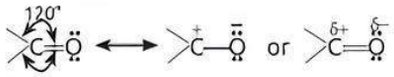
8 Aldehydes, Ketones and Carboxylic Acids

Fastrack Revision

Aldehydes and Ketones

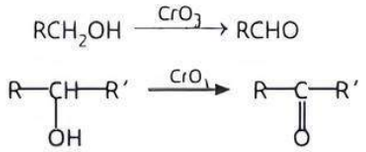
- In aldehydes, the carbonyl group (>C=O) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms.
- **Nature of Carbonyl Group**
  - The carbon and oxygen of the carbonyl group are sp^2 hybridised and the carbonyl double bond contains one σ-bond and one π-bond.



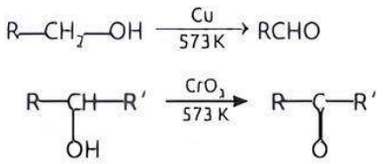
  - The electronegativity of oxygen is much higher than that of the carbon, so their electron cloud is shifted towards the oxygen. Therefore, C—O bond is polar in nature.

Preparation of Aldehydes and Ketones

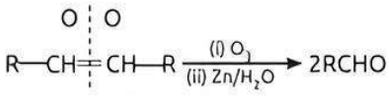
- **By oxidation of Alcohols:**

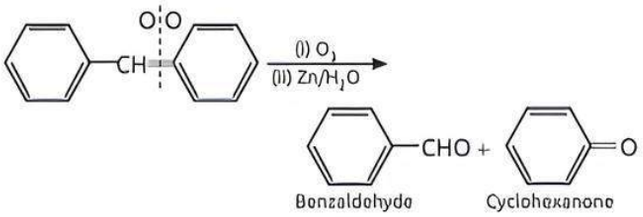


- **By Dehydrogenation of Alcohols:** In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones.

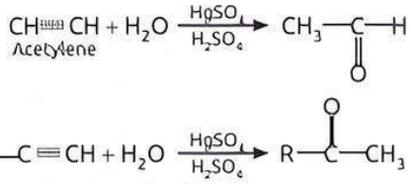


- **By Ozonolysis of Alkenes:**

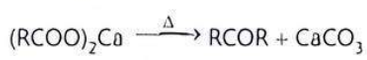




- **By Hydration of Alkynes:** Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.

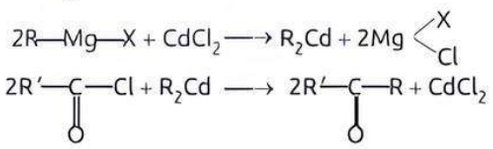


- **By Heating Ca Salt of Acid:**

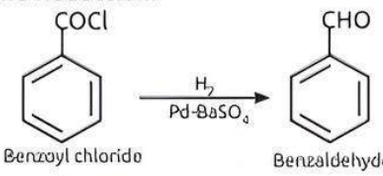


- **From Nitriles (Stephen reaction):**

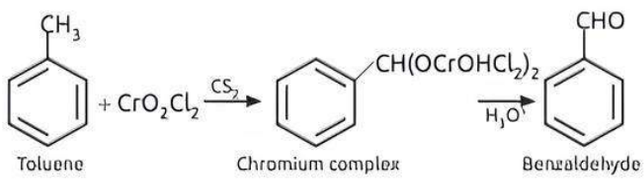
- **From Acyl Chlorides:**



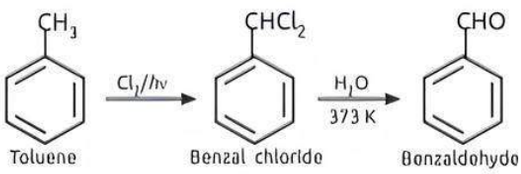
- **Rosenmund Reduction:**



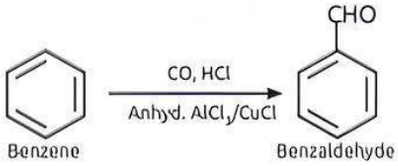
  - Formaldehyde cannot be prepared by this method as HCOCl is highly unstable.
- **Etard Reaction:**



- **Side Chain Halogenation Followed by Hydrolysis of Toluene:**



- **Gattermann-Koch Synthesis:**



▶ **By Decarboxylation and Dehydration of Aromatic Acids:**

$$C_6H_5COOH + HCOOH \xrightarrow[300°C]{MnO} C_6H_5CHO + H_2O + CO_2$$

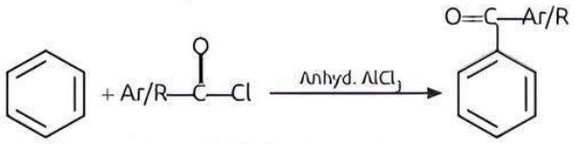
$$C_6H_5COOH + HOOCH_3 \xrightarrow[100°C]{MnO} C_6H_5COCH_3 + H_2O + CO_2$$

▶ **From Nitriles:**

$$CH_3CH_2C{\equiv}N + C_6H_5MgBr \xrightarrow{\text{Ether}} CH_3CH_2C(NMgBr)C_6H_5 \xrightarrow[-Mg(OH)Br]{-NH_3,\ H_3O^+} C_2H_5COC_6H_5$$

(1-Phenylpropanone)

▶ **Friedel-Crafts Acylation:**

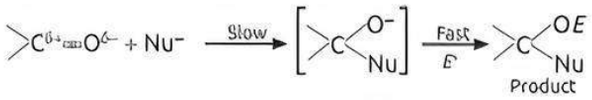


Physical Properties of Aldehydes and Ketones

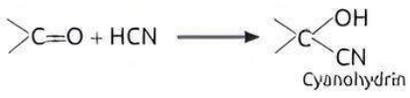
- Methanal (HCHO) is a gas at room temperature and its 40% aqueous solution is known as **formalin**. It is a reducing agent in silvering of mirrors and decolourising vat dyes.
- Ethanal (CH_3CHO) is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.
- The boiling point of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
- Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.

Chemical Reactions of Aldehydes and Ketones

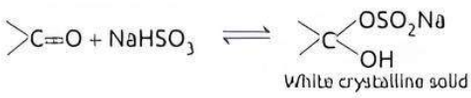
▶ **Nucleophilic Addition Reactions:**



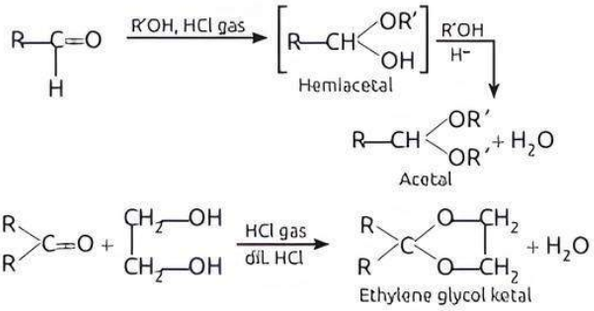
- **Addition of Hydrogen Cyanide:**



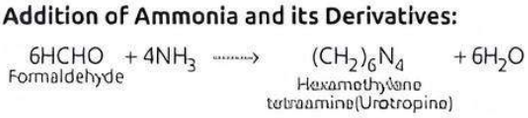
- **Addition of Sodium Hydrogen Sulphite:**



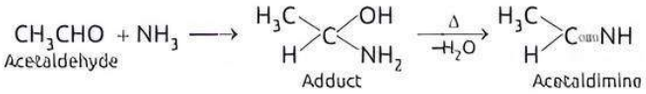
- **Addition of Lower Alcohols:**

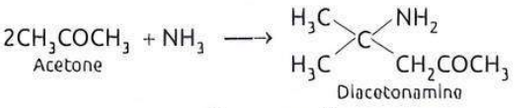


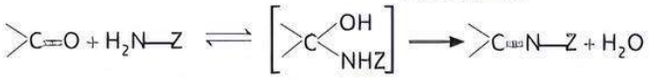
- **Addition of Ammonia and its Derivatives:**



Urotropine on controlled nitration gives the well known explosive, **RDX (Research and Development explosive).**



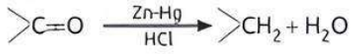




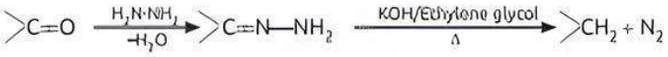
where, Z = alkyl, aryl, —OH, —NH_2, —C_6H_5NH, —NH_2CONH_2 etc.

▶ **Reduction:** Aldehydes and Ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride [$LiAlH_4$].

- **Clemmensen Reduction:**



- **Wolff-Kishner Reduction:**

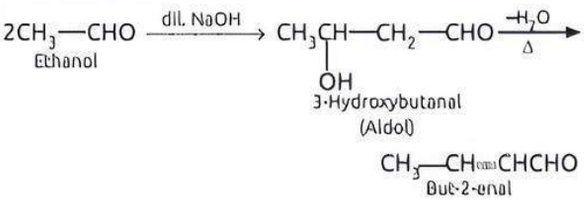


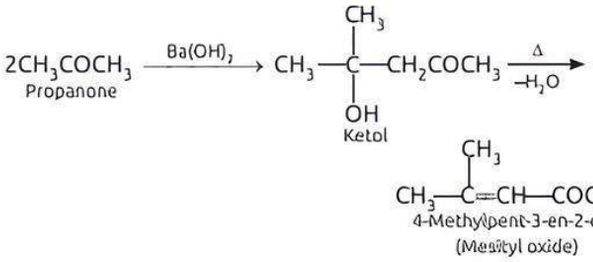
▶ **Oxidation:** Aldehydes get easily oxidised to carboxylic acids by HNO_3, $KMnO_4$, $K_2Cr_2O_7$, etc., or even by mild oxidising agent.

$$RCHO \xrightarrow{(O)} RCOOH$$

▶ **Reactions due to α-hydrogen:** The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-hydrogen.

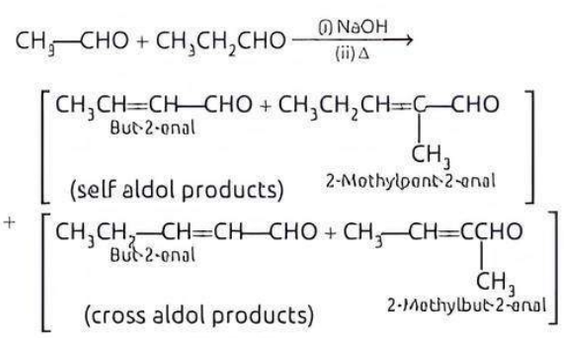
- **Aldol Condensation:**

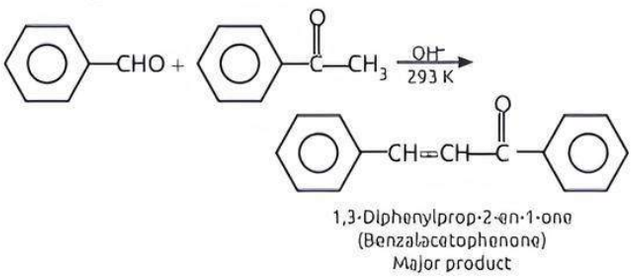




Its further condensation gives phorone.

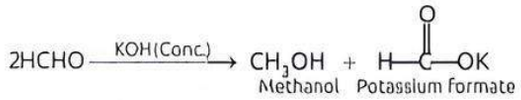
- **Cross Aldol Condensation:** Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation or Claisen reaction.**

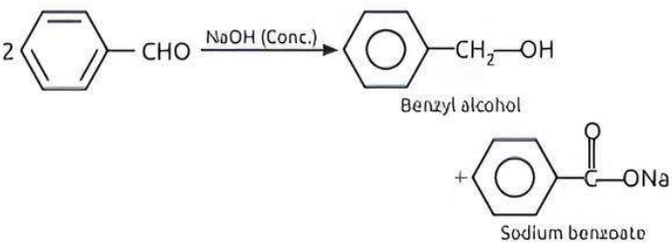




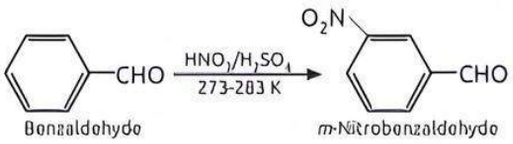
▶ **Other Reactions:**

- **Cannizzaro Reaction:**





- **Electrophilic Substitution Reaction:** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows +R effect, therefore it acts as a deactivating and *meta*-directing group.

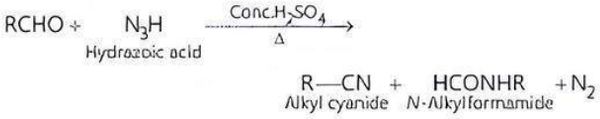


- **Baeyer-Villiger Oxidation:** With Caro's acid (H_2SO_5) or perbenzoic acid (C_6H_5O) or peracetic acid (CH_3CO_3H), aliphatic ketones give ester.

$$R_2CO + R'CO_3H \longrightarrow RCOOR + RCOOH$$

- **Tischenko's Reaction:** It is a modified form of Cannizzaro reaction.

- **Schmidt Reaction:**



Tests to Distinguish between Aldehydes and Ketones:

- **Tollen's Test:** Aldehydes give bright silver mirror with Tollen's reagent (ammoniacal silver nitrate).

$$RCHO + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow RCOO^- + 2Ag\downarrow + H_2O + NH_4^+ + 3NH_3$$

(Silver mirror)

- **Fehling's Test:** Fehling's solution gives a reddish-brown precipitate with aldehydes (except benzaldehyde).

$$R—CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O(s)\downarrow + 3H_2O$$

(Fehling's solution; Red ppt.)

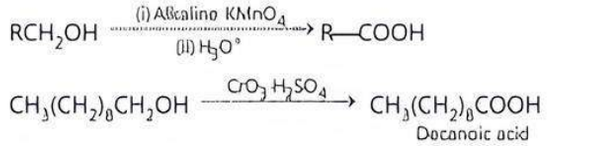
- **Benedict Solution:** With it, aldehydes (except benzaldehyde) give red ppt. of Cu_2O.
- **Schiff's Reagent:** It is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing SO_2. Aldehydes give pink colour with this reagent but ketones do not.

Carboxylic Acids

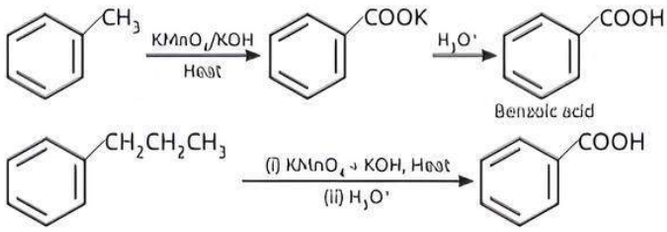
These are the compounds which have $-\overset{\overset{O}{\|}}{C}-OH$ group [carboxyl group]. The word 'carboxyl' is a combination of two words–carbonyl ($>C=O$) and hydroxyl ($-OH$).

Methods of Preparation of Monocarboxylic Acids

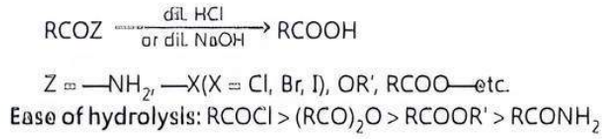
▶ **From Primary Alcohols and Aldehydes:**



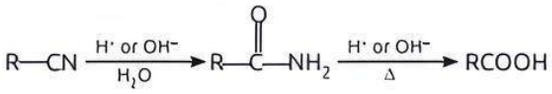
▶ **From Alkyl Benzenes:** Alkyl benzene when treated with strong oxidising agent like H_2CrO_4 (chromic acid), acidic or alkaline $KMnO_4$ gives benzoic acid.

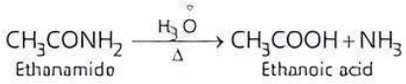


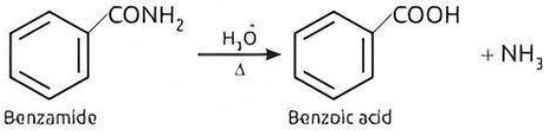
▶ **From Acid Derivatives:**



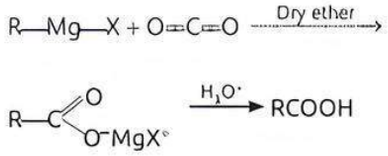
▶ **From Nitriles and Amides:**



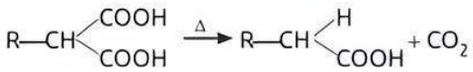




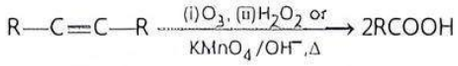
▶ **From Grignard Reagents:**



▶ **By Heating Geminal Dicarboxylic Acids:**



▶ **From Alkynes:**



Physical Properties of Carboxylic Acids

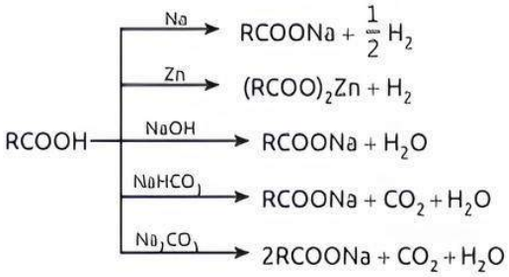
- Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids.
- The lower carboxylic acids are freely miscible with water due to the presence of intermolecular hydrogen bonding with H_2O molecules. However, the solubility in water decreases gradually due to increase in the size of alkyl group.
- Monocarboxylic acids have higher boiling points as compared to the alcohols of comparable molecular masses due to the presence of stronger intermolecular hydrogen.
- Melting points of aliphatic monocarboxylic acids show alternation or oscillation effect, *i.e.* the m.p. of an acid with even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms.

Chemical Properties of Carboxylic Acids

▶ **Reactions Involving Cleavage of O—H Bond:**

Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair of O of —OH group.

- **Reactions with Metals and Alkalies:**



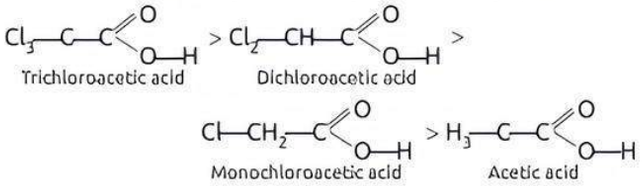
- **Acidity:** Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

The electron releasing substituents (+I effect) decrease the acidic strength of the carboxylic acids by destabilising the carboxylate ion.

Order of +I effect: $-H < -CH_3 < -C_2H_5 < -C_3H_7$

Therefore, the order of acidic strength is

$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$

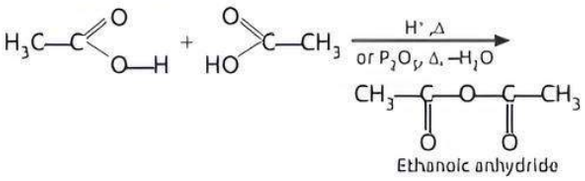


$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

This is because –I effect decreases in the order: F > Cl > Br > I.

▶ **Reactions Involving Cleavage of C—O—H Bond**

- **Formation of Anhydride:**



- **Esterification:**

$$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

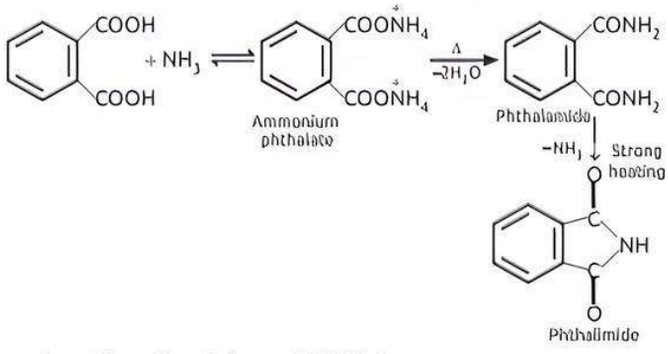
- **Reactions with PCl_5, PCl_3 and $SOCl_2$:**

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

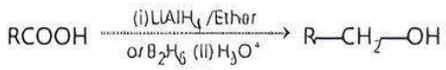
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

- **Reaction with Ammonia:**



▶ **Reactions Involving —COOH Group:**

- **Reduction**



- **Decarboxylation:**

$$RCOONa \xrightarrow[\Delta]{NaOH,CaO\ (Ratio\ 3:1)} R{-}H + Na_2CO_3$$

▶ **Substitution Reactions in the Hydrocarbon Part:**

$$R{-}CH_2{-}COOH \xrightarrow[(ii)H_2O]{(i)X_2/Red\ phosphorus} R{-}\underset{\underset{X}{|}}{CH}{-}COOH \quad (X = Cl, Br)$$

The reaction is known as **Hell-Volhard-Zelinsky** reaction.

▶ **Arndt-Eistert Reaction:** It is method of converting lower carboxylic acids to their higher homologues.

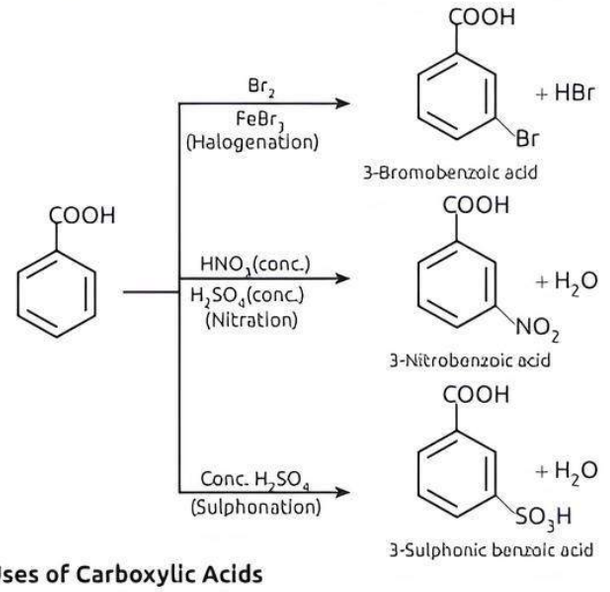
$$RCOOH \xrightarrow{PCl_5} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow{HOH} RCH_2COOH$$

Diazo ketone

▶ **Reducing Property:** Among carboxylic acids, formic acid is the only acid that acts as reducing agent. It reduces acidified $KMnO_4$ to $MnSO_4$, $HgCl_2$ to Hg, Tollens' reagent to silver mirror and Fehling's solution to red ppt. and itself gets oxidised to CO_2 and H_2O.

$$HCOOH + HgCl_2 \longrightarrow Hg + 2HCl + CO_2$$

▶ **Electrophilic Substitution Reactions of Aromatic Acids:**



▶ **Uses of Carboxylic Acids**

- Formic acid is used in leather tanning, textile dyeing and finishing.
- Acetic acid is used in the manufacture of rayon and in plastics, in rubber and silk industries, in cooking and in vinegar (a 8-10% solution of acetic acid).
- Benzoic acid and its salts are used as urinary antiseptics.
- Formic acid can act as a reducing agent.

Practice Exercise

Multiple Choice Questions

Q 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

Q 2. Which of the following does not reduce Fehling's solution?

a. CH_3COOH b. HCOOH
c. HCHO d. CH_3CHO

Q 3. What is IUPAC name of the ketone *A*, which undergoes iodoform reaction to give CH_3CH ⋯ $C(CH_3)COONa$ and yellow precipitate of CHI_3? *(CBSE SQP 2023-24)*

a. 3-Methylpent-3-en-2one
b. 3-Methylbut-2-en- one
c. 2, 3-Dimethylethanone
d. 3-Methylpent-4-one

Q 4. Which of the following reagents would one choose to transform CH_3COCl into acetone? *(CBSE 2023)*

a. $(CH_3)_2Cd$ b. CH_3MgBr
c. CH_3Cl d. $(CH_3O)_2Mg$

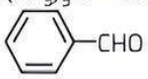
Q 5. The oxidation of toluene to benzaldehyde by chromyl chloride is called: *(CBSE SQP 2022-23)*

a. Etard reaction
b. Riemer-Tiemann reaction
c. Stephen's reaction
d. Cannizzaro's reaction

Q 6. Acetic acid reacts with hydrazoic acid at 0° in the presence of conc. H_2SO_4 to give:

a. methane b. methyl amine
c. methyl cyanide d. ethyl amine.

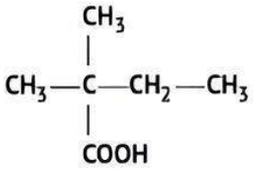
Q 7. Which of the following does not give Cannizzaro reaction? *(CBSE 2023)*

a. $(CH_3)_3C-CHO$ b. $(CH_3)_2CH-CHO$
c.  d. HCHO

Q 8. Aldehydes and ketones react with hydroxylamine to form: *(CBSE 2023)*

a. hydrazones b. cyanohydrins
c. semicarbazones d. oxime

Q 9. What is the correct IUPAC name of the given compound? *(CBSE 2020)*



a. 2, 2-dimethylbutanoic acid
b. 2-carboxyl-2-methylpropanoic acid
c. 2-ethyl-2-methylpropanoic acid
d. 3-methylbutane carboxylic acid

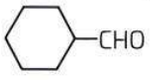
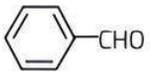
Q 10. Which of the following is most reactive in nucleophilic addition reactions? *(CBSE 2023)*

a. HCHO b. CH_3CHO
c. CH_3COCH_3 d. $CH_3COC_2H_5$

Q 11. The reagent that can be used to distinguish acetophenone and benzophenone is: *(CBSE 2023)*

a. 2, 4-dinitrophenyl hydrazine
b. aqueous $NaHSO_3$
c. Fehling solution
d. I_2 and NaOH

Q 12. Which of the following does not give aldol condensation reaction? *(CBSE 2023)*

a. CH_3–CHO
b. 
c. 
d. CH_3COCH_3

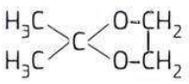
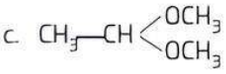
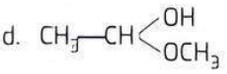
Q 13. Which of the following compounds will undergo self-condensation in the presence of dilute NaOH solution? *(CBSE 2023)*

a. C_6H_5CHO
b. CH_3CH_2CHO
c. $(CH_3)_3C-CHO$
d. $H-CHO$

Q 14. Which does not form iodoform on heating with I_2 and base?

a. Acetone
b. Ethanol
c. Methanol
d. Acetaldehyde.

Q 15. Which of the following is an 'Acetal'? *(CBSE 2023)*

a. $CH_3CH_2-OCH_3$
b. 
c. 
d. 

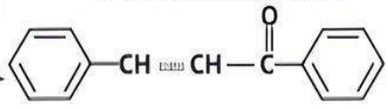
Q 16. $C_6H_5CHO + CH_3COCH_3 \xrightarrow[\Delta]{OH^-} C_6H_5CH=CH-COCH_3$,

This reaction is known as: *(CBSE 2023)*

a. Aldol condensation
b. Cross-Aldol condensation
c. Cannizzaro's reaction
d. Friedel-Crafts reaction.

Q 17. Which of the following tests/reactions is given by aldehydes as well as ketones? *(CBSE SQP 2022-23)*

a. Fehling's test
b. Tollen's test
c. 2, 4 DNP test
d. Cannizzaro reaction

Q 18. $A + B \xrightarrow{\text{dil. NaOH}}$ 

Identify *A* and *B*: *(CBSE SQP 2023-24)*

a. *A* = 1-phenylethanal, *B* = acetophenone
b. *A* = Benzophenone, *B* = formaldehyde
c. *A* = Benzaldehyde, *B* = Acetophenone
d. *A* = Benzophenone, *B* = Acetophenone

Assertion & Reason Type Questions

Directions (Q. Nos. 19-24): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

Q 19. Assertion (A): Benzoic acid is a weaker acid than formic acid.

Reason (R): Phenyl group destabilises the carboxylate anion due to conjugation.

Q 20. Assertion (A): Acetic acid does not undergo haloform reaction.

Reason (R): Acetic acid has no α-hydrogen atom.

Q 21. Assertion (A): Formic acid and acetic acid can be distinguished by Tollen's reagent.

Reason (R): Formic acid is a stronger acid than acetic acid.

Q 22. Assertion (A): Strong oxidising agents oxidise toluene and its derivatives to benzoic acids.

Reason (R): It is possible to stop the oxidation of toluene at the aldehyde stage with suitable reagents. *(CBSE SQP 2023-24)*

Q 23. Assertion (A): Nitration of benzoic acid gives meta nitrobenzoic acid.

Reason (R): Carboxyl group deactivates the ortho and para positions in the ring.

Q 24. Assertion (A): Carboxylic acids do not give characteristic reactions of carbonyl group.

Reason (R): The carbonyl group is sterically hindered in carboxylic acid.

Answers

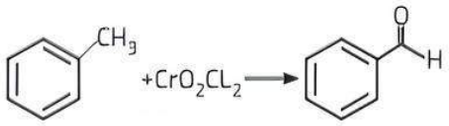
1. (b) Butan-2-ol **2.** (a) CH_3COOH

3. (a) 3-Methylpent -3-en-2-one

4. (a) $(CH_3)_2Cd$

5. (a) Etard reaction

Etard reaction involves the oxidation of aromatic methyl groups or heterocyclic bound methyl groups to an aldehyde using chromyl chloride. For example, toluene can be oxidized to benzaldehyde using the Etard reaction as shown:



6. (b) methyl amine

7. (b) Aldehydes that do not have an α-hydrogen atom undergo self-oxidation and reduction (disproportionation) reaction on heating with

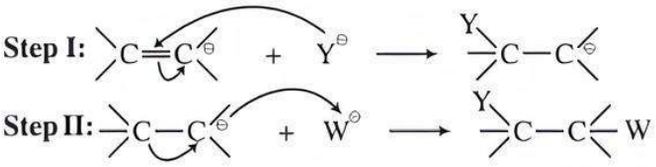
concentrated alkali. In $(CH_3)_2$ CH—CHO, alpha hydrogens are present. So, it does not undergo Cannizzaro reaction.

8. (d) Oxime
9. (a) 2, 2-dimethylbutanoic acid
10. (a) Reactivity towards nucleophilic addition reactions are influenced by the groups attached to carbonyl carbon. More electron-deficient this carbon, more is the reactivity. Presence of alkyl groups decrease the reactivity by decreasing the electron deficiency. Hence, HCHO is more reactive towards nucleophilic addition reactions.
11. (d) I_2 and NaOH are used to distinguish the two. On reacting with acetophenone, iodine molecules react with methyl groups and form methyl iodide leading to the formation of yellow precipitate which shows that the compound is acetophenone. On the other hand, if I_2 and NaOH reacts with benzophenone, then it will not give any precipitate because benzophenone has a ring that does not lead any precipitate.
12. (c) Benzaldehyde will not give aldol condensation reaction due to absence of α- H atom.
13. (b) CH_3CH_2CHO has α-hydrogen atom, hence it will undergo self-condensation in the presence of dil. NaOH solution.
14. (c) Methanol
15. (c) An acetal is an organic molecule where two separate oxygen atoms are single bonded to a central carbon atom. They have the general structure of $R_2C(OR')_2$.
16. (b) Cross-Aldol condensation
17. (c) 2, 4 DNP test
    Fehling's test, Tollen's test and Cannizzaro reaction are shown by alcohols only and not by aldehydes or ketones.
18. (c) A = Benzaldehyde, B = Acetophenone
    This is an example of crossed Aldol condensation.
19. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
20. (c) Acetic acid behaves as an acid in the presence of OH^- ions and does not create CHX_3 haloform. So, it does not undergo the haloform reaction. Hence, the assertion is true, but reason is false because the acetic acid has three alpha hydrogens.
21. (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
22. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
23. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
24. (c) Assertion (A) is true due to the lone pairs on oxygen atom attached to hydrogen atom in the —COOH group that are involved in resonance and hence making the carbon atom less electrophilic. So, carboxylic acids do not give characteristic reactions of carbonyl group.
    Reason (R) is false because the carbonyl group in carboxylic acid has both single and double bond characters due to resonance.

Case Study Based Questions

Case Study 1

Nucleophilic addition reactions are encountered in compounds having polar functional groups (C=O, C≡N, C=S). In the first step, a nucleophile with its pair of electrons attacks the carbon atom of a double or triple bond, forming a carbanion. It is followed by a second step in which this carbanion reacts with a positive species.



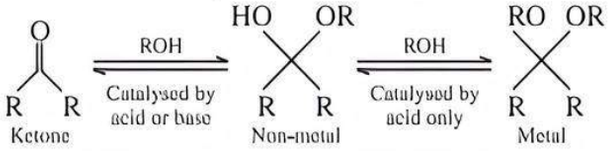
When the olefin contains a good leaving group (as defined for nucleophilic substitution), substitution is a side reaction. (*i.e.* a nucleophilic substitution at a vinylic substrate).

Addition of HCN to carbonyl group and addition of alcohol to carbonyl group is a nucleophilic addition reaction.

Addition of HCN to carbonyl group: In this reaction cyanide ion (CN^-) acts as a nucleophile which attacks the carbon of carbonyl group, the carbon-oxygen double bond breaks followed by capture of proton and a cyanohydrin is formed.

Addition of alcohol to carbonyl compounds:

Aldehydes and ketones react with one mole of alcohol to form hemiacetal or hemiketal, respectively. Reaction with second mole of alcohol gives acetal or ketal. In this reaction, the alcohol with lone pair of electrons of oxygen atom acts as a nucleophile.

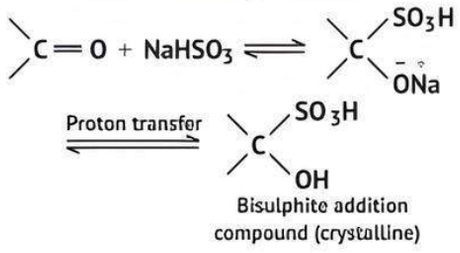


Read the given passage carefully and give the answer of the following questions:

Q 1. Identify the example in which both nucleophilic addition and nucleophilic addition elimination reaction occur respectively in the carbonyl compound.

a. Reduction to alcohols
b. Addition of sodium sulphide
c. Tollen's test
d. Reaction with alcohols

Q 2. Consider the following reaction:



Bisulphite addition compound (crystalline)

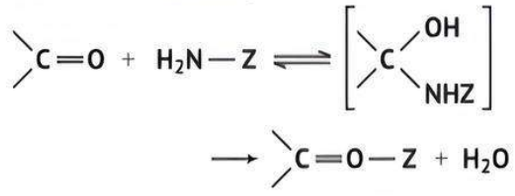
In the given reaction, equilibrium lies largely to the right hand side for most aldehydes and the left for most ketones due to:

a. electronic reasons b. steric reasons
c. bonding reasons d. Both a. and b.

Q 3. Which of the following alternative is correct for the treatment of ketones with ethylene glycol in the presence of dry HCl?

a. The product obtained is ethylene glycol hemi-ketal
b. In this reaction, electrophilicity of carbonyl carbon decreases
c. HCl protonates the oxygen of the carbonyl group
d. The product thus obtained is cyanohydrin

Q 4. Consider the following reaction:



Which of the following statements is/are true about the above reactions?

a. $H_2N - Z$ tends to add to the carbon of carbonyl group of aldehydes and ketones
b. The reaction is reversible and catalysed by acid
c. The equilibrium favours the product formation due to rapid dehydration of the intermediate
d. All of the above

Answers

1. (d) Reaction with alcohols
2. (b) steric reasons
3. (c) HCl protonates the oxygen of the carbonyl group
4. (c) The equilibrium favours the product formation due to rapid dehydration of the intermediate

Case Study 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 reactions 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.

Read the given passage carefully and give the answer of the following questions: *(CBSE 2023)*

Q 1. Write the name of the product when an aldehyde reacts with excess alcohol in presence of dry HCl.

Q 2. Why carboxylic acid is a stronger acid than phenol?

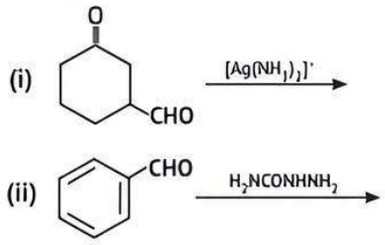
Q 3. (i) Arrange the following compounds in increasing order of their reactivity towards CH_3MgBr :

$CH_3CHO, (CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_3, CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

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

OR

Write the main product in the following:



Answers

1. An aldehyde react with excess alcohol in the presence of dry HCl to yield alkoxy alcohol intermediate known as hemiacetals which further reacts with one more molecule of alcohol to give a gem-dialkoxy compound known as acetal.
2. Carboxylic acid is a stronger acid than phenol because the negative charge in carboxylate anion is more spread out compared to the phenoxide ion as there are two electronegative O-atoms in carboxylic anion compared to one in phenoxide ion. In the resonance structures of carboxylate anion, the negative charge is present on the O-atoms while in resonance of phenoxide ion, negative charge is also present on electropositive carbon atom which leads to less stability of phenoxide ion than carboxylate anion.
3. (i) $CH_3CHO > CH_3-\overset{\overset{O}{\|}}{C}-CH_3 > (CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_3$

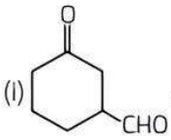
   Aldehydes are more reactive than ketones towards Grignard reagents due to less steric hindrance. Grignard reagents attack if the bulkiness is low.

   (ii) Propanal and propanone can be distinguished by the Tollen's test. Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But propanone being a ketone does not reduce Tollen's reagent.

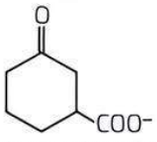
$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$
Propanal — Tollen's reagent

$$CH_3CH_2COO^- + Ag\downarrow + 4NH_3 + 2H_2O$$
Propanoate ion — Silver mirror

OR

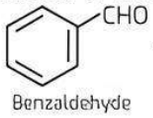
(i) 

$$\xrightarrow[3OH^-]{2(Ag(NH_3)_2)^+}$$



$$+2Ag + 4NH_3 + 2H_2O$$

The main product obtained is silver mirror due to the formation of silver metal.

(ii) 
Benzaldehyde

$$\xrightarrow{H_2NCONHNH_2}$$


Benzaldehyde semicarbazone

The main product obtained is Benzaldehyde semicarbazone.

Very Short Answer Type Questions

Q 1. Give a chemical test to differentiate between aldehyde and ketone.

Ans. On heating with Fehling's solution, aldehydes (acetaldehyde) give red precipitate of Cu_2O whereas ketones (acetone) give no reaction.

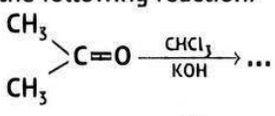
$$\underset{\text{acetaldehyde}}{CH_3CHO} + \underset{\text{Fehling Solution}}{2CuO} \xrightarrow{\Delta} \underset{\text{red ppt.}}{Cu_2O\downarrow} + CH_3COOH$$

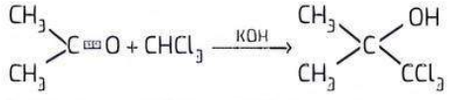
Q 2. Explain Schmidt reaction by giving example.

Ans. **Schmidt Reaction:** The reaction in which carboxylic acid reacts with hydrazoic acid in the presence of concentrated H_2SO_4 to give primary amine, is called Schmidt reaction. *e.g.*,

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Aniline}}{C_6H_5NH_2} + CO_2 + N_2$$

Q 3. Complete the following reaction.

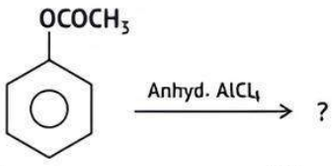


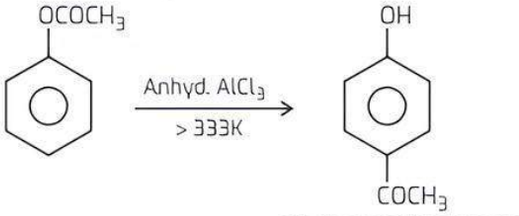
Ans. 

Q 4. Oxidation of CH_3—CHO is easier than CH_3COCH_3. Why? *(CBSE 2019)*

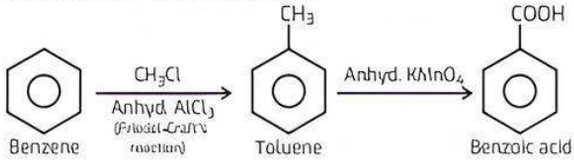
Ans. CH_3—CHO contains H atom on the carbonyl group but ketones like CH_3COCH_3 do not have it. Cleavage of C—H bond in CH_3CHO is easier than cleavage of C—C bond in $CH_3CO\,CH_3$. Hence, CH_3—CHO oxidises easily.

Q 5. Complete the following equation.

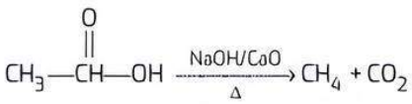


Ans. 
p-hydroxy acetophenone

Q 6. Write the chemical reaction of preparation of benzoic acid from benzene.

Ans. 
Benzene — Toluene — Benzoic acid

Q 7. Write the chemical equation for the decarboxylation reaction of an organic acid.

Ans. 

i.e., $CH_3COOH \xrightarrow{NaOH/CaO} \underset{\text{Sodium acetate}}{CH_3COONa}$

$$\xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$$

Q 8. Write the chemical equation of the reaction of formic acid with Tollen's reagent.

Ans. $HCOOH + \underset{\text{Tollen's reagent}}{Ag_2O} \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2\uparrow + H_2O$

Q 9. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Why? *(CBSE 2019)*

Ans. CH_3CHO is sterically hindered than CH_3CHO due to the presence of alkyl group on both sides on the carbonyl carbon, making them less reactive towards nucleophilic attack because both methyl groups have electron releasing tendency due to-*I* effect. These alkyl groups make ketone less reactive by donating an electron to a carbonyl group. Therefore, CH_3CHO is more reactive towards reaction with HCN.

Note: As +*I* effect increases, steric hindrance increases and hence reactivity decreases.

Q 10. *p*-nitrobenzoic acid has lower pK_a value than benzoic acid. Why? *(CBSE 2019)*

Ans. As *p*-nitrobenzoic acid contains —NO_2 group which is an electron withdrawing group resulting in higher acidity than benzoic acid. Greater is the acidic character, lower is the pK_a value. Thus, pK_a value of *p*-nitrobenzoic acid is lower than that of benzoic acid.

Q 11. How will you convert benzoic acid into benzene?

Ans. Benzoic acid can be converted into benzene by fusing with soda lime (NaOH/CaO).

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[\text{Fuse}]{NaOH} \underset{\text{Sod. benzoate}}{C_6H_5COONa} \xrightarrow[\text{Fuse}]{NaOH/CaO} \underset{\text{Benzene}}{C_6H_6}$$

Q 12. Complete the following reactions:

(i) $R-CH_2COOH \xrightarrow{X_2/\text{Red P}} ?$

(ii) $2CH_3COOH \xrightarrow{P_2O_5/\text{Heat}} ?$

Ans. (i) $\underset{\text{Carboxylic acid}}{R-CH_2COOH} \xrightarrow[\text{(HVZ reaction)}]{X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid}}{R-CH(X)COOH}$

(ii) $\underset{\text{Ethanoic acid}}{2CH_3COOH} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Ethanoic anhydride}}{(CH_3CO)_2O} + H_2O$

Q 13. How will you convert benzoic acid to benzaldehyde?

Ans. $\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[\text{Reduction}]{LiAlH_4/\text{ether}} \underset{\text{Benzal alcohol}}{C_6H_5CH_2OH} \xrightarrow[\text{Controlled oxidation}]{PCC} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

Q 14. Name the reagents used in the following reactions?

(i) $CH_3-CHO \xrightarrow{?} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(ii) $CH_3-COOH \xrightarrow{?} CH_3COCl$

Ans. (i) CH_3MgBr / H_3O^+, (ii) PCl_5 or PCl_3 or $SOCl_2$

Q 15. How will you convert:

(i) Acetic acid to methane

(ii) Benzoic acid to benzaldehyde.

Ans. (i) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow[\text{Heat}]{NaOH/CaO} \underset{\text{Methane}}{CH_4}$

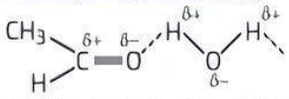
(ii) $\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow[BaSO_4]{H_2/Pd} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

Q 16. Arrange the following compounds in increasing order of acidic strength: 2, 4-dinitrobenzoic acid, 4-methoxybenzoic acid, 4- nitrobenzoic acid.

Ans. The increasing order of acidic strength is:
4-methoxybenzoic acid < 4-nitrobenzoic acid < 2, 4-dinitrobenzoic acid.

Q 17. Why is ethanal soluble in water?

Ans. Ethanal is soluble in water due to formation of intermolecular hydrogen bonding.



Q 18. Give a chemical test to distinguish between benzaldehyde and benzoic acid.

Ans. Benzoic acid gives a brisk effervescence with saturated $NaHCO_3$ solution but benzaldehyde fails to respond to this test.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + H_2O + \underset{\text{Brisk effervescence}}{CO_2}\uparrow$$

Q 19. Distinguish between the following:

(i) $CH_3-CO-CH_2CH_3$ **and** $CH_3-CH_2-CH_2-CHO$

(ii) Ethanal and ethanoic acid.

Ans. (i) $CH_3-CO-CH_2CH_3$ responds to iodoform reaction (gives yellow precipitate) while $CH_3-CH_2-CH_2-CHO$ fails to give.

(ii) Ethanoic acid gives a brisk effervescence with $NaHCO_3$ solution while ethanal fails to give.

Q 20. Write the structures of *A*, *B*, *C* and *D* in the following reactions:

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow{H_2/Pd\text{-}BaSO_4} [A] \xrightarrow{NaOH\ (conc.)} B + C$$

$$\xrightarrow{CH_3MgBr/H_3O^+} [D]$$

Ans. $\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow{H_2/Pd\text{-}BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaOH\ (conc.)}$

$$\underset{\text{Benzyl alcohol}}{\underset{(B)}{C_6H_5CH_2OH}} + \underset{\text{Sod. benzoate}}{\underset{(C)}{C_6H_5COONa}} \xrightarrow{CH_3MgBr/H_3O^+} \underset{\text{2-Phenylethanol}}{\underset{(D)}{C_6H_5CH(OH)CH_3}}$$

Q 21. How will you convert propanone to propene?

Ans. $\underset{\text{Propanone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-CH(OH)-CH_3}$

$$\xrightarrow[443K]{H_2SO_4\ (conc.)} \underset{\text{Propene}}{CH_3CH=CH_2}$$

Q 22. Predict the product of reaction:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \xrightarrow{HCN} ?$$

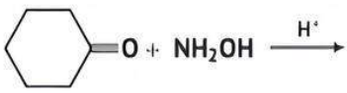
Ans. $\underset{\text{Propanone}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O} + HCN \longrightarrow \underset{\text{Propanone cyanohydrin}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CN}$

Q 23. How will you convert benzoyl chloride into benzaldehyde?

Ans. It can be done with Rosenmund's reduction (H_2 in the presence of $Pd/BaSO_4$)

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow{(Pd/BaSO_4)} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

Q 24. Write the products of the following reactions:

(i) 

(ii) $2C_6H_5CHO + NaOH\ (conc.) \longrightarrow$

Ans. (i) 

(ii) $C_6H_5CH_2OH$ (benzyl alcohol),
C_6H_5COONa (sodium benzoate).

Q 25. Out of $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$ which gives iodoform test?

Ans. $CH_3CH_2CH_2COCH_3$ is a 2-methylketone. It gives iodoform test.

Q 26. Why does not $(CH_3)_3CCHO$ undergo aldol condensation?

Ans. $(CH_3)_3CCHO$ does not undergo aldol condensation due to absence of α-hydrogen atom.

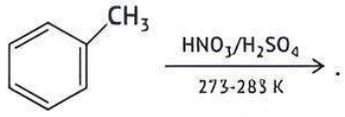
Q 27. How will you convert propanone to propan-2-ol?

Ans. $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2 \xrightarrow{Pb/BaSO_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$

Propanone → Propan-2-ol

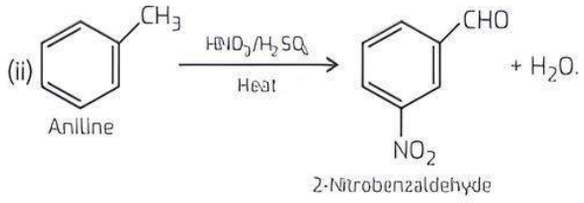
Q 28. Complete the following reactions:

(i) $2H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{conc. KOH}}$

(ii)  $\xrightarrow[273\text{-}283\ K]{HNO_3/H_2SO_4}$.

Ans. (i) $2H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}} CH_3OH + HCOOK$

Methyl alcohol; Pot. formate

(ii) 

Aniline → 2-Nitrobenzaldehyde

Q 29. Complete the following:

$$2CH_3CHO \xrightarrow{\text{Dil. NaOH}} A \xrightarrow[-H_2O]{\text{heat}} B$$

Ans. $2CH_3CHO \xrightarrow[\text{Aldol Condensation}]{\text{Dil. NaOH}} CH_3CH(OH)CH_2CHO$

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

But-2-one

Q 30. Give the names of the reagents which can bring about the following conversions:

(i) Propan-1-ol to propanal.

(ii) Pent-3-en-2-ol to pen-3-en-2-one.

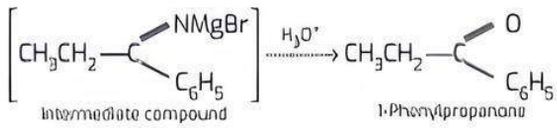
Ans. (i) Pyridine chlorochromate (P.C.C.)

(ii) Pyridine chlorochromate (P.C.C.)

Q 31. How will you convert ethyl cyanide to 1-phenylpropanone?

Ans. $CH_3CH_2C\equiv N + C_6H_5MgBr \xrightarrow{\text{Anhyd. ether}}$

Ethyl cyanide; Phenyl mag. bromide



Intermediate compound → 1-Phenylpropanone

Q 32. Give a simple test to distinguish between:

(i) Pentan-2-one and pentan-3-one

(ii) Benzaldehyde and acetophenone.

Ans. (i) Pentan-2-one is a methyl ketone. It gives iodoform test (yellow ppt.) but pentan-3-one does not respond to this test since it is not a methyl ketone.

(ii) Acetophenone ($C_6H_5COCH_3$) being a methyl ketone responds to iodoform test (yellow ppt.) but benzaldehyde (C_6H_5CHO) does not give this test.

Q 33. How would you prepare but-2-enal from ethanal?

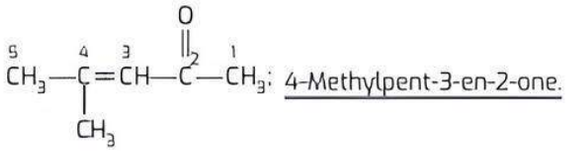
Ans. $CH_3CHO + HCH_2CHO \longrightarrow CH_3CH(OH)CH_2CHO$

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

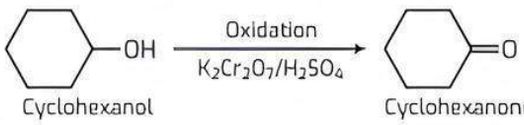
but-2-enal (Crotonaldehyde)

Q 34. Give IUPAC name of the organic compound:

$(CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-CH_3$.

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

Q 35. How will you convert cyclohexanol to cyclohexanone?

Ans. 

Cyclohexanol → Cyclohexanone

Q 36. Name the reagent that can be used to convert:

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol.

Ans. (i) Pyridinium chlorochromate (PCC).

(ii) $LiAlH_4$ or H_2 in the presence of nickel catalyst (catalytic hydrogenation)

Q 37. Complete the following:

(i) $CH_3COCH_3 + HI \xrightarrow{\text{Red P/423 K}}$

(ii) $CH_3\equiv CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2}$

Ans. (i) $CH_3COCH_3 + 4HI \xrightarrow{\text{Red P/423 K}} CH_3CH_2CH_3 + H_2O + 2I_2$

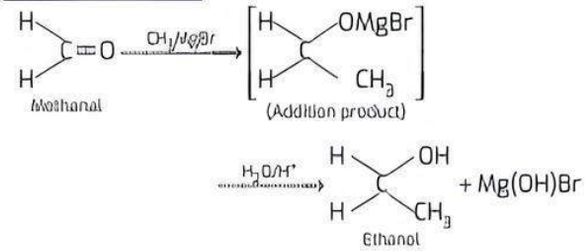
Propanone → Propane

(ii) $CH_2=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + 2HCl + Pd$

Ethene → Ethanal

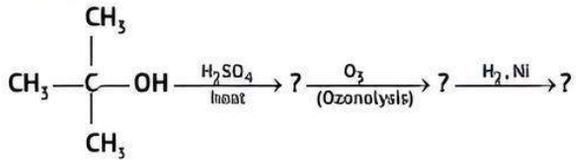
Q 38. What happens when methanal is treated with methyl magnesium bromide and then hydrolysed?

Ans. Ethanol is formed.

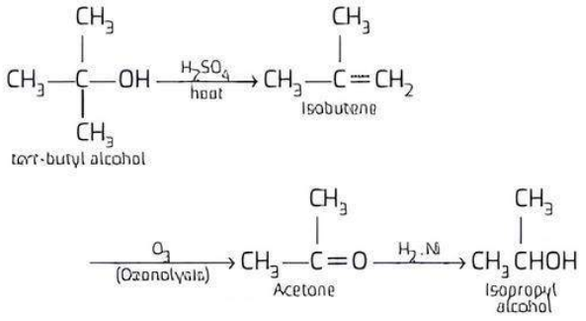


Methanal → (Addition product) → Ethanol

Q 39. Complete the following:

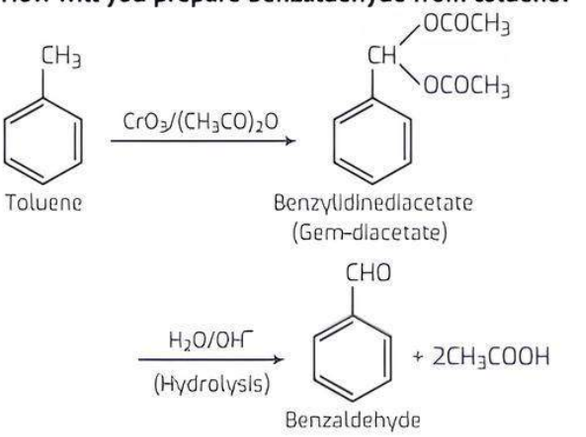


Ans.



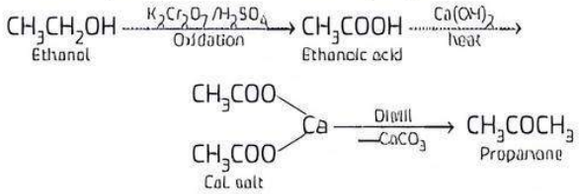
Q 40. How will you prepare benzaldehyde from toluene?

Ans.



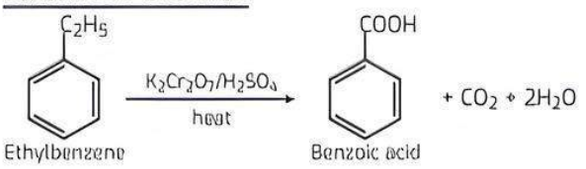
Q 41. How will you convert ethanol to propanone?

Ans.



Q 42. What happens when ethylbenzene is heated with acidified $K_2Cr_2O_7$?

Ans. Benzoic acid is formed.

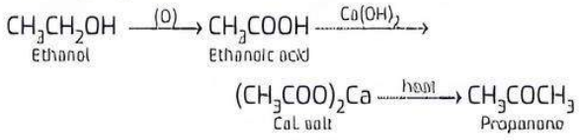


Q 43. How will you prepare ethylamine from acetaldehyde?

Ans.

Q 44. How is propanone obtained from ethanol?

Ans.



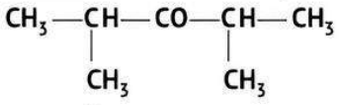
Q 45. Give a chemical test to distinguish between benzaldehyde and acetone.

Ans. Acetone (CH_3COCH_3), being a methyl ketone, gives a positive iodoform test (forms yellow precipitate) but benzaldehyde does not respond to this test.

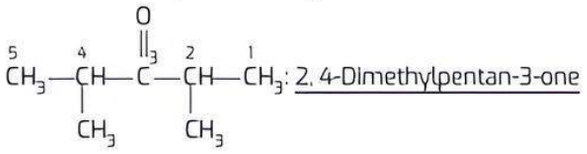
Q 46. Give a chemical test to distinguish between ethanal and propanal. *(CBSE 2013)*

Ans. This distinction can be done by iodoform test which is given by ethanal and not by propanal.

Q 47. Write IUPAC name of the compound

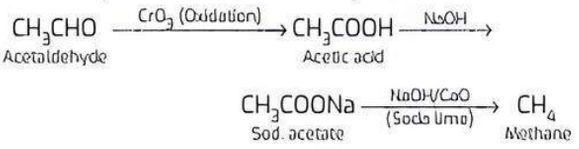


Ans.



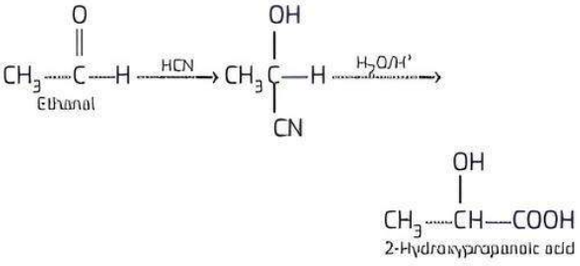
Q 48. How will you convert acetaldehyde into methane?

Ans.



Q 49. How will you convert ethanal to 2-hydroxypropanoic acid?

Ans.



Short Answer Type-I Questions

Q 1. Arrange the following compounds in increasing order of their boiling points. *(NCERT INTEXT)*

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans. Molar mass of the given compounds are in the range of 44 to 46. CH_3CH_2OH exhibits extensive hydrogen bonding and exists as aggregate molecule. Thus, among the given compounds, boiling point is highest for CH_3CH_2OH (ethanol). CH_3CHO is more polar than CH_3OCH_3. Consequently, the dipole-dipole interactions will be more in CH_3CHO as compared to CH_3OCH_3 and $CH_3CH_2CH_3$ (which have weak van der Waals' forces of attraction). Thus, the given compounds can be arranged in the increasing order of their boiling points in the following manner.

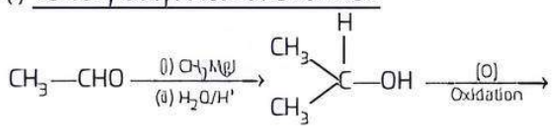
$CH_3—CH_2—CH_3 < CH_3—O—CH_3 < CH_3—CHO < CH_3CH_2OH$

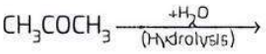
Q 2. What happens when:

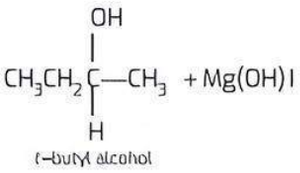
(i) Propanone is treated with methylmagnesium iodide and then hydrolysed, and

(ii) Benzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$? *(CBSE 2020)*

Ans. (i) Tertiary butyl alcohol is formed.







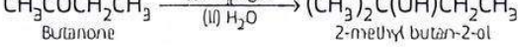
(ii) Acetophenone is formed.

Q 3. What happens when:

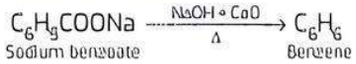
(i) Butanone is treated with methylmagnesium bromide and then hydrolysed and

(ii) Sodium benzoate is heated with soda lime. *(CBSE 2020)*

Ans. (i) 2-methylbutan-2-ol is formed.



(ii) Benzene is formed.

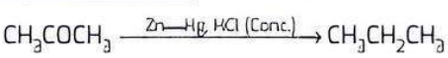


Q 4. What happens when:

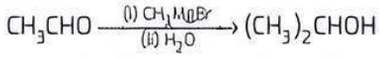
(i) Acetone is treated with Zn(Hg)/Conc. HCl and

(ii) Ethanal is treated with methylmagnesium bromide and then hydrolysed? *(CBSE 2020)*

Ans. (i) Propane is formed.

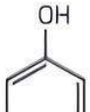


(ii) Propan-2-ol or Isopropyl alcohol is formed.



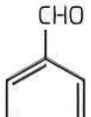
Q 5. An aromatic compound '*A*' on treatment with $CHCl_3$ and KOH gives two compounds, both of which give same product '*B*' when distilled with zinc dust. Oxidation of '*B*' gives '*C*' with molecular formula $C_7H_6O_2$. Sodium salt of '*C*' on heating with soda lime gives '*D*' which may also be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

Ans. *A* =



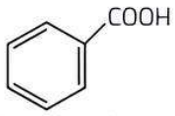
Phenol

B =



Benzaldehyde

C =



Benzoic acid

D =

Benzene

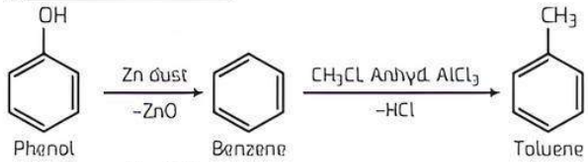
COMMON ERROR

While finding the final product, students write complete reaction and make mistakes.

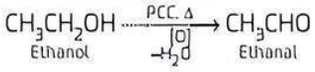
Q 6. How do you convert the following:

(i) Phenol to Toluene (ii) Ethanol to Ethanal *(CBSE 2019)*

Ans. (i) Phenol to Toluene:

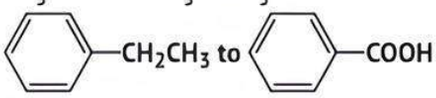


(ii) Ethanol to Ethanal :



Q 7. Do the following conversions in not more than two steps: *(CBSE 2023)*

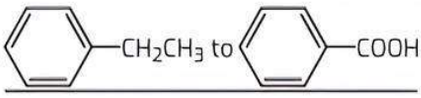
(i) CH_3COOH to CH_3COCH_3

(ii) 

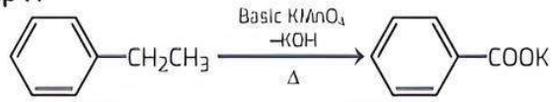
Ans. (i) CH_3COOH to CH_3COCH_3

Step 1: $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$

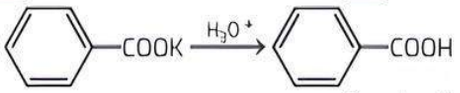
Step 2: $(CH_3COO)_2Ca \xrightarrow[\text{distillation}]{\text{Dry}} CH_3COCH_3$

(ii) 

Step 1 :



Step 2 :



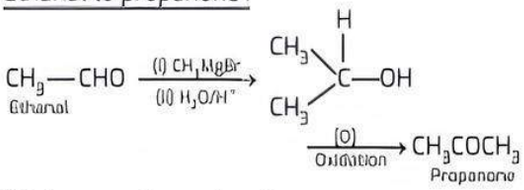
Benzoic acid

Q 8. How do you convert the following?

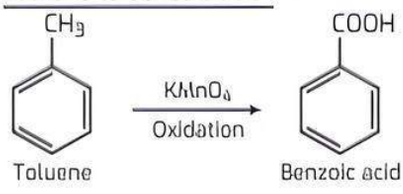
(i) Ethanal to propanone

(ii) Toluene to Benzoic acid

Ans. (i) Ethanal to propanone :



(ii) Toluene to benzoic acid :



Note: Aniline does not undergo Friedel-Craft reaction as it forms salt with $AlCl_3$, which is used as catalyst.

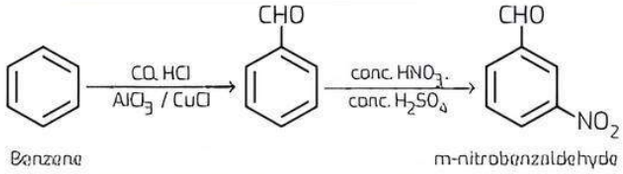
Q 9. Convert the following:

(i) Benzene to *m*-nitrobenzaldehyde

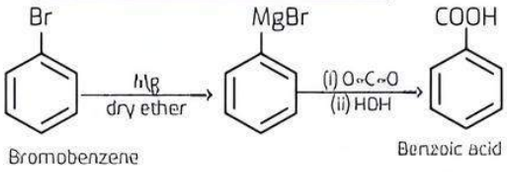
(ii) Bromobenzene to benzoic acid

(CBSE SQP 2023-24)

Ans. (i) Benzene to m-nitrobenzaldehyde



(ii) Bromobenzene to benzoic acid :



Q 10. Write the reaction and IUPAC name of the product formed when 2-Methylpropanal (isobutyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis. *(CBSE SQP 2022-23)*

Ans. When 2-Methylpropanal (Isobutyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis, the following reactions occur:

$$(CH_3)_2CHCHO + C_2H_5MgBr \xrightarrow{\text{dry ether}} (CH_3)_2CHCH(C_2H_5)(OMgBr)$$

$$(CH_3)_2CHCH(C_2H_5)(OMgBr) \xrightarrow{H^+/H_2O} (CH_3)_2CHCH(C_2H_5)(OH)$$

The IUPAC name of the product formed is 2-Methylpentan-3-ol.

Q 11. Account for the following:

(i) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(ii) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. *(CBSE 2018)*

Ans. (i) Due to presence of strong —COOH group, aromatic carboxylic acid does not undergo Friedel-Craft reaction.

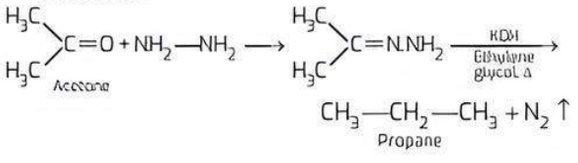
(ii) More is the value of pK_a, lower the acidic nature of carboxylic acid and *vice-versa*. The groups which show-I effect, if present in benzoic acid are stronger acids than that show +*I* effect or has no group. As nitro group (—NO_2) show –*I* effect, thus it has lower pK_a value than that of benzoic acid.

Q 12. Write the equations involved in the following reactions:

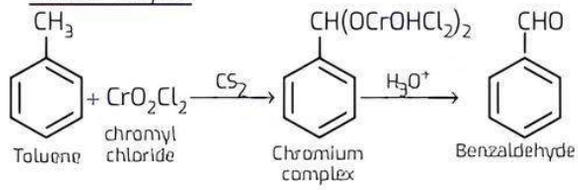
(i) Wolff-Kishner Reduction

(ii) Etard Reaction *(CBSE 2017)*

Ans. **(i) Wolff-Kishner Reduction:** The carbonyl group of aldehydes and ketones is reduced to —CH_2 group on treatment with hydrazine followed by heating with KOH in high boiling solvent like ethylene glycol. This reaction is known as Wolff-Kishner reduction.



(ii) Etard Reaction: Toluene reacts with chromyl chloride in presence of CS_2 followed by hydrolysis to produce Benzaldehyde.



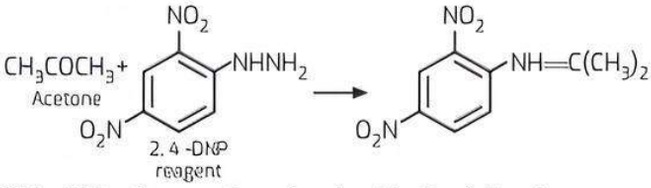
Q 13. (i) Out of *p*-tolualdehyde and *p*-nitrobenzaldehyde, which one is more reactive towards nucleophilic addition reactions, why?

(ii) Write the structure of the product formed when acetone reacts with 2,4 -DNP reagent.

(CBSE SQP 2023-24)

Ans. (i) *p*-nitrobenzaldehyde is more reactive towards the nucleophilic addition reaction than *p*-tolualdehyde as nitro group is electron withdrawing in nature. Presence of nitro group decrease electron density, hence facilitates the attack of nucleophile. Presence of —CH_3 leads to +*I* effect as —CH_3 is electron releasing group.

(ii)



Q 14. Write the reactions involved in the following:

(i) Hell-Volhard Zelinsky reaction

(ii) Decarboxylation reaction *(CBSE 2017)*

Ans. **(i) Hell-Volhard Zelinsky reaction:** Carboxylic acids having α-hydrogen atom are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. This reaction is known as Hell-Volhard Zelinsky reaction.

$$R—CH_2—COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2,\ Red\ P} R—\underset{\underset{X}{|}}{CH}—COOH$$

α-halocarboxylic acid (X = Cl, Br)

(ii) Decarboxylation: It refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salt is heated with sodalime.

$$CH_3COONa \xrightarrow[\text{mixture of NaOH and CaO)}]{\text{Sodalime (3 : 1 ratio}} CH_4 + Na_2CO_3$$

Sodium ethanoate — Methane

Q 15. Write the reactions involved in the following reactions:

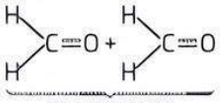
(i) Clemmensen reduction

(ii) Cannizzaro reaction *(CBSE 2017)*

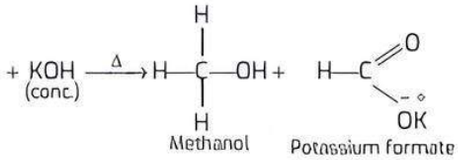
Ans. (i) Clemmensen reduction: The carbonyl group of aldehydes and ketones is reduced to $-CH_2$ group on treatment with zinc-amalgam and concentrated hydrochloric acid. This reaction is known as Clemmensen reaction.

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} -CH_2 + H_2O$$

(ii) Cannizzaro reaction: Aldehydes which do not have α-hydrogen atom undergo self oxidation reaction on treatment with conc. alkali. This reaction is known as Cannizzaro reaction.



Formaldehyde



Methanol Potassium formate

Q 16. Give reasons:

(i) *p*-Nitrobenzoic acid has higher K_a value than benzoic acid.

(ii) Acetone is soluble in water but benzophenone is not.

Ans. (i) In *p*-Nitrobenzoic acid, $-NO_2$ group present at para position in the ring is an electron withdrawing group. Under its influence, the release of H^+ ion from the acid becomes easier as compared to benzoic acid in which no such group is present. Therefore, K_a value of *p*-nitrobenzoic acid is more (3.6×10^{-4}) as compared to benzoic acid (6.3×10^{-5}).

(ii) Acetone (CH_3COCH_3) is soluble in water to small extent due to the presence of polar carbonyl group which is involved in hydrogen bonding with H_2O *i.e.*, molecules of water. Benzophenone ($C_6H_5COC_6H_5$) has two phenyl groups which are quite big in size. They try to mask the polar carbonyl group to a large extent. As a result, hydrogen bonding is negligible and therefore, benzophenone does not dissolve in water.

Q 17. Give reasons:

(i) Formic acid is stronger acid than acetic acid.

(ii) Alpha (α)-Hydrogens of aldehydes and ketones are acidic. *(CBSE 2023)*

Ans. (i) Acetic acid has the presence of methyl group ($-CH_3$ group) which is electron releasing in nature and hence electron density increases on oxygen atom of O—H bond. This makes the removal of H^+ ions difficult. But formic acid has no such case due to which it is a stronger acid than acetic acid.

(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. Thus, α-hydrogens of aldehydes and ketones are acidic.

Q 18. Complete each synthesis of filling the missing starting materials, reagents or products (*X*, *Y*)

(i) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{NaOH} X$

(ii) $CH_3CH_2CH_2CH_2OH \longrightarrow Y$

Ans. (i) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{NaOH}$

$CH_3COONa + C_6H_5CH_2OH$

Benzyl alcohol

(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow{KMnO_4\ (Y)} CH_3CH_2CH_2COOH$

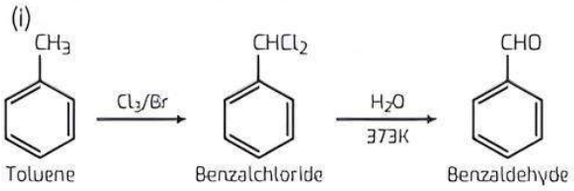
Butan-1-ol Butanoic acid

Q 19. How will you bring about the following conversion in not more than two steps ?

(i) Toluene to Benzaldehyde

(ii) Ethyl cyanide to 1-Phenylpropanone.

Ans. (i)



Toluene Benzalchloride Benzaldehyde

(ii) $CH_3CH_2C{\equiv}H \xrightarrow{PhMgBr} \left[CH_3CH_2-\underset{Ph}{\underset{|}{C}}=NMgBr\right] \xrightarrow{H_2O/H^+} CH_3CH_2-\underset{Ph}{\underset{|}{C}}=O$

Ethyl cyanide 1-Phenylpropanone

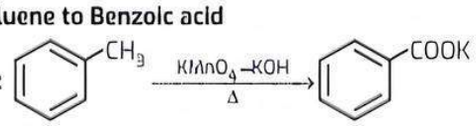
Q 20. Do the following conversions in not more than two steps:

(i) Toluene to Benzoic acid

(ii) Benzaldehyde to 1-Phenylethanol *(CBSE 2023)*

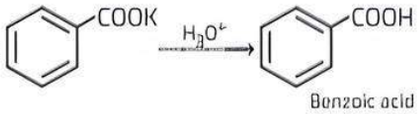
Ans. (i) Toluene to Benzoic acid

Step 1:



Toluene

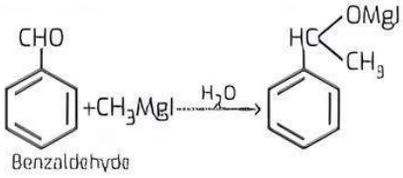
Step 2:



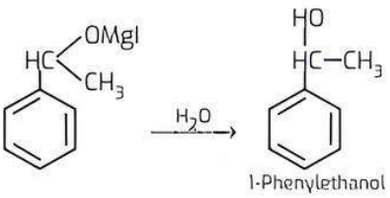
Benzoic acid

(ii) Benzaldehyde to 1-Phenylethanol

Step 1:



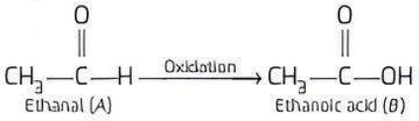
Benzaldehyde

Step 2: 

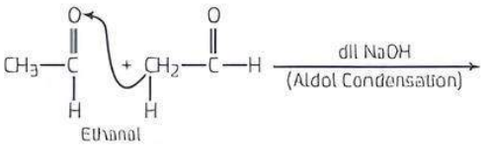
1-Phenylethanol

Q 21. A compound (*A*) on oxidation gives *B* ($C_2H_4O_2$), (*A*) reacts with dil. NaOH and on subsequent heating forms (*C*). The compound (*C*) on catalytic hydrogenation gives (D). Identify *A*, *B*, *C*, *D* and write down the reaction involved.

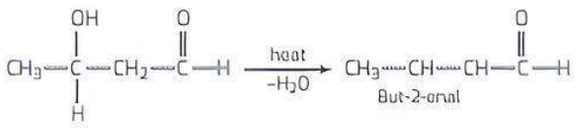
Ans. Since the compound (*A*) upon oxidation gives the compound *B* ($C_2H_4O_2$), it is accepted to be an aldehyde with the formula, C_2H_4O. It is ethanal. The reactions involved are given:



Ethanal (*A*) Ethanoic acid (*B*)



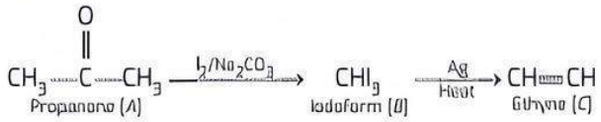
Ethanal



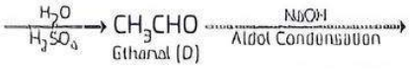
3-Hydroxybutanal But-2-enal

Q 22. An organic compound [*A*], whose molecular formula is C_3H_6O, gives iodoform reaction and forms compound [*B*]. Compound [*B*], when heated with silver powder, converts into compound [*C*]. Compound [*C*] reacts with dil. sulphuric acid and mercuric sulphate to obtain compound [*D*], which gives Aldol condensation reaction. Write down the names of all compounds from [*A*] to [*D*] and also write the chemical equations for each step.

Ans. The compound [*A*] can be either an aldehyde or a ketone. Since it gives iodoform test, it is a methylketone and is propanone. As a result of iodoform reaction, the compound [*A*] gives iodoform [*B*]. When heated with silver powder, iodoform changes into ethyne [*C*]. Ethyne upon hydration in the acidic conditions gives ethanal [*D*] which responds to Aldol condensation. The chemical reactions involved are listed.



Propanone (*A*) Iodoform (*B*) Ethyne (*C*)



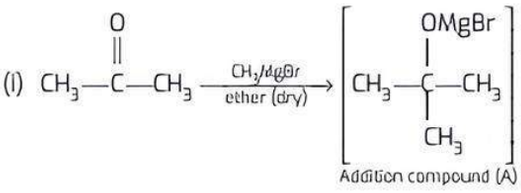
Ethanal (D)

$CH_3CH(OH)CH_2CHO$
3-Hydroxybutanal

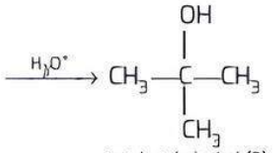
Q 23. Complete the following reactions:

(i) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow[\text{ether (dry)}]{CH_3MgBr} A \xrightarrow{H_3O^+} B$

(ii) $CH_3—CH_2—CH_2—CHO \xrightarrow{Ni/H_2} A$

Ans. (i) 

Addition compound (A)

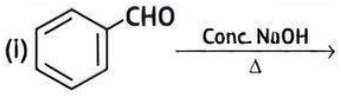


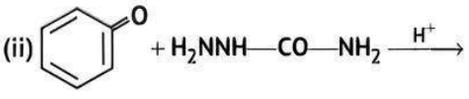
tert-butyl alcohol (B)

(ii) $CH_3—CH_2—CH_2—CHO \xrightarrow{Ni/H_2}$
Butanal

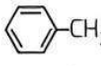
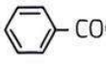
$CH_3CH_2—CH_2—CH_2OH$
Butan-1-ol (A)

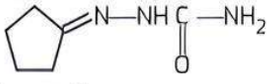
Q 24. Write the products of the following reactions:

(I) 

(ii) 

(CBSE 2023)

Ans. (i) The products obtained are  (Benzyl alcohol) and  (Sodium benzoate).

(ii) The product obtained is 

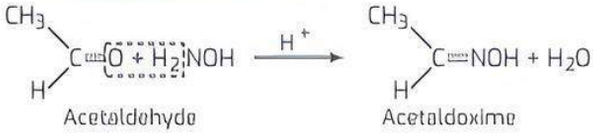
(cyclopentanone semicarbazone).

Q 25. What happens when:

(I) Acetaldehyde reacts with NH_2OH?

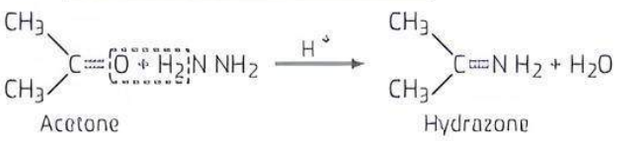
(ii) Acetone reacts with $NH_2—NH_2$?

Ans. (I) Acetaldoxime is formed.



Acetaldehyde Acetaldoxime

(II) Hydrazone of acetone is formed.



Acetone Hydrazone

Q 26. How will you convert 2-Methylpent-2-enal to:

(i) 2-Methylpentane

(ii) 2-Methylpentanal?

Ans. (i) $CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CHO \xrightarrow[\text{Reduction}]{\text{Wolff-Kishner}}$ 2-Methylpent-2-enal

$CH_3CH_2CH{=}CH_2 \xrightarrow{H_2/Pt} CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}H{-}CH_3$ 2-Methylpentane

(ii) $CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CHO \xrightarrow[HCl]{CH_3OH} CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}H(OCH_3)_2$ 2-Methylpent-2-enal

$\xrightarrow{H_2/Pt} CH_3CH_2CH\overset{CH_3}{\overset{|}{C}}H(OCH_3)_2$

$\xrightarrow[\text{(Hydrolysis)}]{HCl, H_2O} CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCHO$ 2-Methylpentanal

Q 27. Give reasons to support the answer:

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

(ii) 3-Hydroxy pentan-2-one shows positive test to Tollen's reagent. *(CBSE SQP 2022 Term-2)*

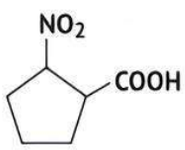
Ans. (i) The alpha hydrogen atoms are acidic in nature due to presence of electron withdrawing carbonyl group. These can be easily removed by a base and the carbanion formed is resonance stabilised.

(ii) Tollen's reagent is a weak oxidising agent not capable of breaking the C—C bond in Ketones. Thus, ketones cannot be oxidised using Tollen's reagent which itself gets reduced to Ag.

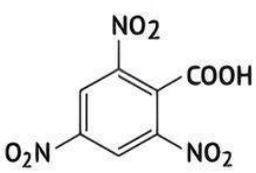
Q 28. Give the IUPAC name of the following compounds:

(i) $C_6H_5CH_2CH_2COOH$ **(ii)** $(CH_3)_2C{=}CH\,COOH$

(iii)



(iv)

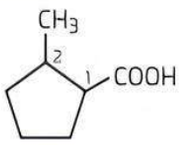


(NCERT INTEXT)

Ans. (i) $C_6H_5\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$ 3-Phenylpropanoic acid

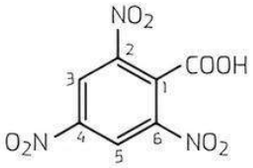
(ii) $\overset{4}{C}H_3-\overset{3}{\overset{|}{\underset{CH_3}{C}}}=\overset{2}{C}H-\overset{1}{C}OOH$ 3-Methylbut-2-enoic acid

(iii)



2-Methylcyclopentanecarboxylic acid

(iv)



2, 4, 6-Trinitrobenzoic acid

Q 29. Write the chemical equations for the following conversion (in not more than 2 steps)

(i) Acetaldehyde to butane-1, 3-diol

(ii) Acetone to propene

Ans. (i) Acetaldehyde to butane-1, 3-diol

$CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{NaOH} CH_3-\underset{OH}{\underset{|}{C}}HCH_2CHO$

Acetaldehyde — Acetaldol

$\xrightarrow[\text{(reduction)}]{LiAlH_4} CH_3-\underset{OH}{\underset{|}{C}}H-CH_2-\underset{OH}{\underset{|}{C}}H_2$

Butane-1,3-diol

(ii) Acetone to Propene

$CH_3COCH_3 \xrightarrow[\text{(reduction)}]{NaOH} CH_3-\underset{OH}{\underset{|}{C}}H-CH_3$

Acetone — Sec-propyl alcohol

$\xrightarrow[\text{heat}]{H_2SO_4\,(Conc.)} CH_3-CH{=}CH_2$

Propene

Q 30. 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 Term-2)*

Ans. (i) No, benzoic acid does not undergo Friedel-Craft reaction because the carboxylic group is deactivating and the Lewis acid catalyst and carboxylic groups are bonded.

(ii) Oxidation of aldehyde is easier than ketone due to presence of H-atoms linked to carbonyl group carbon which is absent in ketones.

Q 31. Arrange the following in the increasing order of their property indicated:

(i) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)

(ii) 4-Nitrobenzoic acid, benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxy benzoic acid (Acid strength) *(CBSE 2022 Term-2)*

Ans. (i) The +I effect of the alkyl group increases in the order:

Ethanal < Propanal < Propanone < Butanone.

(ii) The strength of the given acid increases as:

4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

Q 32. Explain the following reactions:

(i) Wolff-Kishner reduction

(ii) Cannizzaro reaction *(CBSE 2022 Term-2)*

Ans. (i) Wolff-Kishner reduction is an indirect reduction of an aldehyde or ketone to the corresponding hydrocarbon due to the effect of heat on the hydrazone or semicarbazone derivative with an alcoholic solution of sodium ethoxide or with solid potassium hydroxide.

(ii) As per the definition, the Cannizzaro reaction involves the reaction of aldehydes with caustic alkali in which one molecule of aldehyde is reduced to the corresponding alcohol and another molecule is oxidised to the salt of the corresponding acid.

Q 33. Show how each of the following compound can be converted into benzoic acid?

(i) Ethylbenzene (ii) Acetophenone

(iii) Bromobenzene (iv) Phenylethene (Styrene)

(NCERT INTEXT)

Ans. (i) $C_6H_5CH_2CH_3$ (Ethylbenzene) $\xrightarrow[\text{heat}]{KMnO_4/OH^-}$ C_6H_5COOK (Pot. benzoate) $\xrightarrow{H_3O^+}$ C_6H_5COOH (Benzoic acid)

(ii) $C_6H_5COCH_3$ (Acetophenone) $\xrightarrow[\text{(Iodoform reaction)}]{I_2/NaOH}$ C_6H_5COOK (Pot. benzoate) $\xrightarrow{H_3O^+}$ C_6H_5COOH (Benzoic acid)

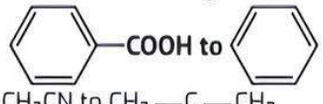
(iii) C_6H_5Br (Bromobenzene) $\xrightarrow[\text{(dry ether)}]{Mg}$ C_6H_5MgBr (Phenyl mag. bromide) $\xrightarrow{C=O}$ $C_6H_5C(=O)OMgBr$ (Addition compound) $\xrightarrow{H_3O/H^+}$ C_6H_5COOH (Benzoic acid)

(iv) $C_6H_5CH=CH_2$ (Styrene) $\xrightarrow[\text{heat}]{KMnO_4/OH^-}$ C_6H_5COOK (Pot. benzoate) + $HCOOK$ (Pot. formate)

C_6H_5COOK (Pot. Benzoate) $\xrightarrow{H_3O^+}$ C_6H_5COOH (Benzoic acid) + $HCOOH$ (Formic acid)

Q 34. Do the following conversions in not more than two steps : *(CBSE 2023)*

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

(ii)  to

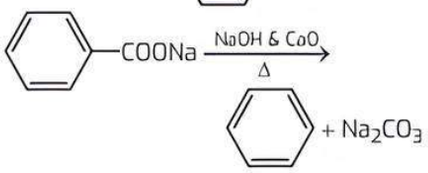
Ans. (i) CH_3CN to $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Step 1: $CH_3CN + CH_3MgBr \xrightarrow{\text{ether}} CH_3-C(=NMgBr)-CH_3$

Step 2: $CH_3-C(=NMgBr)-CH_3 \xrightarrow{H_2O} CH_3-C(=O)-CH_3$

(ii)  to

Step 1: 

Step 2: 

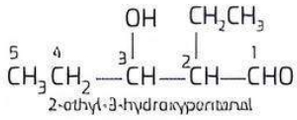
Short Answer Type-II Questions

Q 1. Write structural formulae 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.

(NCERT EXERCISE)

Ans. (i) Propanal as electrophile and butanal as nucleophile:

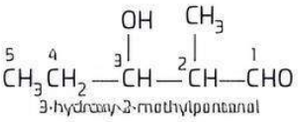
CH_3CH_2CHO (Propanal) + $CH_3CH_2CH_2CHO$ (Butanal) $\longrightarrow$



2-ethyl-3-hydroxypentanal

(ii) Propanal as electrophile as well as nucleophile:

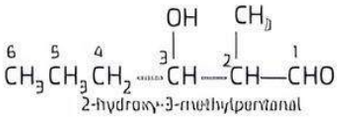
CH_3CH_2CHO (Propanal) + $CH_3CH_2CH_2CHO$ (Butanal) $\longrightarrow$



3-hydroxy-2-methylpentanal

(iii) Propanal as nucleophile and butanal as electrophile:

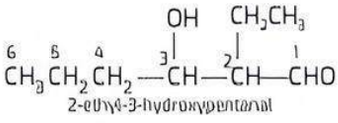
CH_3CH_2CHO (Propanal) + $CH_3CH_2CH_2CHO$ (Butanal) $\longrightarrow$



2-hydroxy-3-methylpentanal

(iv) Butanal as electrophile as well as nucleophile:

$CH_3CH_2CH_2CHO$ (Butanal) + $CH_3CH_2CH_2CHO$ (Butanal) $\longrightarrow$



2-ethyl-3-hydroxypentanal

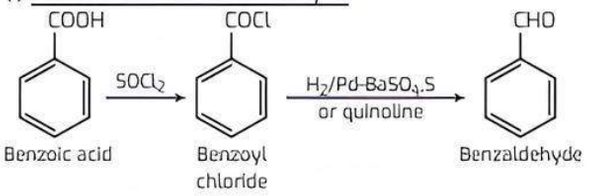
Q 2. Do the following conversions in not more than two steps:

(i) Benzoic acid to Benzaldehyde

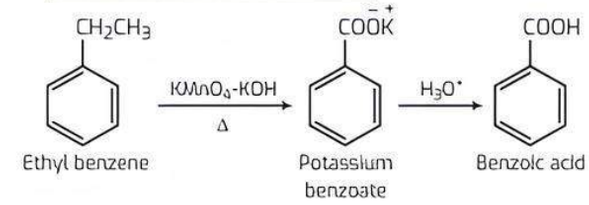
(ii) Ethyl benzene to Benzoic acid

(iii) Propane to Propene *(CBSE 2017)*

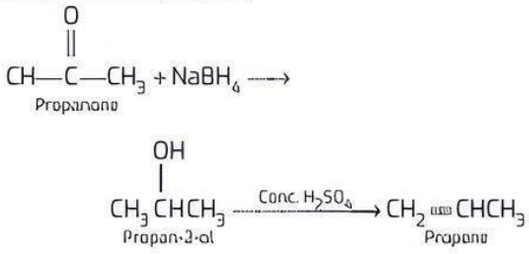
Ans. (i) Benzoic acid to benzaldehyde



(ii) Ethyl benzene to benzoic acid



(iii) Propanone to propene

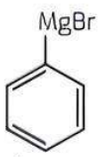


Q 3. Write structure of compound *A*, *B* and *C* in each of the following reactions:

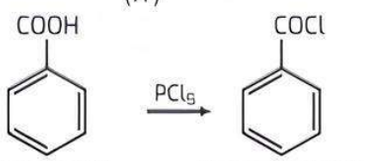
(i) $C_6H_5Br \xrightarrow{Mg/dry\ ether} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_2(g)} B \xrightarrow{PCl_5} C$

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

(CBSE 2017)

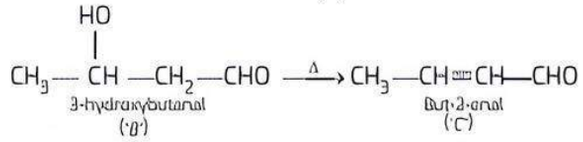
Ans. (i) $C_2H_5Br \xrightarrow[ether]{Mg/dry}$  $\xrightarrow[(b)\ H_3O^+]{(a)\ CO_2(g)}$

Phenyl magnesium bromide ('A')



(ii) $CH_3CN \xrightarrow[H_3O^+]{(a)\ SnCl_2/HCl} CH_3CHO \xrightarrow{dil.\ NaOH}$

Acetaldehyde ('A')



Q 4. Explain why:

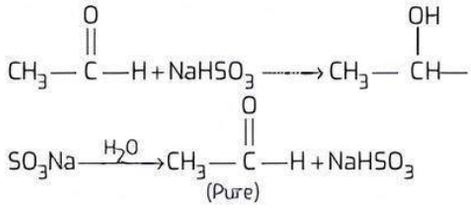
(i) Carboxyl group in benzoic acid is meta directing.

(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.

(iii) Carboxylic acids do not give characteristic reactions of carbonyl group. *(CBSE 2023)*

Ans. (i) In benzoic acid, the carboxyl group is meta-directing because it is electron withdrawing group with —R effect. There is +ve charge on *ortho* and *para* positions So, electrophilic substitution takes place at *meta* position.

(ii) Aldehydes and ketones form addition compounds with $NaHSO_3$ whereas impurities do not form such. So, on hydrolysis, aldehydes and ketones are obtained further.



(iii) This is due to the lone pairs on oxygen atom attached to hydrogen atom in the —COOH group that are involved in resonance and hence make the carbon atom less electrophilic. So, carboxylic acids do not give characteristic reactions of carbonyl group.

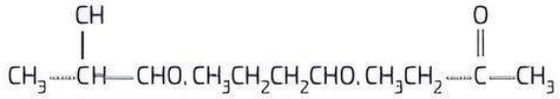
Q 5. (*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollen's test whereas isomer (*B*) does not give Tollen's test but gives positive Iodoform test. Isomers (*A*) and (*B*) on reduction with Zn (Hg)/Conc. HCl give the same product (*D*).

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

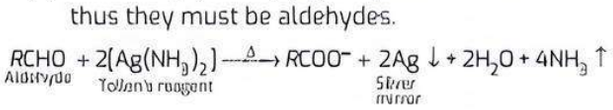
(ii) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN?

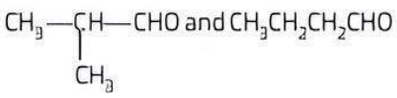
(CBSE 2018)

Ans. (i) The possible functional isomers of carbonyl compound with molecular formula, C_4H_8O are:

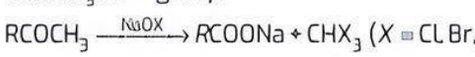


(a) Isomers (*A*) and (*C*) gives positive Tollen's test, thus they must be aldehydes.

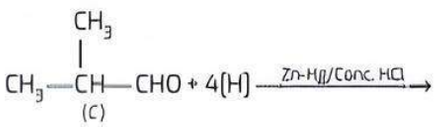




(b) Isomer (*B*) does not give Tollen's test, but gives positive Iodoform test thus it must be a ketone with CH_3CO— group.



(c) Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give some product (*D*).



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + H_2O$$

$$\underset{(A)}{CH_3-CH_2-CH_2-CHO} + 4[H] \xrightarrow{Zn\text{-}Hg/Conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3} + H_2O$$

$$\underset{(B)}{CH_3CH_2CH_3} + 4[H] \xrightarrow[Conc.\ HCl]{Zn\text{-}Hg/} \underset{(C)}{CH_3CH_2CH_2CH_3} + H_2O$$

Hence, the structure of (*A*), (*B*), (*C*) and (*D*) are:

$$\underset{(A)}{CH_3CH_2CHO} \quad \underset{(B)}{CH_3CH_2COCH_3} \quad \underset{(C)}{CH_3\underset{\underset{CH_3}{|}}{C}HCHO} \quad \underset{(D)}{CH_3CH_2CH_2CH_3}$$

COMMON ERROR

Improper analysis of the question may result in wrong conclusion or incorrect product.

(ii) The isomer (*B*) is least reactive towards addition of HCN because, aldehydes are more reactive towards nucleophilic addition reactions than ketones due to inductive and steric effects.

Q 6. What happens when:

(i) Formic acid reacts with conc. H_2SO_4?

(ii) Acetic acid reacts with Cl_2 in the presence of red P?

(iii) Calcium acetate is heated?

Ans. (i) Dehydration takes place resulting in formation of CO.

$$HCOOH \xrightarrow[-H_2O]{H_2SO_4\ (heat)} CO$$

(ii) Trichloroacetic acid is formed.

$$CH_3COOH \xrightarrow[Red\ P]{3Cl_2} CCl_3COOH + 3HCl$$

(iii) Acetone is formed.

$$\underset{Cal.\ acetate}{(CH_3COO)_2Ca} \xrightarrow{heat} \underset{Acetone}{CH_3COCH_3} + CaCO_3$$

Q 7. How are following conversions carried out?

(i) Ethyl cyanide to ethanoic acid

(ii) Butan-1-ol to butanoic acid

(iii) Benzoic acid to *m*-bromobenzoic acid.

Ans. (i)

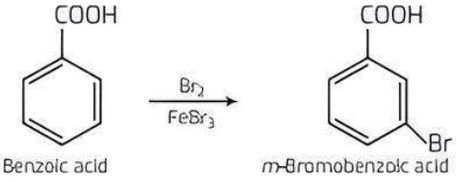
$$\underset{\text{Ethyl cyanide}}{CH_3CH_2C\equiv N} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[heat]{NH_3} CH_3CH_2CONH_2$$

$$\downarrow Br_2/KOH$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xleftarrow[(O)]{KMnO_4/H_2SO_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xleftarrow[heat]{HONO} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

(ii) $$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[(O)]{KMnO_4/H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(iii)



Benzoic acid — *m*-Bromobenzoic acid

Q 8. An organic compound [*A*] with molecular formula $C_8H_{16}O_2$ was hydrolysed with dilute sulphuric acid to give a carboxylic acid [*B*] and an alcohol [*C*]. Oxidation of [*C*] with chromic acid produced [*B*]. The alcohol [*C*] on dehydration gave but-1-ene. Write equations for the reactions involved.

(NCERT EXERCISE)

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

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

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

The equations for the reaction are given as :

$$\underset{\substack{\text{Butylbutanoate (A)}\\(C_8H_{16}O_2)}}{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} \xrightarrow{H_2O/H^+}$$

$$\underset{\text{Butanoic acid (B)}}{CH_3CH_2CH_2COOH} + \underset{\text{Butan-1-ol (C)}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\text{Butanoic acid (B)}}{CH_3CH_2CH_2COOH} \xleftarrow[(oxidation)]{H_2CrO_4} \underset{\text{Butan-1-ol (C)}}{CH_3CH_2CH_2CH_2OH}$$

$$\xrightarrow[-H_2O]{(Dehydration)} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

Q 9. An organic compound '*A*', having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives '*B*'. '*B*' does not reduce Fehling's solution but gives a yellow precipitate of the compound '*C*' with I_2/NaOH. Deduce the structures of *A*, *B* and *C*.

(CBSE 2023)

Ans. Since compound *B* gives positive iodoform test, this means it contains —$COCH_3$ (methyl ketone) group *i.e.*, it is a ketone. Moreover, *B* is obtained by the oxidation of *A*. So, it must be a 2° alcohol.

Hence, the structure of compound *A* is $R-\underset{\underset{OH}{|}}{CH}-CH_3$.

Comparing with the molecular formula, C_3H_8O, the compound *A* is $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ (Propan-2-ol).

The reaction is as follows:

$$\underset{(A)}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[573K]{Cu} \underset{\text{Acetone}\ (B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

$$\text{Acetone} \xrightarrow[Solution]{Fehling} \text{No reaction}$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3COONa + 3NaI + \underset{\text{Iodoform}\ (C)}{CHI_3}\downarrow + 3H_2O$$

Hence, we have the following structures:

$A = CH_3CH(OH)CH_3$

$B = CH_3COCH_3$

$C = CHI_3$

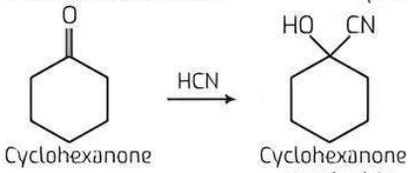
Q 10. Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.

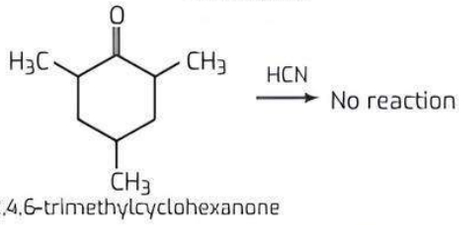
(ii) There are two $—NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazone.

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

Ans. (i)



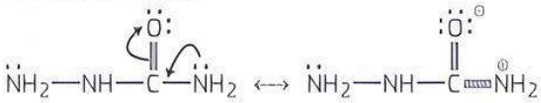
Cyclohexanone — Cyclohexanone cyanohydrin



2,4,6-trimethylcyclohexanone

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

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



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

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{ROH} \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftharpoons}} \underset{\text{Ester}}{RCOOR} + H_2O$$

In order that the reaction may proceed in the forward direction, ester or water formed in the reaction must be removed. Sulphuric acid added in esterification helps in removing molecules of H_2O as it is a dehydrating agent.

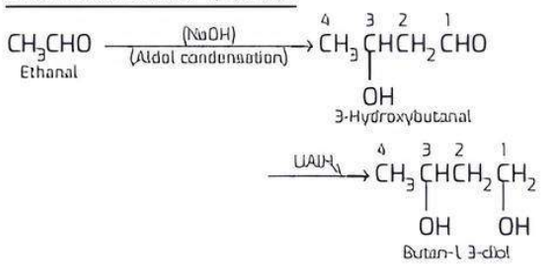
Q 11. How will you convert ethanal to the following compounds?

(i) Butane-1, 3-diol

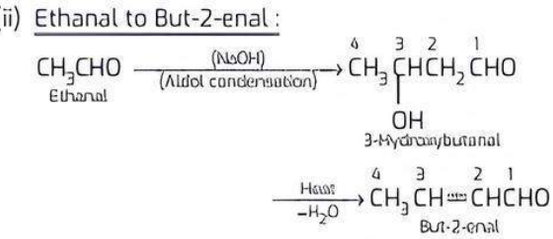
(ii) But-2-enal

(iii) But-2-enoic acid

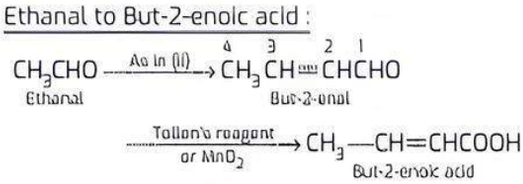
Ans. (i) Ethanal to Butane-1, 3-diol :



(ii) Ethanal to But-2-enal :



(iii) Ethanal to But-2-enoic acid :



Note: Both Tollen's reagent and MnO_2 are weak oxidising agents. These oxidise only the aldehydic group without affecting the double bond.

Q 12. Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reactions:

(i) Ethanal, propanal, propanone, butanone

(ii) Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, acetophenone

Ans. (i) The increasing order of reactivity of the carbonyl compounds towards nucleophilic addition reactions is:

butanone < propanone < propanal < ethanal

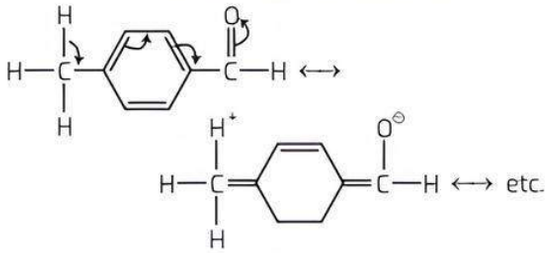
The reactivity is based upon two factors. These are steric factors and electronic factors.

(ii) The increasing order of reactivity is:

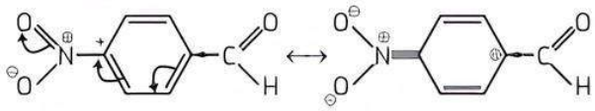
acetophenone < *p*-tolualdehyde < benzaldehyde < *p*-nitrobenzaldehyde

Explanation: Acetophenone, being a ketone is the least reactive towards nucleophilic addition. All others are aldehydes. Among them, *p*-tolualdehyde is less reactive than benzaldehyde because CH_3 group present at the para position w.r.t. — CHO group will increase the electron density on the carbonyl carbon atom due to hyper conjugation

effect. As a result, the nucleophile attack occurs to lesser extent as compared to benzaldehyde.



In *p*-nitrobenzaldehyde, the nitro group has an opposing effect. It is electron withdrawing in nature due to –I effect as well as –R effect. The electron density on the carbonyl carbon atom decreases and thus favours the nucleophilic attack.



Q 13. Arrange the following in the increasing order of their property indicated:

(i) Benzoic acid, Phenol, Picric acid, Salicylic acid (pk_a values).

(ii) Acetaldehyde, Acetone, Methyl-tert-butyl ketone (reactivity towards NH_2OH).

(iii) Ethanol, Ethanoic acid, Benzoic acid (boiling point) *(CBSE SQP 2022 Term-2)*

Ans. (i) Picric acid < Salicylic acid < Benzoic acid < Phenol

(ii) Methyl-tert-butyl ketone < Acetone < Acetaldehyde

(iii) Ethanol < Ethanoic acid < Benzoic acid

Note: B.P. of carboxylic acids is higher than alcohols due to extensive hydrogen bonding, the B.P. increases with increase in molar mass.

Q 14. 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*.

Ans. Compound *A* is an alkene. On ozonolysis, it will give carbonyl compounds. As, both *B* and *C* have $>C=O$ group, *B* gives positive Fehling test so it is an aldehyde and it gives iodoform test, so it has $CH_3C(=O)$ group which means that the aldehyde is acetaldehyde.

C does not give Fehling test, so it is a ketone. It gives positive iodoform test so it is a methylketone which means it has $CH_3C(=O)$ group. Compound *A* (C_5H_{10}) on ozonolysis gives *B* (CH_3CHO) + C (CH_3COR). So, *C* is CH_3COCH_3.

$$CH_3CH{=}C(CH_3)_2 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} CH_3CHO + CH_3COCH_3$$

A *B* *C*

$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + Cu_2O + 3H_2O$$

(red ppt.)

$$CH_3COCH_3 + 2Cu^{2+} + 5OH^- \longrightarrow \text{No reaction}$$

$$CH_3CHO + 3I_2 + 3NaOH \longrightarrow CHI_3 + 3HI + HCOONa$$

(Yellow ppt.)

$$CH_3COCH_3 + 3I_2 + 3NaOH \longrightarrow CHI_3 + 3HI + CH_3COONa$$

(Yellow ppt.)

Q 15. (i) Write the IUPAC name of the following organic compound:

$$(CH_3CH_2)_2NCH_3$$

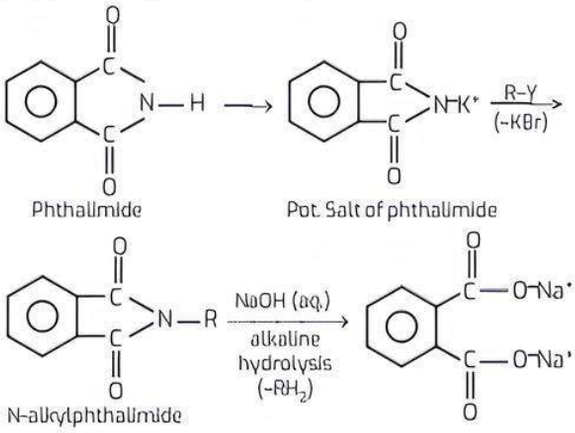
(ii) Write the equations for the following:

(a) Gabriel phthalimide synthesis

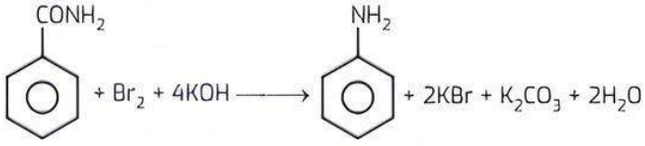
(b) Hoffmann bromamide degradation

Ans. (i) N–ethyl-N-Methylethanamine

(ii) (a) Gabriel phthalimide synthesis:



(b) Hoffmann bromamide degradation:



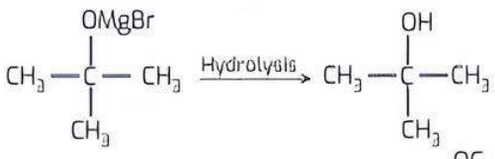
Q 16. What happens when:

(i) Propanone is treated with CH_3Mg Br and then hydrolysed?

(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction?

Ans. (i) $CH_3-C(=O)-CH_3 + CH_3MgBr \longrightarrow$



(ii) $CH_3-CHO \xrightarrow{\text{ethanol (excess)}} CH_3-CH(OC_2H_5)_2$

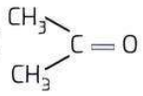
(iii) $2HCHO \xrightarrow{OH^-} HCOOH + CH_3OH$

Q 17. Write the main product in the following reactions:

(i) $2CH_3COCl + (CH_3)_2Cd \longrightarrow$

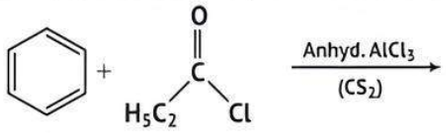
(ii) $CH_3CH_2CHO \xrightarrow{Zn(Hg)/conc.HCl}$

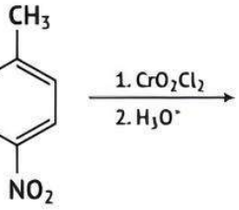
(iii) 

Ans. (i)  (ii) $CH_3—CH_2—CH_3$

(iii) 

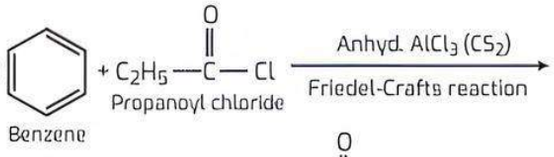
Q 18. Write the structure of the products of the following:

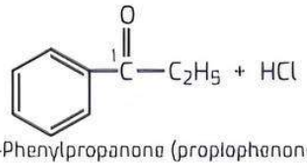
(i) 

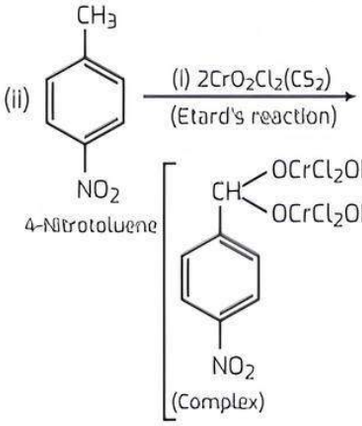
(ii) 

(iii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

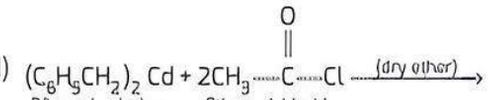
(iv) $H_3CC{\equiv}CH \xrightarrow{Hg^{2+}, H_2SO_4}$

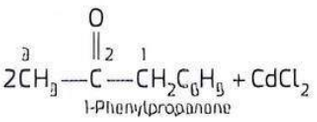
Ans. (i) 
Benzene — Propanoyl chloride — Anhyd. $AlCl_3$ (CS_2), Friedel-Crafts reaction

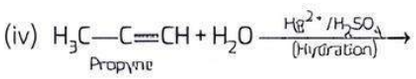

1-Phenylpropanone (propiophenone)

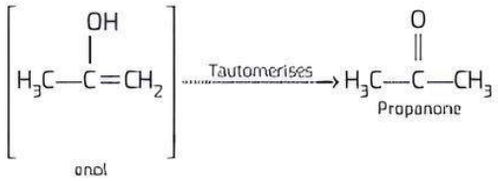
(ii) 
4-Nitrotoluene — (I) $2CrO_2Cl_2(CS_2)$, (Etard's reaction)

(Complex) — H_3O^+ — 4-Nitrobenzaldehyde

(iii) 
Dibenzylcadmium — Ethanoyl chloride — (dry ether)


1-Phenylpropanone

(iv) 
Propyne — Hg^{2+}/H_2SO_4 (Hydration)


enol — Tautomerises — Propanone

Long Answer Type Questions

Q 1. Arrange the following in increasing order of the property 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)

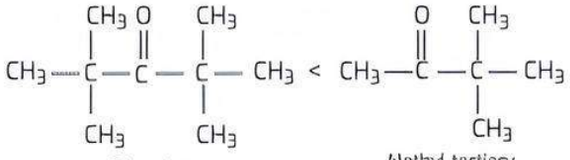
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3, 5-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength). *(NCERT EXERCISE)*

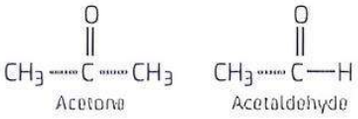
Ans. (i) Cyanohydrin derivative is formed as a result of the reaction in which the nucleophile (CN^- ion) attack carbon atom of the carbonyl group. The order of reactivity :

(a) decreases with increase in +I effect of the alkyl group.

(b) decreases with increase in steric hindrance due to the size as well as number of the alkyl groups.

In the light of the above information, the decreasing order of reactivity is:

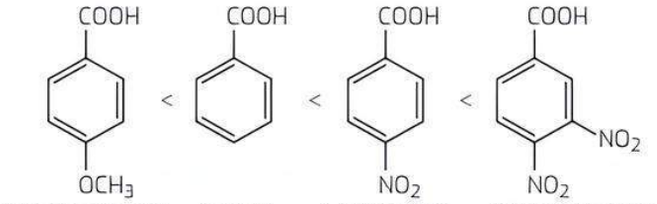

DI-tertiary butyl ketone — Methyl tertiary butyl ketone


Acetone — Acetaldehyde

(ii) We know that alkyl group +I effect decreases the acidic strength. The +I effect of isopropyl group is more than that of *n*-propyl group. Similarly, bromine (Br) with -I effect increases the acidic strength. Closer its position in the carbon atom chain w.r.t. carboxyl (COOH) group, more will be its -I effect and stronger will be the acid. In the light of this, the increasing order of acidic strength is:

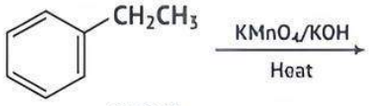
$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

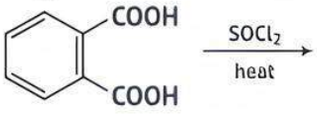
(iii) We have learnt that the electron donating group (OCH_3) decreases the acidic strength of the benzoic acid. At the same time, the electron withdrawing group (NO_2) increases the same. Keeping this in mind, the increasing order of acidic strength is:



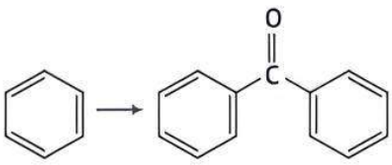
4-Methoxybenzoic acid | Benzoic acid | 4-Nitrobenzoic acid | 3,4-Dinitrobenzoic acid

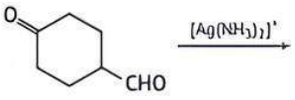
Q 2. Complete each synthesis by giving starting material, reagent or product.

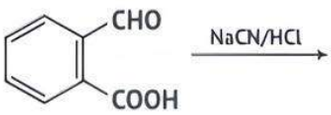
(i) 

(ii) 

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

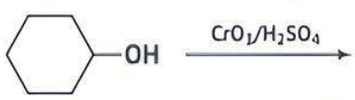
(iv) 

(v) 

(vi) 

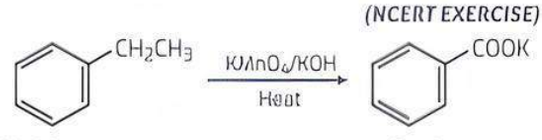
(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil. NaOH}}$

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

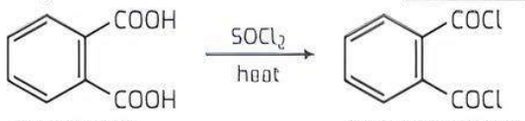
(ix) 

(x) 

(NCERT EXERCISE)

Ans. (i) 

Ethyl benzene | Pot. benzoate

(ii) 

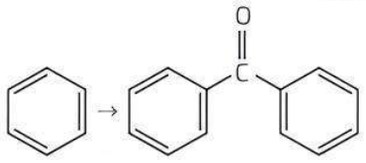
Phthalic acid | Phthaloyl chloride

(iii) $C_6H_5CH{=}O + H_2NCONHNH_2 \longrightarrow$

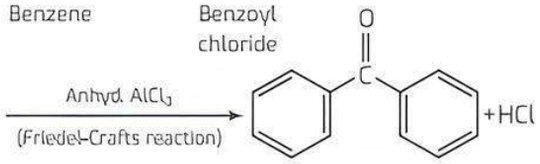
Benzaldehyde | Semicarbazide

$C_6H_5CH{=}NCONH_2 + H_2O$

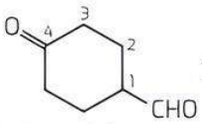
Benzaldehyde semicarbazone

(iv) 

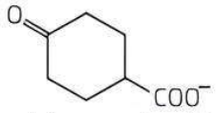
Benzene | Benzoyl chloride



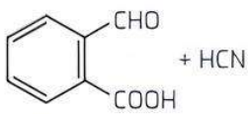
Benzophenone

(v) 

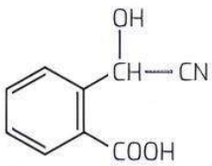
4-Oxocyclohexane-carbaldehyde



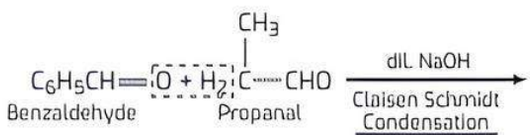
4-Oxocyclohexanecarboxylate anion

(vi) 

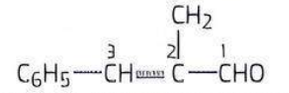
2-Formylbenzoic acid



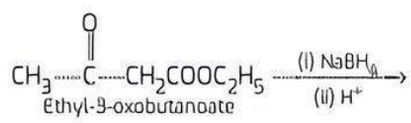
2-(1-hydroxycyanomethyl) benzoic acid

(vii) 

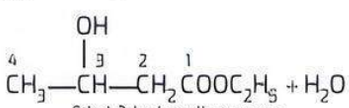
Benzaldehyde | Propanal | Claisen Schmidt Condensation



2-Methyl-3-phenylprop-2-enal

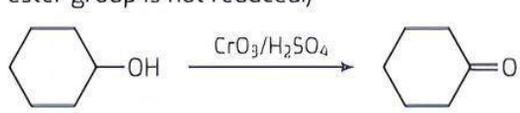
(viii) 

Ethyl-3-oxobutanoate

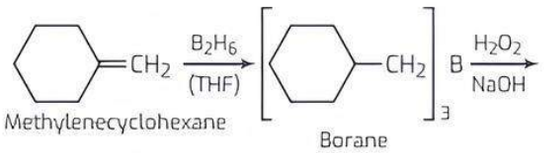


Ethyl-3-hydroxylbutanoate

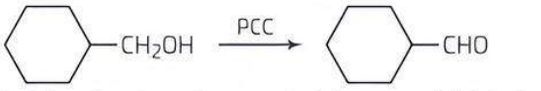
(Only the ketonic group is reduced by $NaBH_4$. The ester group is not reduced.)

(ix) 

Cyclohexanol | Cyclohexanone

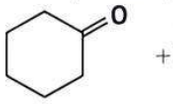
(x) 

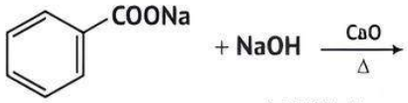
Methylenecyclohexane — Borane



Cyclohexylmethanol — Cyclohexanecarbaldehyde

Q 3. (i) Write the product (s) in the following reactions:

(a) 

(b) 

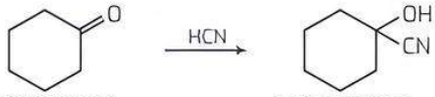
(c) $CH_3—CH=CH—CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL\text{-}H} ?$

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

(a) Butanal and Butan-2-one

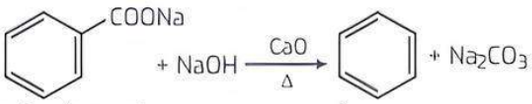
(b) Benzoic acid and Phenol *(CBSE 2017)*

Ans. (i) (a) Cyclohexanone reacts with hydrogen cyanide (HCN) to form cyclohexanone cyanohydrin.



Cyclohexanone — Cyclohexanone cyanohydrin

(b) The sodium benzoate reacts with soda lime to give benzene.



Sodium benzoate — Benzene

(c) But-2-en-1-nitrile on reaction with DIBAL-H followed by water gives but-2-en-1-ol

$$CH_3—CH=CH—CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL\text{-}H} CH_3CH=CH—CHO$$

But-2-en-1-nitrile — But-2-en-1-ol

(ii) (a) Butanal being an aldehyde reduces Tollen's reagent to shiny silver mirror but butan-2-one being a ketone does not reduces Tollen's reagent.

$$CH_3CH_2CH_2CHO + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \xrightarrow{\Delta}$$

$$CH_3CH_2CH_2COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Silver mirror

$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{\text{Tollen's reagent}} \text{No silver mirror}$$

(b) Benzoic acid and phenol can be distinguished by ferric chloride test. Phenol reacts with neutral $FeCl_3$ to form ferric phenoxide complex giving violet colouration.

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

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

$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{Ferric benzoate (buff colour ppt)}}{(C_6H_5COO)_3Fe} + 3HCl$$

Q 4. (i) Write the reaction involved in the following :

(a) Etard reaction

(b) Stephen reduction

(ii) How will you convert the following in not more than two steps :

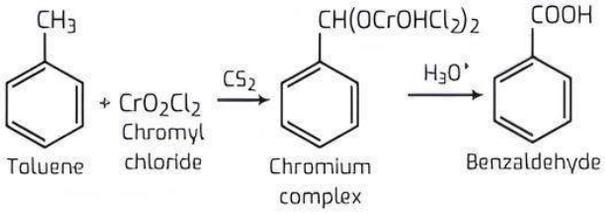
(a) Benzoic acid to Benzaldehyde

(b) Acetophenone to Benzoic acid

(c) Ethanoic acid to 2-hydroxyethanoic acid.

(CBSE 2017)

Ans. (i) (a) Etard Reaction : Toluene reacts with chromyl chloride in presence of CS_2 followed by hydrolysis to produce benzaldehyde.

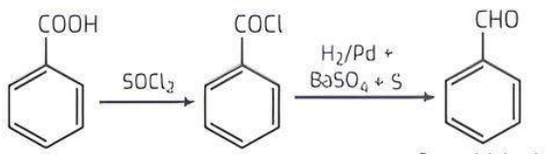


Toluene — Benzaldehyde

(b) Stephen Reduction: Alkyl nitrites on reduction with stannous chloride and hydrochloric acid in dry ether gives corresponding imine hydrochlorides which on acid hydrolysis, give corresponding aldehydes.

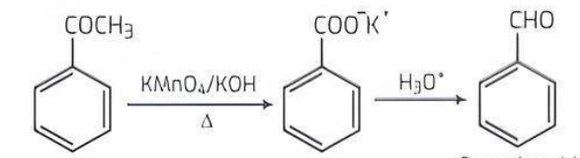
$$\underset{\text{Alkyl nitrites}}{R—CN} + 2(H) \xrightarrow[\text{Reduction}]{SnCl_2 + HCl} \underset{\text{Imine}}{RCH=NH} \xrightarrow{H_3O^+} \underset{\text{Aldehyde}}{RCHO}$$

(ii) (a) Benzoic acid to Benzaldehyde:



Benzoic acid — Benzaldehyde

(b) Acetophenone to Benzoic acid:



Acetophenone — Benzoic acid

(c) Ethanoic acid to 2-hydroxyethanoic acid:

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{Cl_2/\text{red P}} ClCH_2COOH$$

$$\xrightarrow{KOH\ (aq)} \underset{\text{2-hydroxy ethanoic acid}}{OH—CH_2COOH}$$

Q 5. (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)*

Ans. (i) (a) Ethanal to But -2-en-1-al:

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{(NaOH)}} \underset{\text{3-Hydroxybutanal}}{CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{But-2-enal}}{CH_3CH=CHCHO}$$

(b) Propanoic acid to 2-chloropropanoic acid:

$$CH_3CH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2/Red\,P} \underset{\text{2-chloropropanoicacid}}{CH_3-\overset{\overset{Cl}{|}}{C}H-COOH}$$

(ii) Compound *B* gives positive Fehling's test. this shows that it is an aldehyde and it gives iodoform test which signifies that it has $-COCH_3$ group as well.

Thus, structure of 'B' is $HC(=O)-\overset{\overset{H}{|}}{C}=O$ (Ethanal).

Compound *C* does not give Fehling's test which signifies that it is a ketone and since it gives iodoform test, thus, it has $-COCH_3$ group.

Thus, structure of 'C' is $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (Acetone).

Since, *B* and *C* are obtained on ozonolysis of alkene C_5H_{10}, it must have the following structure:

$CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$ (2-methyl but-2-ene)

The reactions are :

- **Ozonolysis:**

$$\underset{\text{(A)}}{CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} \underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

- **Iodoform reaction :**

$$\underset{\text{(B)}}{CH_3CHO} \xrightarrow[I_2]{NaOH} CHI_3 + HCOONa \quad \text{(Iodoform)}$$

$$\underset{\text{(C)}}{CH_3COCH_3} \xrightarrow[I_2]{NaOH} CH_3COONa + CHI_3 \text{ (Iodoform)}$$

Q 6. (i) How can you convert each of the following compounds to benzoic acid?

(a) Acetophenone

(b) Ethylbenzene

(c) Bromobenzene

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

(a) O_2N-CH_2-COOH, $F-CH_2-COOH$, $CN-CH_2COOH$

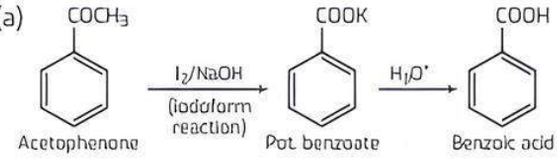
(Acidic character)

(b) Ethanal, Propanal, Butanone, Propanone

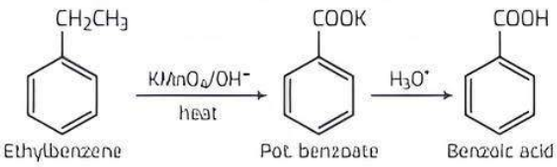
(Reactivity in nucleophilic addition reactions)

(CBSE 2023)

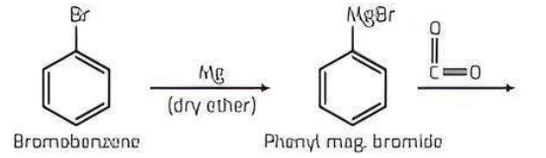
Ans. (i) (a)

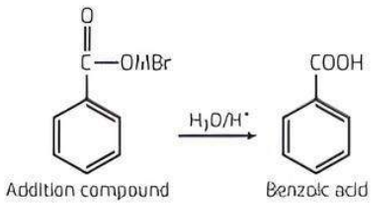


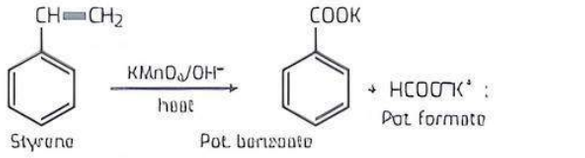
(b)

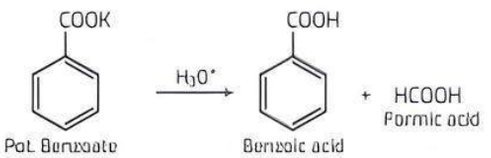


(c)









(ii) (a) The presence of electron withdrawing group increases the acidic strength and $-I$ effect of NO_2, F and CN are as follows: $F < CN < NO_2$

Hence, the increasing order of acidic character of the given compounds is :

$$F \cdots CH_2 - COOH < CN \cdots CH_2 \cdots COOH < O_2N \cdots CH_2 \cdots COOH$$

(b) The increasing order of reactivity of the carbonyl compounds towards nucleophilic addition reactions is:

butanone < propanone < propanal < ethanal

The reactivity is based upon two factors. These are steric factors and electronic factors.

Q 7. (i) An organic compound (*X*) having molecular formula $C_5H_{10}O$ can show various properties depending on its structures.

Draw each of the structures if it:

(a) gives positive iodoform test.

(b) shows Cannizzaro's reaction.

(c) reduces Tollens' reagent and has a chiral carbon.

(ii) Write the reaction involved in the following:

(a) Wolff-Kishner reduction

(b) Hell-Volhard Zelinsky reaction *(CBSE 2023)*

Ans. (i) (a) $CH_3-\underset{\underset{O}{\|}}{C}-CH(CH_3)_2$

(b) $(CH_3)_3CHO$

(c) $(CH_3)-\underset{\underset{CHO}{|}}{CH}-CH_2CH_3$

(ii) **(a) Wolff-Kishner Reduction:** The carbonyl group of aldehydes and ketones is reduced to $-CH_2$ group on treatment with hydrazine followed by heating with KOH in high boiling solvent like ethylene glycol. This reaction is known as Wolff-Kishner reduction.

$$H_3C-\underset{\text{Acetone}}{\underset{H_3C}{\overset{}{>}}C=O} + NH_2-NH_2 \longrightarrow H_3C-\underset{H_3C}{\overset{}{>}}C=N.NH_2$$

$$\xrightarrow[\text{Ethylene glycol, }\Delta]{KOH} CH_3-CH_2\cdots\cdots CH_3 + N_2\uparrow$$

Propane

(b) Hell-Volhard Zelinsky Reaction: Carboxylic acids having α-hydrogen atom are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. This reaction is known as Hell-Volhard Zelinsky reaction.

$$R-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2,\ Red\ P} R-\underset{\underset{X}{|}}{CH}-COOH$$

α-halocarboxylic acid
(X = Cl, Br)

Q 8. A hydrocarbon (*A*) with molecular formula C_5H_{10} on ozonolysis give two products (*B*) and (*C*). Both (*B*) and (*C*) give a yellow precipitate when heated with iodine in presence of NaOH while only (*B*) give a silver mirror on reaction with Tollen's reagent.

(i) Identify (*A*), (*B*) and (*C*).

(ii) Write the reaction of *B* with Tollen's reagent.

(iii) Write the equation for iodoform test for *C*.

(iv) Write down the equation for aldol condensation reaction of *B* and *C*. *(CBSE SQP 2022-23)*

Ans. Since, the hydrocarbon has molecular formula $C_5H_{10}O$ and it undergoes ozonolysis, so *A* must be an alkene. *B* gives yellow precipitate with iodine in the presence of NaOH and gives silver mirror with Tollen's reagent so *B* must be an aldehyde. *C* doesn't give silver mirror with Tollen's reagent, so it must be a methyl ketone.

(i) *A* is an alkene.

B is an aldehyde with $-CH_3$ group.

C is a methyl ketone.

or, *A* : $CH(CH_3)=C(CH_3)_2$

B : CH_3CHO

C : $O=C(CH_3)_2$

(ii) The reaction of *B* with Tollen's reagent is:

$$CH_3CHO + [Ag(NH_3)_2] + OH^- \longrightarrow CH_3COO^- + Ag + NH_3 + H_2O$$

(iii) The equation for iodoform test for *C* is:

$$CH_3COCH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3COONa$$

(iv) The equation for aldol condensation reaction of *B* and *C* is as shown:

$$CH_3COCH_3 + CH_3CHO \xrightarrow{Ba(OH)_2} (CH_3)_2C(OH)CH_2COCH_3 + CH_3CH(OH)CH_2CHO + (CH_3)_2(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3 \xrightarrow{Heat} (CH_3)_2C=CHCOCH_3 + CH_3CH=CHCHO + (CH_3)C=CHCHO + CH_3CH=CHCOCH_3$$

Here, four products are obtained through mixed aldol reaction of *B* and *C* as:

$B-B + C-C + B-C + C-B$

Q 9. An organic compound (*A*) with molecular formula $C_2Cl_3O_2H$ is obtained when (*B*) reacts with Red *P* and Cl_2. The organic compound (*B*) can be obtained on the reaction of methyl magnesium chloride with dry ice followed by acid hydrolysis.

(i) Identify *A* and *B*.

(ii) Write down the reaction for the formation of *A* from *B*. What is this reaction called?

(iii) Given any one method by which organic compound *B* can be prepared from its corresponding acid chloride.

(iv) Which will be the more acidic compound (*A*) or (*B*)? Why?

(v) Write down the reaction to prepare methane from the compound (*B*). *(CBSE SQP 2022-23)*

Ans. (i) When *B* reacts with Red *P* and Cl_2, *A* is formed which must be a halogenated compound. Also, *B* is formed by the reaction of methyl magnesium chloride with dry ice (Grignard reagent) followed

by acid hydrolysis so, it is a carboxylic acid. *A* has molecular formula $C_2Cl_3O_2H$ having two carbon atoms, so *B* will also have two carbon atoms only and it must be an acetic acid.

A: CCl_3COOH

B: CH_3COOH

(ii) The reaction for the formation of *A* from *B* is:

$$CH_3COOH \xrightarrow[(ii)\ H_2O]{(i)\ Red\ P/Cl_2} CCl_3COOH$$

This reaction is called as Hell-Volhard Zelinsky reaction.

(iii) The organic compound *B* can be prepared from its corresponding acid chloride using the following method:

$$CH_3COCl \xrightarrow{H_2O} CH_3COOH$$

(iv) *A* will be more acidic due to the presence of 3 Cl groups (electron withdrawing groups) which increase acidity of carboxylic acid.

(v) The reaction to prepare methane from the compound B is as shown:

$$CH_3COOH \xrightarrow[(ii)\ Heat]{(i)\ NaOH,\ CO} CH_4 + Na_2CO_3$$

Q 10. (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*.

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

$B \xrightarrow{LiAlH_4} D$

(CBSE 2023)

Ans. (i) (a) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$:

On heating with Fehling's solution, $CH_3CH_2CH_2CHO$ gives red precipitate of Cu_2O whereas $CH_3COCH_2CH_3$ gives no reaction.

$$CH_3CH_2CH_2CHO + 2CuO \xrightarrow{\Delta}$$

$$Cu_2O\downarrow + CH_3CH_2CH_2COOH$$

Red ppt.

(b) Ethanal and Ethanoic acid:

Ethanoic acid gives a brisk effervescence with $NaHCO_3$ solution while ethanal fails to give such a reaction.

(ii) Oxime of acetone: $CH_3-\underset{\displaystyle CH_3}{\overset{}{C}}=N-OH$

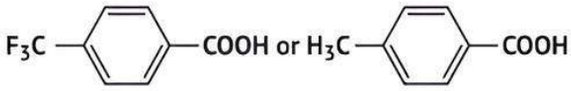
(iii)

$$CH_3COOH \xrightarrow{PCl_5} \underset{(A)}{CH_3COCl} \xrightarrow[BaSO_4]{H_2/Pd-} \underset{(B)}{CH_3CHO} \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \underset{(C)}{CH_3COCH_3}\ (Acetone) + CH_3MgBr$$

$B \xrightarrow{LiAlH_4} \underset{(D)}{CH_3CH_2OH}\ (Ethanol)$

Q 11. (i) Draw structure of the 2, 4-dinitrophenylhydrazone of benzaldehyde.

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

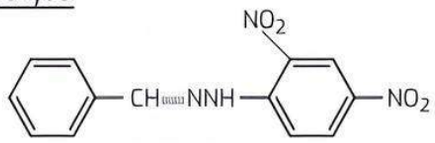


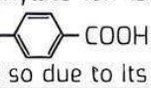
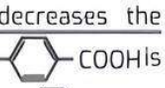
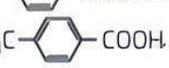
(iii) Write the chemical equation involved in Rosenmund's reduction.

(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)*

Ans. (i) Structure of 2,4-dinitrophenylhydrazone of benzaldehyde:



(ii) In both compounds, the carboxylic acid is attached to the benzene ring, so the carboxylate ion is stabilised by resonance. In  fluorine is also attached to the ring so due to its electron- withdrawing nature, it increases the acidic character of carboxylic acid while in the case of  the $-CH_3$ group is an electron-donating group which decreases the acidity of carboxylic acid. Thus,  is a stronger acid as compared to  .

(iii) The chemical equation involved in Rosenmund's reduction is:

$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow{H_2,\ Pd/BaSO_4} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

(iv) 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. Thus, α-hydrogens of aldehydes and ketones are acidic.

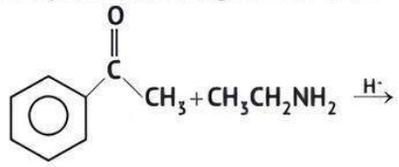
(v) Benzoic acid gives a brisk effervescence with saturated $NaHCO_3$ solution but benzaldehyde fails to respond to this test.

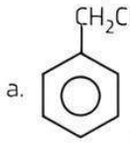
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + H_2O + \underset{\text{Brisk effervescence}}{CO_2}$$

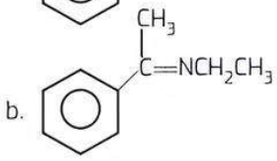
Chapter Test

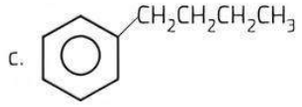
Multiple Choice Questions

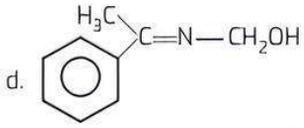
Q 1. Find the product of the given reaction:



a. 

b. 

c. 

d. 

Q 2. Identify (*X*), (*Y*) and (*Z*) reagents in the given sequence of reactions:

$$CH \equiv CH \xrightarrow{X} CH_3CHO \xrightarrow{Y} CH_3CH(OH)CH_3 \xrightarrow{Z} CH_3COCH_3$$

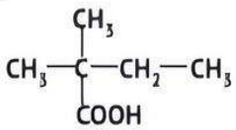
a. $X = H_2SO_4$, $Y = H_2O/OH^-$, $Z = PCl_5$, heat
b. $X = HNO_3$, $Y = Na_2CO_3$, $Z = H_2SO_4$, heat
c. $X = H_2SO_4/Hg^{2+}$, $Y = PCl_5/H_2O$, $Z = K_2Cr_2O_7/OH^-$
d. $X = H_2SO_4/Hg^{2+}$, $Y = CH_3MgBr/H_2O$, $Z = K_2Cr_2O_7/OH^+$

Q 3. Match the column I with column II and mark the appropriate choice.

Column I	Column II
(A) Clemmensen reduction	(i) Conc. KOH
(B) Rosenmund reduction	(ii) Zn/Hg + Conc. HCl
(C) Iodoform reaction	(iii) H_2/Pd-$BaSO_4$
(D) Cannizzaro reaction	(iv) NaOH +I_2

a. (A) → (i), (B) → (iii), (C) → (ii), (D) → (iv)
b. (A) → (iii), (B) → (iv), (C) → (i), (D) → (ii)
c. (A) → (ii), (B) → (iii), (C) → (iv), (D) → (i)
d. (A) → (iv), (B) → (i), (C) → (ii), (D) → (iii)

Q 4. What is the correct IUPAC name of the given compound:



a. 2, 2-dimethylbutanoic acid
b. 2-carboxyl-2-methylpropanoic acid
c. 2-ethyl-2-methylpropanoic acid
d. 3-methylbutane carboxylic acid

Assertion and Reason Type Questions

Directions (Q. Nos. 5-6): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

Q 5. Assertion (A): Ketones can be converted into acids by haloform reaction.

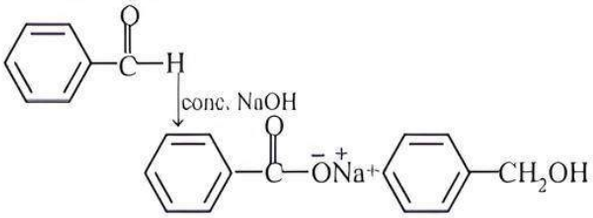
Reason (R): Addition of Grignard reagents to dry ice followed by hydrolysis gives ketone.

Q 6. Assertion (A): Etard reaction helps to stop the oxidation of toluene at the aldehyde stage.

Reason (R): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

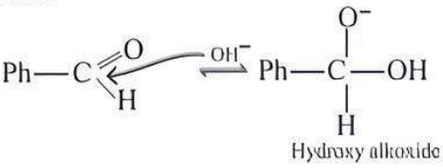
Case Study Based Question

Q 7. When an aldehyde with no α-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to a carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidised and other half is reduced. This reaction is known as Cannizzaro reaction.

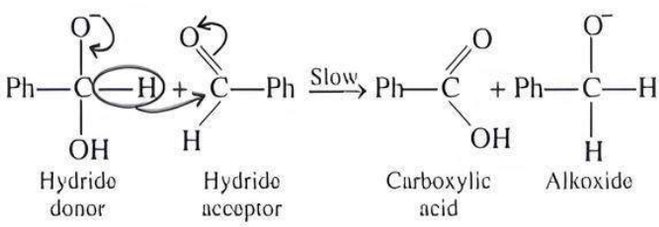


Mechanism:

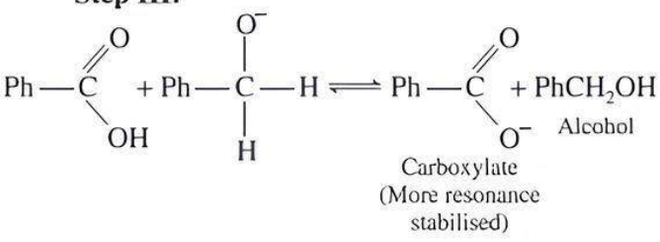
Step I:



Step II:



Step III:



Read the given passage carefully and give the answer of the following questions:

(i) What is given by a mixture of benzaldehyde and fomaldehyde on heating with aqueous NaOH solution?

(ii) Trichloroacetaldehyde is subjected to Cannizzaro reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. Find the other compound.

(iii) In Cannizzaro reaction given below:

$2PhCHO \xrightarrow{^-OH} PhCH_2OH + PhCO_2^-$

Give its slowest step.

OR

Which of the following compounds will undergo Cannizzaro reaction?

Benzophenone, Benzaldehyde,

1-Phenylpropanone, 2-2-Dimethyl butanol

Very Short Answer Type Questions

Q 8. Illustrate decarboxylation reaction giving a suitable example.

Q 9. $(CH_3)_3C—CHO$ does not undergo aldol condensation. Comment.

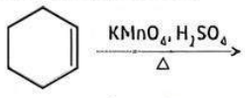
Short Answer Type-I Questions

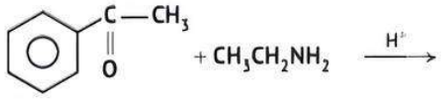
Q 10. Account for the following:

(i) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(ii) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid.

Q 11. Predict the products.

(i) 

(ii) 

Q 12. Write the equations involved in the following reactions:

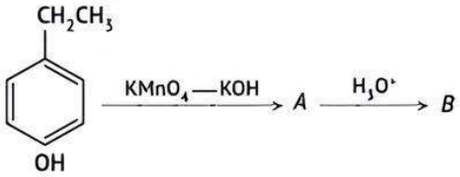
(i) Clemmensen reduction

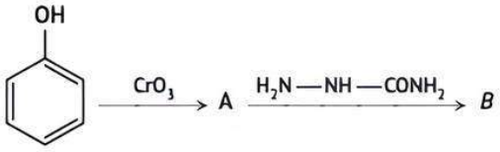
(ii) Wolff-Kishner reduction

Short Answer Type-II Questions

Q 13. An organic compound *A* (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid *B* and an alcohol *C*. Oxidation of *C* with chromic acid also produced *B*. On dehydration, *C* gives but-1-ene. Write the equations for the reactions involved.

Q 14. Write structures of compounds *A* and *B* in each of the following reactions:

(i) 

(ii) 

Q 15. *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 Tollen's test whereas isomer *B* does not give Tollen's 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?

Long Answer Type Questions

Q 16. (i) What is meant by the following terms? Give an example of the reaction in each case.

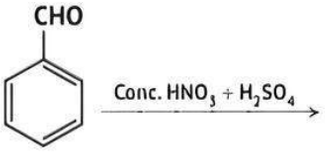
(a) Aldol

(b) Semicarbazone

(ii) Complete the following:

(a) $CH_3COCl \xrightarrow{H_2, Pd/BaSO_4}$

(b) $CH_3—CH=CH—CN \xrightarrow{DIBAL—H}$

(c) 

Q 17. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions: