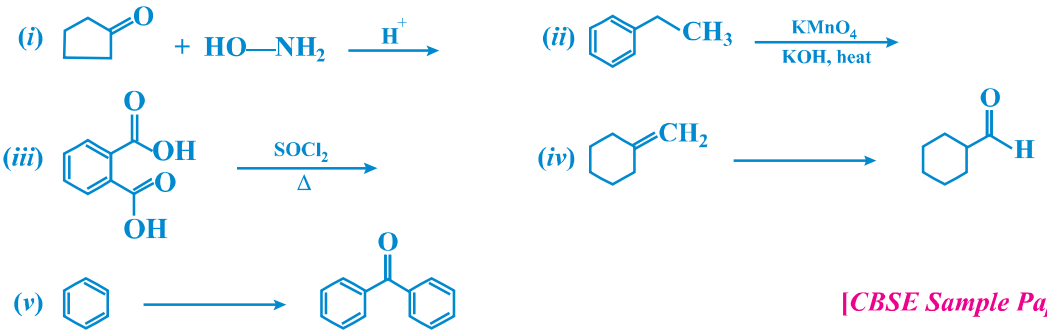
E = $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ Acetone

Reactions are:



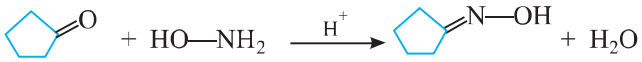


Q. 9. Complete each synthesis by giving missing starting material, reagent or products:

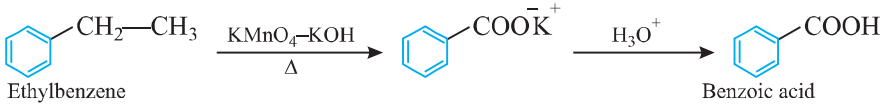


[*CBSE Sample Paper 2017*]

Ans. (*i*)

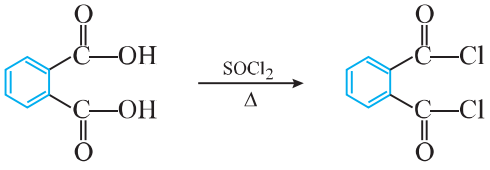


(*ii*)



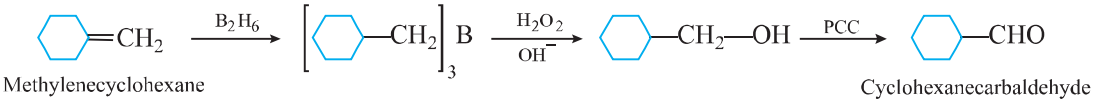
Ethylbenzene — Benzoic acid

(*iii*)



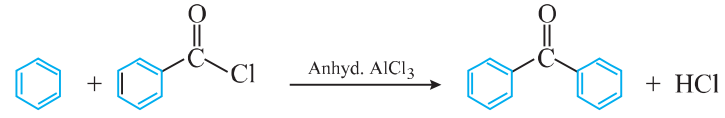
Phthalic acid — Phthaloyl chloride

(*iv*)



Methylenecyclohexane — Cyclohexanecarbaldehyde

(*v*)



Benzene — Benzoyl chloride — Benzophenone

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

$$CH_3CN \xrightarrow[(ii)\ H_2O]{(i)\ SnCl_2—HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\text{Heat}} C$$

$A \xrightarrow{HCN} D$

(*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

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

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

$D = CH_3—\underset{\underset{OH}{|}}{CH}—CN$ 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.

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

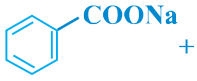
(*b*) Formic acid reduces Tollens' reagent to metallic silver while propionic acid does not.

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

(*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:**

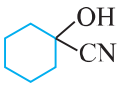
(*a*)  **+ HCN ⟶ ?**

(*b*)  **+ NaOH $\xrightarrow[\Delta]{CaO}$?**

(*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.

$$\underset{\text{Butanal}}{CH_3—CH_2—CH_2—CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$

$$\underset{\text{Butanoate ion}}{CH_3—CH_2—CH_2—COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

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

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

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. **Toluene can be oxidised to benzoic acid by**
   (*a*) $KMnO_4$(alk.) (*b*) $K_2Cr_2O_7$
   (*c*) Both (*d*) None
2. **Carbonyl group undergoes**
   (*a*) Electrophilic addition reaction (*b*) Nucleophilic addition reactions
   (*c*) Both (*d*) None
3. **Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives**
   (*a*) Acetic acid (*b*) Acetaldehyde
   (*c*) Formaldehyde (*d*) Formic acid

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.* (3 × 1 = 3)

4. **Assertion (*A*) :** Acetic acid does not undergo haloform reaction.
   Reason (*R*) : Acetic acid has no alpha hydrogen.
5. **Assertion (*A*) :** 2, 2-Dimethylpropanal undergoes Cannizzaro reaction with conc. NaOH.
   Reason (*R*) : Cannizzaro reaction is a disproportionation reaction.
6. **Assertion (*A*) :** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
   Reason (*R*) : Carboxyl group increases the electron-density at *meta*-position.

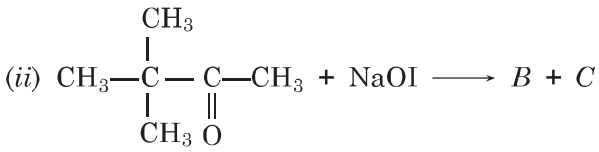
Answer the following questions:

7. Write the IUPAC name of the following compound:

(1)

8. How will you distinguish between ethanol and ethanal? (1)
9. Complete the following reactions by identifying *A*, *B* and *C*.

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

(*ii*) 

(2)

10. 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] **(2)**

11. Write the reagents required in the following reactions: ***[CBSE Allahabad 2015]***

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

(*ii*) $CH_3—COOH \xrightarrow{?} CH_3—CONH_2$ **(2)**

12. 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. **(2)**

13. 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)]*** **(3)**

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

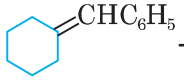
(*i*) Ethyl benzene to benzene

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

(*iii*) Acetone to propene **(3)**

15. 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. **(3)**

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

(*i*)  $\xrightarrow[2.\ Zn/H_2O]{1.\ O_3}$ (A) + (B)

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

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

(*iv*) (D) $\xrightarrow[\Delta]{H_2/Ni}$ (E) **(5)**

Answers

1. (*c*) **2.** (*b*) **3.** (*a*) **4.** (*c*) **5.** (*b*) **6.** (*c*)