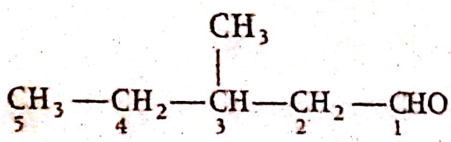
Explanations

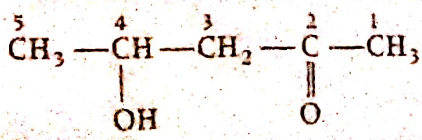
1. $\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CHO}$

Propanal **(1)**

2. 

3-methylpentanal **(1)**

NOTE 'al' represents — CHO group and 'pent' represents chain of five C-atoms.

3. 

IUPAC name 4-hydroxypentan-2-one **(1)**

4. 

p-methylbenzaldehyde
[p means para and 4th position wrt aldehyde group]

(1)

5. Pentan-2-one and pentan-3-one can be distinguished by iodoform test.

On heating with $NaOH + I_2$ or [NaOI], propan-2-one being a methyl ketone forms yellow ppt of iodoform, whereas pentan-3-one does not.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3NaOI \longrightarrow CH_3CO\bar{O}Na^+ + \underset{\text{Iodoform (yellow ppt)}}{CHI_3\downarrow} + 2NaOH$$

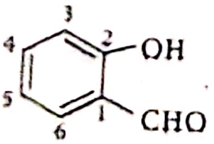
$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{NaOI} \text{No yellow ppt of iodoform}$$

(1)

6. $\overset{3}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$

2-methylpropan-1-al

(1)

7. 

2-hydroxybenzaldehyde

(1)

8. $H_3\overset{4}{C}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}HO$

3-methylbutanal

(1)

9. $\overset{5}{C}H_3-\underset{\underset{Cl}{|}}{\overset{4}{C}H}-\overset{3}{C}H_2-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{1}{C}H_3$

4-chloropentan-2-one

(1)

10. Boiling point is related to attractive forces. Stronger the attractive force, higher is the boiling point.

Ethanol, i.e. CH_3-CH_2-OH undergoes extensive intermolecular hydrogen bonding, therefore, its boiling point is highest among all the given compounds. In contrast, among CH_3-CHO and $CH_3-CH_2-CH_3$, CH_3CHO possess higher boiling point than $CH_3CH_2CH_3$ because CH_3CHO possess dipole-dipole interactions which are stronger than van der Waals' forces of attraction existing in $CH_3CH_2CH_3$.
Hence, the order of their increasing boiling points is:

$$CH_3-CH_2-CH_3 < CH_3-CHO < CH_3-CH_2-OH$$

(1)

11. The structure is $\overset{5}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{4}{C}}=\overset{3}{C}H-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{1}{C}H_3$

4-methylpent-3-en-2-one

(1)

12. **Ethanol to acetone**

$$C_2H_5OH + KMnO_4 \xrightarrow{[O]} CH_3CHO + CH_3MgBr \longrightarrow CH_3\underset{\underset{OMgBr}{|}}{C}H\,CH_3$$

$$\xrightarrow{\text{Hydrolysis}} CH_3\underset{}{\overset{\overset{OH}{|}}{C}H}\,CH_3 \xrightarrow[KMnO_4]{[O]} CH_3\underset{\underset{O}{\|}}{C}\,CH_3$$

(1)

13. $\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{3}{C}H=\underset{2}{C}H-\underset{1}{\overset{\overset{O}{\|}}{C}}-H$

Pent-2-en-1-al

(1)

14. Benzophenone ($C_6H_5COC_6H_5$) and acetophenone ($C_6H_5COCH_3$) can be distinguished by iodoform test. Acetophenone, being a methyl ketone on treatment with I_2 / NaOH [or NaOI] undergoes iodoform reaction to give a yellow ppt. of iodoform. On the other hand, benzophenone does not give this test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow C_6H_5CO\bar{O}\overset{+}{N}a + \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{NaOI} \text{No yellow ppt. of iodoform}$$

(1)

15. Reactivity depends on two factors: steric effect and electronic effect. Lesser the steric hindrance, higher is the reactivity.

On moving from ethanal to butanone, + I-effect and steric hindrance of alkyl group increases due to which the electron density on the carbon atom of the carbonyl group progressively increases and hence, attack by nucleophile becomes slower and slower. Thus, the reactivity increases in the order as:
Butanone < propanone < propanal < ethanal (1)

16. **Cross aldol condensation** When aldol condensation is carried out between two different aldehydes or ketones or between an aldehyde or a ketone and atleast one of them contain α-H, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products. **(1/2)**

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH}$$

$$\underset{\text{But-2-enal}}{CH_3\,CH{=}CH\,CHO} + \underset{\text{2-methylpent-2-enal}}{CH_3CH_2CH{=}\underset{|\atop CH_3}{C}{-}CHO}$$

$$+ \underset{\text{2-methylbut-2-enal}}{CH_3{-}CH{=}\underset{|\atop CH_3}{C}{-}CHO}$$

$$+ \underset{\text{Pent-2-enal}}{CH_3CH_2{-}CH{=}CHCHO}$$ **(1/2)**

17. Refer to solution 5. **(1)**

18. **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 reduction.

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

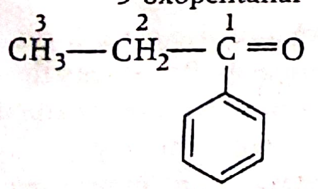
e.g. $$\underset{\text{Propanone}}{(CH_3)_2C{=}O} \xrightarrow[HCl]{Zn\text{-}Hg} \underset{\text{Propane}}{(CH_3)_2CH_2} + H_2O$$ **(1)**

19. $$\overset{1}{CH_3}{-}\overset{2}{\underset{\|\atop O}{C}}{-}\overset{3}{CH}{=}\overset{4}{\underset{|\atop CH_3}{C}}{-}\overset{5}{CH_3}$$

4-methylpent-3-en-2-one. **(1)**

20. $$\overset{5}{H_3C}{-}\overset{4}{H_2C}{-}\overset{3}{\underset{\|\atop O}{C}}{-}\overset{2}{CH_2}{-}\overset{1}{CHO}$$ **(1)**

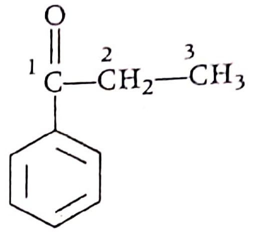
3-oxopentanal

21. 

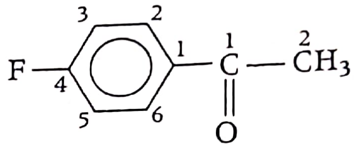
1-phenylpropan-1-one **(1)**

22. **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.

$$\underset{\text{Acetone}}{(H_3C)_2C{=}O} + NH_2{-}NH_2 \longrightarrow (H_3C)_2C{=}NNH_2 \xrightarrow[\text{Ethylene glycol, }\Delta]{KOH} \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3} + N_2\uparrow$$ **(1)**

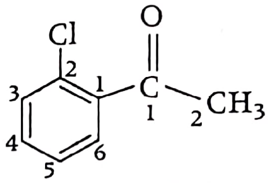
23. 

1-phenylpropan-1-one **(1)**

24. 

4-fluorophenylethanone **(1)**

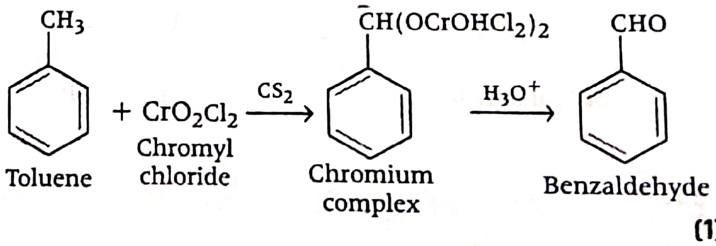
25. It is ammoniacal silver nitrate ($AgNO_3$ + NH_4OH) solution. It is used to test the presence of aldehyde group as it is a mild oxidising agent. **(1)**

26. 

2-chlorophenylethanone **(1)**

27. (i) **Wolff-Kishner Reduction**
Refer to solution 22. **(1)**

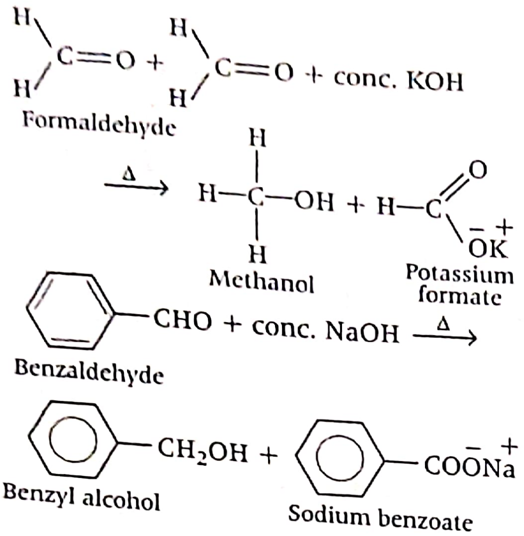
(ii) **Etard Reaction**
Toluene reacts with chromyl chloride in presence of CS_2 followed by hydrolysis produces benzaldehyde.



(1)

28. (i) **Clemmensen reduction** Refer to solution 18.

(ii) **Cannizzaro reaction** Aldehydes which do not have α-H atoms undergo self oxidation and reduction reaction on treatment with conc. alkali. This reaction is known as Cannizzaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



(1)

29. (i) $CH_3—CH = CH_2 \xrightarrow{H_2O/H^+}$ (Propene) $CH_3—CH(OH)—CH_3$ (Propan-2-ol) (1)

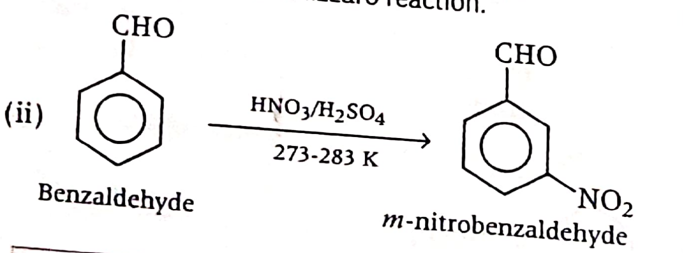
(ii) $CH_3—CH_2—Cl \xrightarrow{aq.\ NaOH}$ (Ethyl chloride)

$CH_3—CH_2—OH \xrightarrow[CrO_3/PCC]{[O]} CH_3—CHO$ (Ethanal) (1)

30. (i) $2H—C(=O)—H \xrightarrow{Conc.\ KOH}$ (Formaldehyde) $H—CH_2—OH + HCO\bar{O}K^+$ (Methanol, Potassium formate)

NOTE It is an example of Cannizzaro reaction. (1)

(ii)

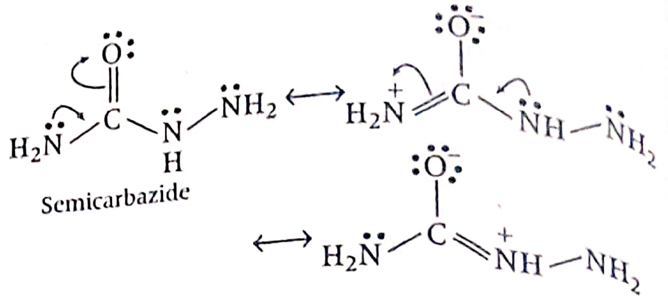


(1)

31.

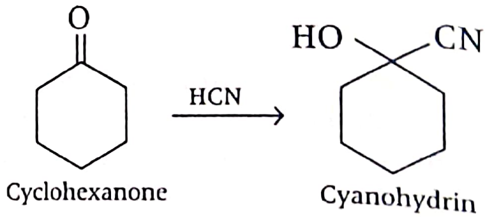
> (i) Lone pair of electrons involved in conjugation with >CO group.
> (ii) +*I*-effect due to methyl groups, steric hindrance, makes a carbonyl compound less reactive.

(i) Although semicarbazide has two $—NH_2$ groups but one of them which is directly attached to >C= O group is involved in resonance as shown below:

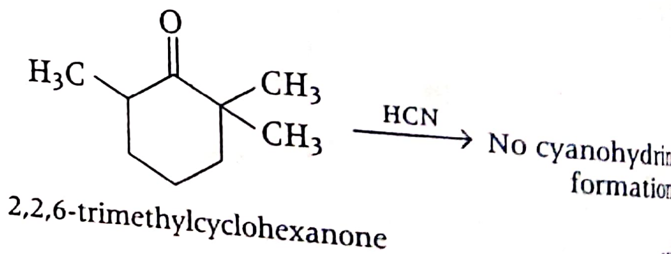


Therefore, the electron density on $—NH_2$ group involved in the resonance decreases. As a result, it cannot act as a nucleophile. In contrast, the lone pair of electrons on the other $—NH_2$ group is not involved in resonance, thus, it can act as a nucleophile and can attack carbonyl carbon atoms of aldehydes and ketones to produce semicarbazones. (1)

(ii) Cyclohexanone forms cyanohydrin according to the following equation:



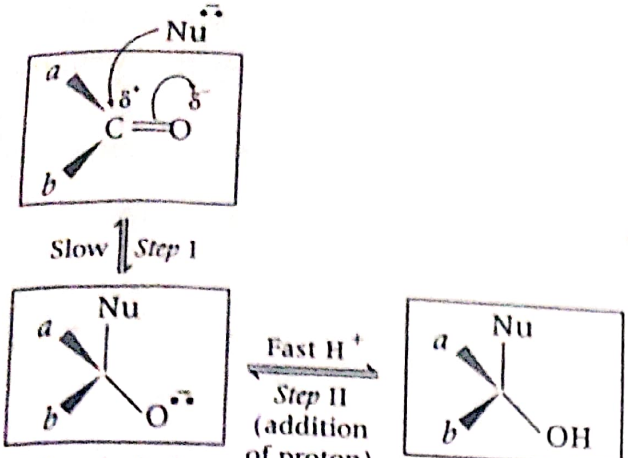
As in cyclohexanone; there is no steric hindrance, therefore the nucleophile CN^- can easily attack the carbonyl carbon. However, in case of 2,2,6-trimethylcyclohexanone, the presence of three methyl groups at α-positions offer steric hindrance and as a result, CN^- cannot attack effectively. For this reason, it does not form a cyanohydrin.



(1)

32. Mechanism of a nucleophilic attack on carbonyl carbon A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2-hybridised orbitals of carbonyl carbon.

The hybridisation of carbon changes from sp^2 to sp^3 and a tetrahedral intermediate is produced. This intermediate immediately accepts a proton from the reaction medium to give electrically neutral product.



Tetrahedral intermediate　　　Addition product

(1)

(1)

33. (i) Stephen Reaction

$$R—CN + SnCl_2 + HCl \downarrow RCH=NH \xrightarrow{H_3O^+} RCHO$$

Imine

(1)

(ii) **Wolff-Kishner Reaction** Refer to solutions 22. (1)

(iii) **Etard Reaction** Refer to solution 27 (ii). (1)

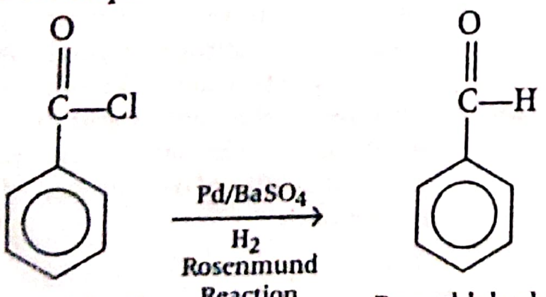
34. (i) Conversion of Propanone to Propane

$$CH_3—\overset{\overset{\large O}{\|}}{C}—CH_3 \xrightarrow[\text{or Wolff-Kishner reduction } NH_2—NH_2 + KOH + \text{glycol}]{\text{Clemmensen reduction, } Zn(Hg)+HCl} CH_3—CH_2—CH_3$$

Propanone　　　Propane

(1)

(ii) Conversion of Benzoyl Chloride to Benzaldehyde



Benzoyl chloride　　　Benzaldehyde (1)

(iii) Conversion of Ethanal to but-2-enal

$$2CH_3CHO \xrightarrow[\text{Aldol condensation}]{\text{Dil. NaOH}} CH_3—\underset{}{\overset{OH}{\overset{|}{C}H}}—CH_2—CHO \xrightarrow[-H_2O]{\Delta} CH_3—CH=CH—CHO$$

Ethanal　　3-hydroxybutanal　　But-2-enal

(1)

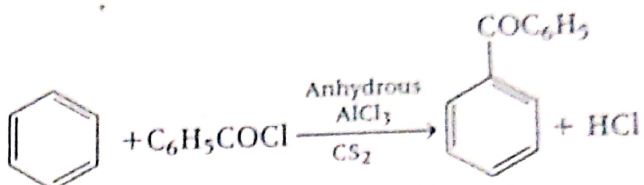
35.

(i) Friedel-Crafts reaction (acylation), i.e. introduction of acyl group in benzene ring.

(ii) Hydration of propyne, i.e. addition of water to propyne and tautomerisation.

(iii) Etard's reaction (aldehyde is formed, i.e. — CH_3 group is converted into — CHO group).

(i)



Benzophenone

(1)

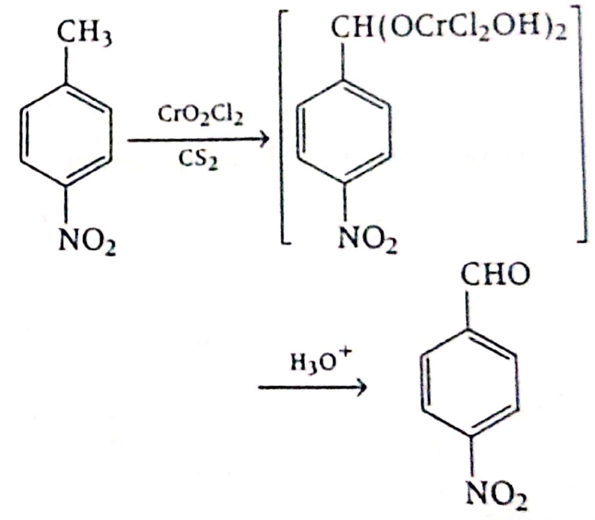
(ii) $H_3C—C\equiv C—H + H_2O \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4}$

$$\left[CH_3—\overset{OH}{\overset{|}{C}}=CH_2\right] \xrightleftharpoons{\text{Tautomerisation}} CH_3—\overset{O}{\overset{\|}{C}}—CH_3$$

Prop-1-en-2-ol (Unstable)　　　Acetone

(1)

(iii)



p-nitrobenzaldehyde

(1)

36. (i) Alcohols are produced by the addition reaction of Grignard's reagents with the carbonyl group of aldehydes and ketones.

Mechanism

Step I The first step of the reaction is the nucleophilic addition of Grignard's reagent to the carbonyl group to form an adduct.

$$>C=\ddot{O} + \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}—X \longrightarrow >\underset{R}{\underset{|}{C}}—O^-\overset{+}{Mg}—X$$

Adduct

(1)

Step **II** Hydrolysis of the adduct yields an alcohol.

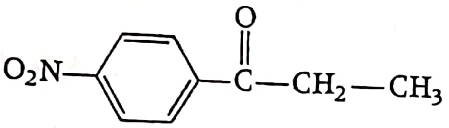
$$>C(R)-\ddot{O}^{-}\overset{+}{Mg}-X \xrightarrow{H_2O} >C(R)-\ddot{O}H + Mg(OH)X$$

Alcohol **(1)**

(ii) (a) 3-methylbutanal

$$H_3\overset{4}{C}-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}(=O)-H$$ **(1/2)**

(b) *p*-nitropropiophenone



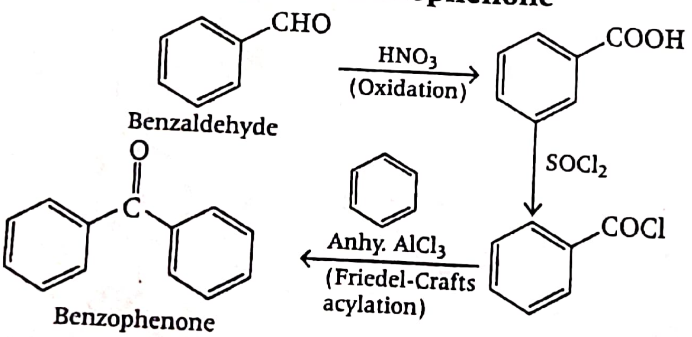
(1/2)

37. (i) Refer to solution 28(ii).

(ii) (a) **Ethanal to 3-hydroxybutanal**

$$\underset{\text{Ethanal}}{2CH_3-CHO} \underset{\text{(Aldol condensation)}}{\overset{\text{Dil. NaOH}}{\rightleftharpoons}} \underset{\text{3-hydroxybutanal}}{\overset{4}{C}H_3-\overset{3}{C}H(OH)-\overset{2}{C}H_2-\overset{1}{C}HO}$$ **(1)**

(b) **Benzaldehyde to benzophenone**



(1)

38. (i) (a) **Propanone oxime** The structure of propanone oxime is:

$$CH_3-C(CH_3)=N-OH$$ **(1)**

NOTE It is formed when propanone reacts with hydroxylamine.

$$(CH_3)_2C=O + \underset{\text{Hydroxylamine}}{H_2-N-OH} \xrightarrow{-H_2O} \underset{\text{Propanone oxime}}{CH_3-C(CH_3)=N-OH}$$

(b) **Semicarbazone of CH_3CHO** The structure of semicarbazone of CH_3CHO is

$$CH_3-CH=N-NH-C(=O)-NH_2.$$ **(1)**

NOTE It is formed when CH_3CHO reacts with semicarbazide.

$$(H_3C)(H)C=O + \underset{\text{Semicarbazide}}{H_2N-NH-C(=O)-NH_2} \xrightarrow{-H_2O} \underset{\text{Semicarbazone}}{CH_3-CH=N-NH-C(=O)-NH_2}$$

(ii) (a) Ethanal, (CH_3CHO) to CH_3-CH_3

$$CH_3CHO \xrightarrow[\text{HCl}]{\text{Zn-Hg}} CH_3-CH_3 + H_2O$$

Clemmensen reduction **(1)**

(b) Ethanal,(CH_3CHO) to

$$CH_3-CH(OH)-CH_2-CHO$$

$$2CH_3CHO \xrightarrow[\text{Aldol condensation}]{\text{Dil. NaOH}} CH_3-CH(OH)-CH_2-CHO$$ **(1)**

(c) Ethanal,CH_3CHO to CH_3CH_2OH

$$CH_3CHO \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} CH_3CH_2OH$$ **(1)**

39. (i) (a) **Aldol condensation** In this reaction two molecules of an aldehyde or ketone condense in presence of dilute alkali (dil NaOH, $Ba(OH)_2$ etc.) to form a β-hydroxy aldehyde or a β-hydroxy ketone respectively. These β-hydroxy aldehydes or ketones are collectively called aldols and the reaction is called aldol condensation. The reaction is based on acidity of α-hydrogen of aldehydes and ketones. **(1)**

For eg:

$$\underset{\text{Ethanal}}{(CH_3)(H)C=O} + \underset{\text{Ethanal}}{H-\overset{\alpha}{C}H_2CHO} \xrightarrow{\text{Dil. NaOH}} \underset{\text{3-hydroxy butanal (Aldol)}}{CH_3-C(OH)(H)-CH_2-CHO}$$

(b) **Cannizzaro reaction** Refer to solution 28 (ii). **(1)**

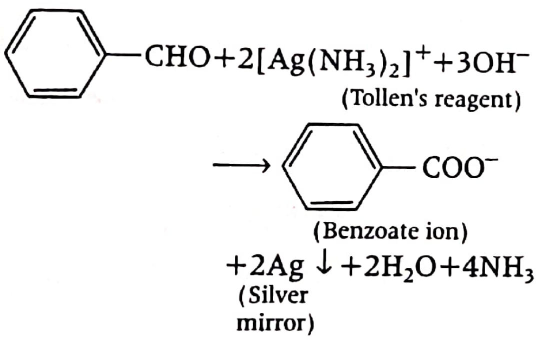
(ii) (a) **Ethanal and propanal** Both can be distinguished by iodoform test. Ethanal contains $CH_3—\overset{O}{\overset{\|}{C}}—$ group, therefore, it undergoes iodoform reaction and gives yellow precipitate of CHI_3. While propanal does not give this test. **(1)**

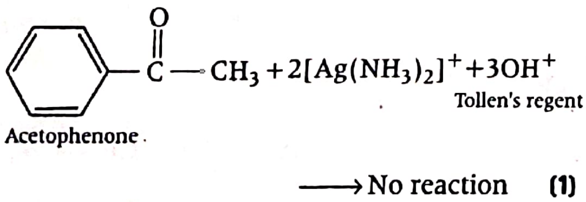
$$\underset{\text{Ethanal}}{CH_3—\overset{O}{\overset{\|}{C}}—H} + 3NaOI \xrightarrow{\Delta}$$

$$CH_3—CO\bar{O}\overset{+}{N}a + 2NaOH + CHI_3\downarrow \text{(yellow ppt)}$$

$$\underset{\text{Propanal}}{CH_3—CH_2—CHO} \xrightarrow[\Delta]{NaOI} \text{No yellow ppt of } CHI_3$$

(b) **Benzaldehyde and acetophenone** Both can be distinguished by Tollen's test. Benzaldehyde contains —CHO group and thus, reduces Tollen's reagent to metallic silver while acetophenone being a ketone does not reduce Tollen's reagent.





(1)

(c) Refer to solution 5. **(1)**

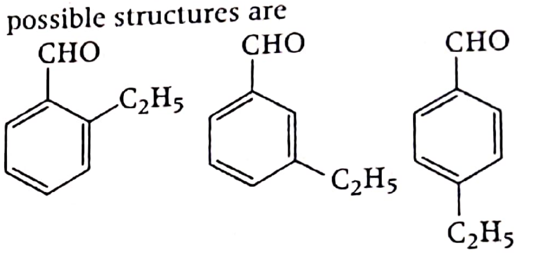
40.

> (i) (a) Carbonyl compounds react with 2,4-DNP.
> (b) Aldehydes (—CHO group containing compounds) reduce Tollen's reagent.
> (c) Aldehydes which don't contain α-H atom undergoes Cannizzaro's reaction.
> (d) Oxidation at successive places shows the presence of two groups at 1, 2-places.
> (ii) (a) Iodoform test
> (b) Tollen's reagent, iodoform test
> (iii) Reactivity decreases as the number of electron donating groups increases.

(i) (a) Since, the compound gives 2,4-DNP derivative, it contains $>C=O$ group. **(1/2)**

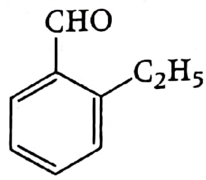
(b) It reduces Tollen's reagent, that means, the carbonyl compound is an aldehyde (— CHO group is present). **(1/2)**

(c) It gives Cannizzaro reaction, so it does not contain any α-hydrogen atom. Thus, its possible structures are



[1/2]

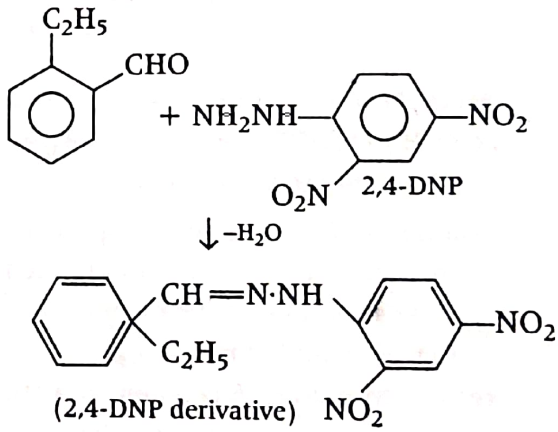
(d) Since, the compound on vigorous oxidation gives 1,2-benzene dicarboxylic acid, the two groups must be present at successive position. Thus, the compound is



(1/2)

The reactions are as follows:

1.



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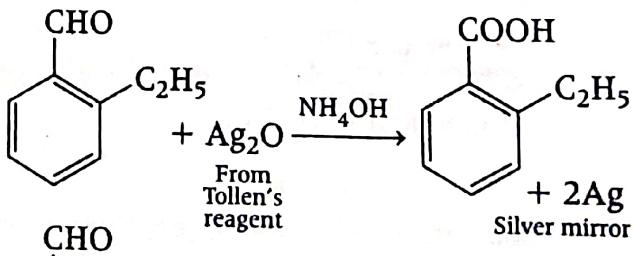
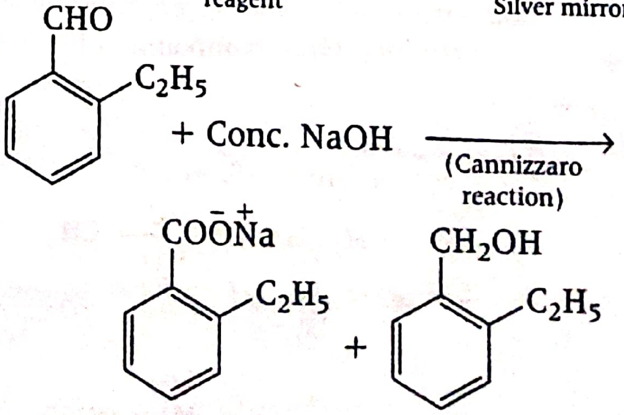
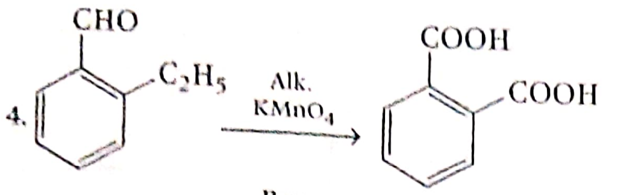


3.





Benzene-1, 2- dicarboxylic acid

(ii) (a) Propanone, because of the presence of $-COCH_3$ group when treated with NaOH and I_2, gives yellow crystals of iodoform.

$$CH_3COCH_3 + 4\,NaOH + 3I_2 \longrightarrow \underset{\text{Iodoform}}{CHI_3}\downarrow + CH_3CO\bar{O}\overset{+}{N}a + 3NaI + 3H_2O$$

In contrast, propanol ($CH_3CH_2CH_2OH$) does not contain $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$ group, so it does not give iodoform test.

(b) Refer to solution 39 (ii) (b). (1)

(iii) The reactivity towards HCN addition decreases as the $+I$-effect of alkyl groups increases as they tend to increase the density of electrophilic carbonyl carbon and makes nucleophilic attack by CN^- difficult. Further, the presence of large number of alkyl groups causes steric hindrance to the nucleophilic attack by CN^- at carbonyl carbon. Hence, reactivity increases as: (1)

Methyl t-butyl ketone < acetone < acetaldehyde

i.e. $[CH_3COC(CH_3)_3] < (CH_3COCH_3) < (CH_3CHO)$

(Reactivity towards HCN) (1)

41. (i) Compound B gives a yellow ppt. with $I_2/NaOH$, i.e. positive iodoform test and not reduce Fehling's solution, it means that it contains $-COCH_3$ (methyl ketone) group, and is a ketone. Moreover, B is obtained by the oxidation of A, thus A must be a 2° alcohol. (As only 2° alcohol give ketones on oxidation with Cu at 573 K). Hence, the structure of compound A is $R\underset{\displaystyle OH}{\underset{|}{CH}}CH_3$.

Comparing with the given molecular formula gives $R = CH_3$. Thus, compound A is $\underset{\text{Propan-2-ol}}{CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_3}$

The reactions are as follows :

$$\underset{(A)}{CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_3} \xrightarrow[573\text{ K},\ -H_2]{Cu} \underset{\text{Acetone } (B)}{CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_3}$$

$$\underset{(B)}{\text{Acetone}} \xrightarrow[\text{solution}]{\text{Fehling's}} \text{No reaction}$$

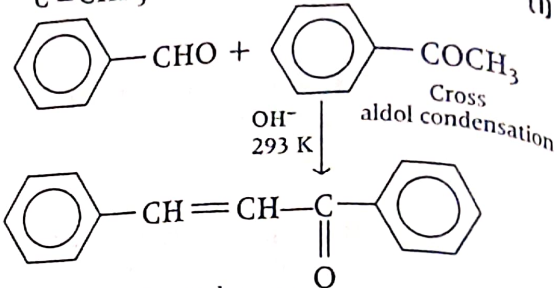
$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3CO\bar{O}\overset{+}{N}a + 3NaI + \underset{\text{Iodoform } (C)}{CHI_3}\downarrow + 3H_2O$$

Thus, $A = CH_3CH(OH)CH_3$ (1)

$B = CH_3COCH_3$ (1)

$C = CHI_3$ (1)

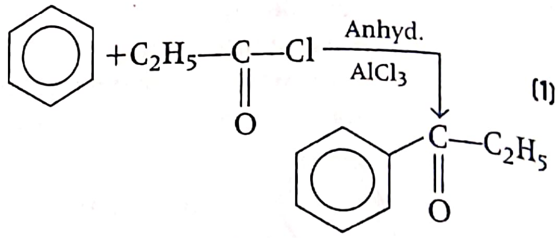
(ii) (a)



Benzalacetophenone

[or 1,3-diphenylprop-2-en-1-one] (1)

(b)



(1)

1-phenylpropan-1-one

42. (i)

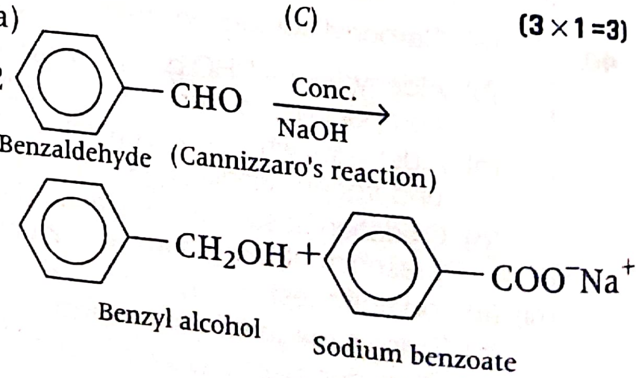
$$CH_3CHO \xrightarrow{(i)\ C_2H_5MgCl} \left[CH_3-\overset{\displaystyle OMgCl}{\overset{|}{CH}}-C_2H_5 \right] \xrightarrow{(ii)\ H_2O}$$

$$\underset{(A)}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-C_2H_5} \xrightarrow[H_2SO_4]{\text{conc.}} \underset{\text{But-2-ene } (B)}{CH_3CH=CHCH_3}$$

$$\xrightarrow{\text{HBr/Peroxide}} \underset{\text{2-bromobutane } (C)}{H_3C-\underset{\displaystyle H}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3}$$

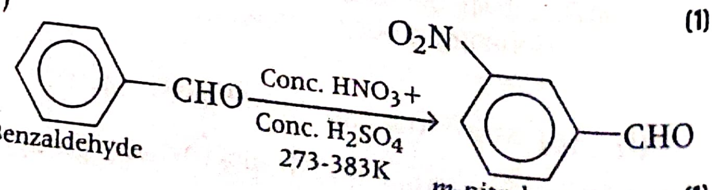
(3 × 1 = 3)

(ii) (a)



(1)

(b)



m-nitrobenzaldehyde (1)

43. Since, A gives haloform test, it must contain $—COCH_3$ group. Thus, its possible formula is $C_2H_5COCH_3$. Since, A on reduction gives B which on heating with sulphuric acid gives C that forms mono-ozonide (i.e. undergoes ozonolysis) this suggests that C is alkene which is formed by dehydration of alcohol. Hence, B is alcohol. Therefore, $C_2H_5COCH_3$ on reduction gives butan-2-ol (A) which on dehydration gives but-2-ene (C). Ozonolysis of but-2-ene gives only acetaldehyde (E). The reactions involved are:

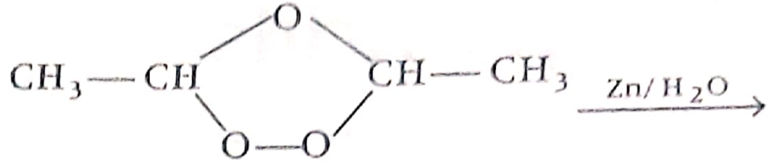
$$\underset{\substack{(A)\\ \text{Butan-2-one}}}{CH_3COCH_2CH_3} \xrightarrow[\text{LiAlH}_4]{[H]}$$

$$\underset{(B)}{CH_3—\underset{\large OH}{\underset{|}{CH}}—\underset{\text{Butan-2-ol}}{CH_2CH_3}} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4 / \Delta} \quad (1)$$

(1)

$$\underset{(C)\ \text{But-2-ene}}{CH_3—CH=CH—CH_3} \xrightarrow{O_3}$$

(1)



(D)

Mono-ozonide

$$\underset{\substack{(E)\\ \text{Acetaldehyde}}}{2CH_3CHO} \quad (1)$$

(A) gives iodoform reaction as

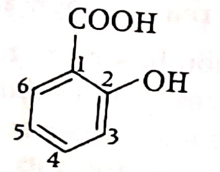
$$CH_3COCH_2CH_3 + 3I_2 + 4NaOH \longrightarrow$$

$$CHI_3 + C_2H_5CO\overset{-}{O}\overset{+}{N}a + 3NaI + 3H_2O \quad (1)$$

Explanations

1. $\overset{4}{C}H_3 - \overset{3}{C}H(OH) - \overset{2}{C}H_2 - \overset{1}{C}OOH$

3-hydroxybutanoic acid (1)

2. 

2-hydroxybenzoic acid (1)

3. $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_3PO_3]{Br_2/P} \underset{\alpha-\text{bromoacetic acid}}{CH_2(Br) - COOH}$ (1)

NOTE This reaction is an example of Hell-Volhard-Zelinsky reaction.

4. Phenol and benzoic acid can be distinguished by ferric chloride test. Phenol reacts with neutral $FeCl_3$ to form ferric phenoxide complex giving violet colouration. (1/2)

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

But benzoic acid reacts with neutral $FeCl_3$ to give a buff coloured precipitate of ferric benzoate. (1/2)

$$\underset{\text{Benzoic acid}}{3C_6H_5COOH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate} \\ \text{(Buff coloured ppt.)}}}{(C_6H_5COO)_3Fe} + 3HCl$$

5. **Decarboxylation** refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salt are heated with sodalime. e.g. (1/2)

$$\underset{\substack{\text{Sodium} \\ \text{ethanoate}}}{CH_3CO\bar{O}\overset{+}{N}a} \xrightarrow[\Delta]{\text{Sodalime (mixture of NaOH and CaO in 3 : 1 ratio)}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$ (1/2)

6. Hexane-1, 6-dioic acid

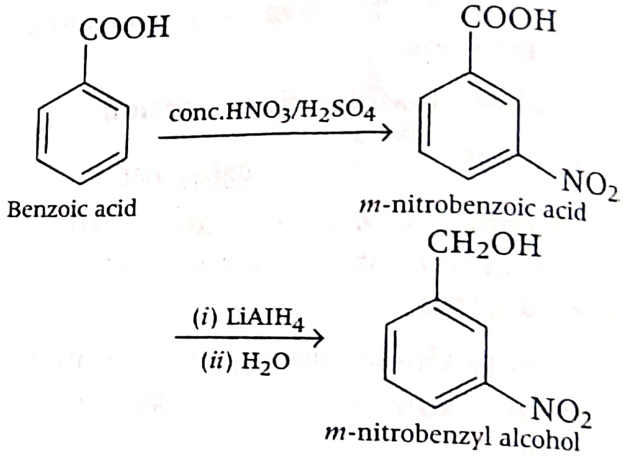
$HOOC - (CH_2)_4 - COOH$ (1)

7. **Hell-Volhard-Zelinsky (HVZ) 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. The reaction is known as Hell-Volhard Zelinsky reaction.

$$R - CH_2 - COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2,\ \text{Red phosphorus}} \underset{\substack{\alpha\text{-halocarboxylic acid} \\ (X = Cl, Br)}}{R - CH(X) - COOH}$$ (1)

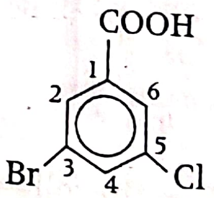
8. **Benzoic acid to *m*-nitrobenzyl alcohol**



(1)

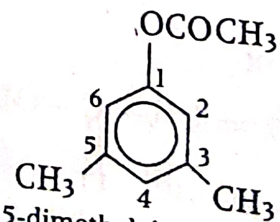
9. $\underset{6}{C}H_3 - \underset{5}{C} \equiv \underset{4}{C} - \underset{3}{C}H = \underset{2}{C}H - \underset{1}{C}(=O) - OH$

Hex-2-en-4-yn-1-oic acid (1)

10. 

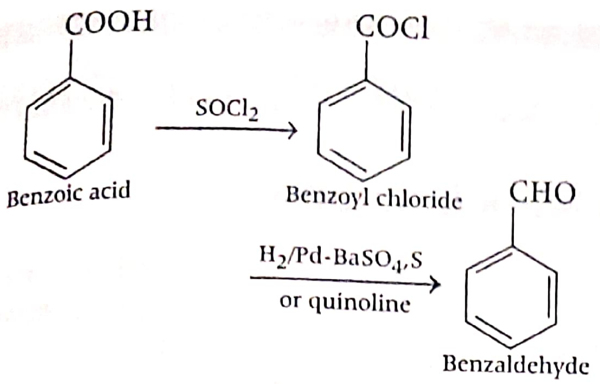
3-bromo-5-chlorobenzoic acid (1)

NOTE Naming will be done in alphabetical manner.

11. 

3, 5-dimethylphenylethanoate (1)

12. Benzaldehyde is easily obtained from benzoyl chloride, so convert benzoic acid into benzoyl chloride and then do Rosenmund's reduction.

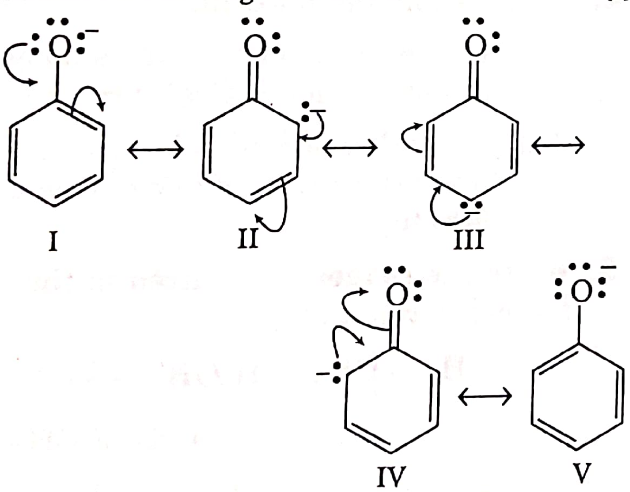


(1)

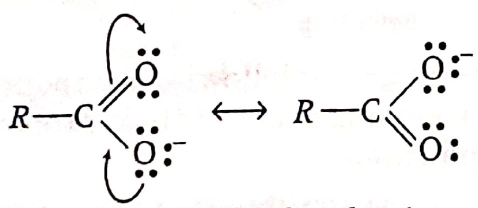
13. (i) **Hell-Volhard-Zelinsky reaction** Refer to solution 7.
(ii) **Decarboxylation reaction** Refer to solution 5. (1)
(In sodalime, the ratio of NaOH and CaO is 3 : 1.) (1)

14. Comparative effectiveness of delocalisation of negative charge is responsible for the acidic strength. A resonating structure having negative charge on more electronegative atom, is more stable.

(i) Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom whereas in case of carboxylate ion, the ion is stabilised by equivalent resonance structures, in which negative charge is on more electronegative atom. (1)



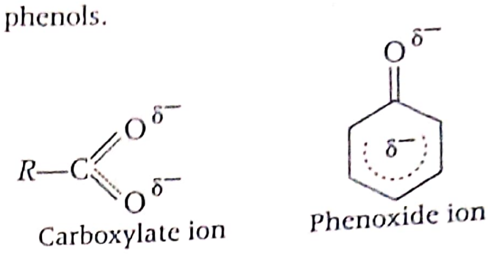
Resonance structures of phenoxide ion



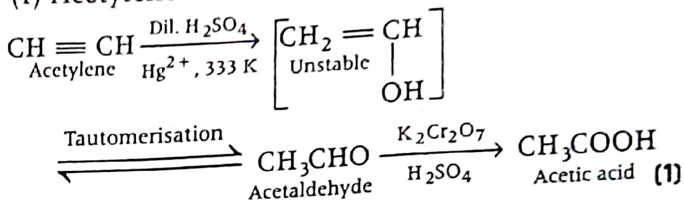
Resonance structures of carboxylate ion

(ii) In carboxylate ion, the negative charge is delocalised over two electronegative oxygen atoms, whereas in phenoxide ion the negative charge is less effectively delocalised over one oxygen atom and less electronegative carbon atoms. Thus, the carboxylate is more stabilised than phenoxide ion.

Hence, carboxylic acids are more acidic than phenols. (1)

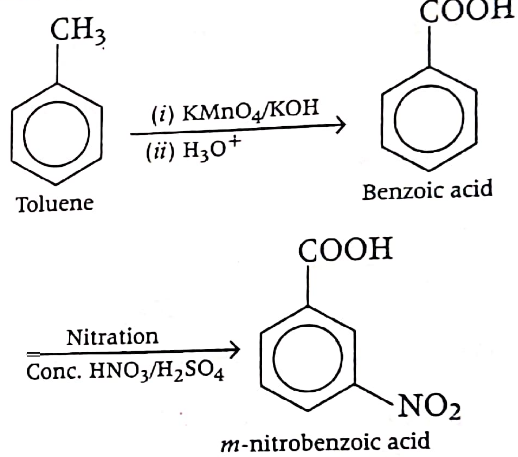


15. (i) Acetylene to acetic acid



(1)

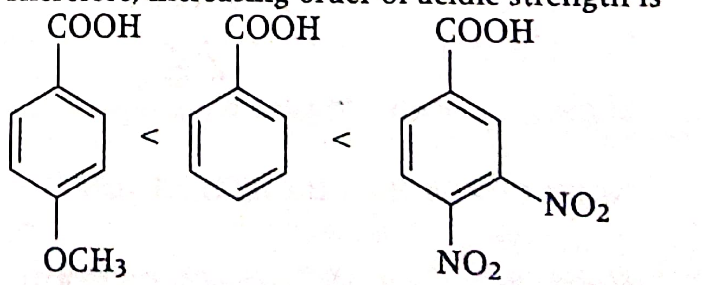
(ii) Toluene to *m*-nitrobenzoic acid



(1)

16. Presence of electron withdrawing group increases the acidity, whereas presence of electron releasing groups decreases the acidity.

Since, electron releasing group decreases the acidic strength, therefore, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Further, since, electron withdrawing groups increase the acidic strength, therefore presence of two electron withdrawing groups in 3, 4-dinitrobenzoic acid makes it a stronger acid.
Therefore, increasing order of acidic strength is



4-methoxy benzoic acid < Benzoic acid < 3,4-dinitrobenzoic acid (1½)

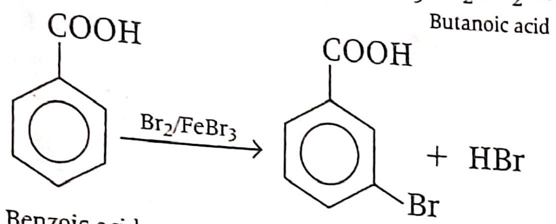
(ii) The $+I$-effect decreases while $-I$-effect increases the acidic strength of carboxylic acids. Therefore,

$(CH_3)_2CHCOOH$ is weaker acid than other two acids containing a chain of three C-atoms because isopropyl group, $(CH_3)_2CH$-exerts greater $+I$-effect. As we know, $-I$-effect decreases with distance, therefore $CH_3CH_2CH(Br)COOH$ is a stronger acid than $CH_3CH(Br)CH_2COOH$. Thus, the overall acidic strength increases in the order.

$$(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$$ **(1½)**

17. (i) $\underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{C_2H_5COOH} \xrightarrow{NH_3/\Delta} C_2H_5CONH_2 \xrightarrow{Br_2/KOH} C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH \xrightarrow{\text{Alkaline } KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$ **(1)**

(ii) $\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[(ii)\ \text{Dil. } H_2SO_4]{(i)\ K_2Cr_2O_7} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$ **(1)**

(iii) 

Benzoic acid   *m*-bromobenzoic acid **(1)**

18.

> (i) Ester produces a carboxylic acid and alcohol on hydrolysis.
> (ii) Ester *A* has 8 carbon atoms, calculate number of *C* atoms in acid and alcohol.
> (iii) Guess the alcohol and acid according to the given reactions.
> (iv) Now guess the ester.
> (v) Write all the related equations.

Compound *C* on dehydration gives but-1-ene ($CH_3CH_2CH{=}CH_2$), so it must be butan-1-ol. When subjected to oxidation *C* gives butanoic acid *B*. Thus, compound *A* is

$$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3.$$

The reactions involved are as follows :

$$\underset{(A)}{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} \xrightarrow{H_2O/H^+} \underset{(B)}{CH_3CH_2CH_2COOH} + \underset{(C)}{CH_3CH_2CH_2CH_2OH}$$ **(1)**

$$\underset{(C)}{CH_3CH_2CH_2CH_2OH} \xrightarrow{CrO_3} \underset{(B)}{CH_3CH_2CH_2COOH}$$ **(1)**

$$\underset{(C)}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2}$$ **(1)**

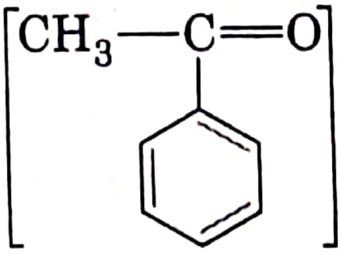
Explanations

1. Given, molecular formula = C_8H_8O,

which gives positive DNP and iodoform test and it neither reduces Tollen's reagent nor decolourise bromine water which means it has one carbonyl group to which one —CH_3 group is directly bonded.

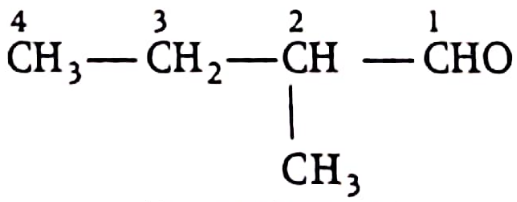
Also, degree of unsaturation = 5;

Therefore, structure of (*A*) is



(1)

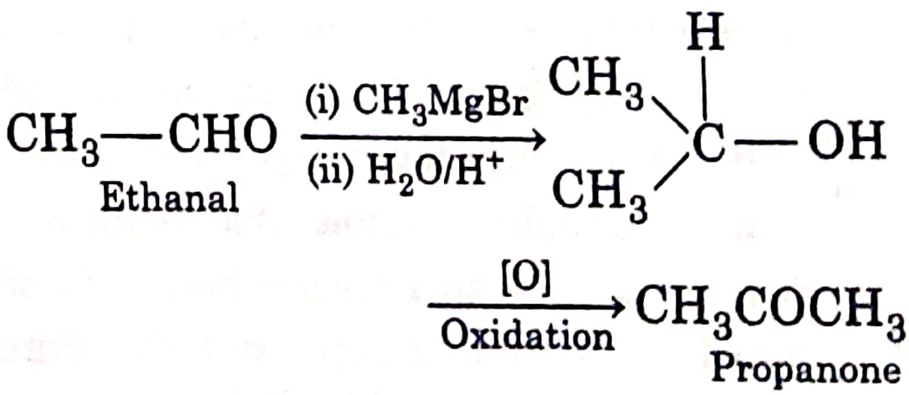
2.



2-methyl butanal

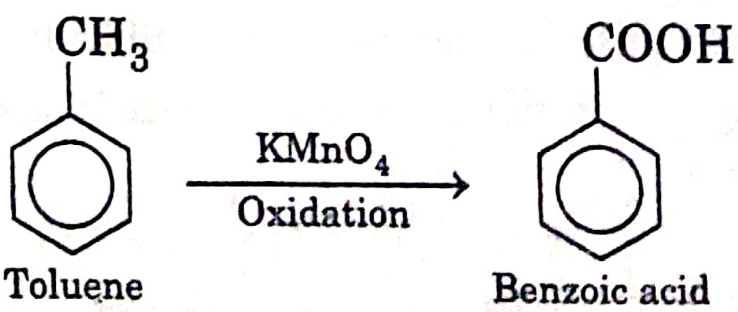
(1)

3. (i) **Ethanal to propanone**



(1)

(ii) **Toluene to benzoic acid**



4. (i) Due to presence of strong —COOH group, aromatic carboxylic acids not undergo for Friedel-Crafts reaction. **(1)**

(ii) As we know, more be the value of K_a, more is the acidic strength of compound and

$$pK_a = -\log[K_a]$$

Therefore, $pK_a \propto \frac{1}{K_a}$ i.e.

More is the value of pK_a, lower be the acidic nature of carboxylic acid and *vice-versa*.

The groups which shows (–) *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 has lower pK_a value than that of benzoic acid. **(1)**

5. (i) $CH_2{=}CH{—}CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_2{=}CH{—}CHO$

Here, PCC is Pyridinium chlorochromate, a 1 : 2 complex of chromium trioxide pyridine ($CrO_3 \cdot 2C_5H_5N$). It only oxidises — OH group and not the double bond. **(1)**

(ii) $CH_3{—}COOH \xrightarrow[-H_2O]{NH_3/Heat} CH_3{—}CONH_2$ **(1)**

6. (i) The increasing order of their reactivity towards nucleophilic addition reaction is

$$\underset{H_3C}{\overset{C_6H_5}{>}}C{=}O < \underset{H_3C}{\overset{H_3C}{>}}C{=}O < \underset{H}{\overset{H_3C}{>}}C{=}O$$

On moving from

$$CH_3CHO \rightarrow CH_3{—}\overset{\overset{O}{\|}}{C}{—}CH_3 \longrightarrow C_6H_5{—}\overset{\overset{O}{\|}}{C}{—}CH_3$$

+*I*-effect, i.e. electron donating effect of alkyl group increases which increases the electron density on C-atom of carbonyl group, and in $C_6H_5COCH_3$ phenyl group get resonance stabilised, makes it stable. Due to this reason it is less reactive towards nucleophilic addition as the attack of nucleophile becomes lower. Further, steric effects of methyl and phenyl groups around carbonyl carbon atom makes the attack of nucleophile on carbonyl carbon difficult. **(1)**

(ii) The correct increasing order of their acidic character is :

$$CH_3{—}\overset{\overset{O}{\|}}{C}{—}OH < \overset{\overset{Cl}{|}}{C}H_2{—}\overset{\overset{O}{\|}}{C}{—}OH < \overset{\overset{F}{|}}{C}H_2{—}\overset{\overset{O}{\|}}{C}{—}OH$$

F-being more electronegative element produces greater–*I*-effect than Cl-atom due to which F-atom withdraw electrons from O—H bond and thereby making O—H bond weaker and hence, facilitates the release of H^+ ion from O—H bond. Hence, FCH_2COOH is stronger acid than $ClCH_2COOH$ and CH_3COOH. In CH_3COOH, due to +*I*-effect of methyl group, electron density in O—H bond increases. As a result, release of H^+ ions from acetic acid becomes more difficult. **(1)**

7. (i) $CH_3{—}\overset{\overset{O}{\|}}{C}{—}CH_3 \xrightarrow{NaBH_4} CH_3{—}\overset{\overset{OH}{|}}{C}H{—}CH_3$ **(1)**

(ii) $C_6H_5{—}CH_2{—}CH_3 \xrightarrow[\Delta]{KMnO_4 - KOH} C_6H_5{—}CO\bar{O}K^+$ **(1)**

8. (i) Cl is an electron withdrawing group, thus, increases the acidity of carboxylic acid by stabilising the conjugate base through delocalisation of the negative charge by inductive effect. While in acetic acid no such group is present which stabilises the conjugate base. That's why, chloroacetic acid because of the presence of electron withdrawing group is more acidic than acetic acid (where no such group is present). **(1)**

(ii) If the medium is too acidic, the ammonia derivatives being basic in nature will form their respective ammonium salts. Due to the absence of lone pair of electrons on the nitrogen atom, these ammonium salts will no longer be nucleophilic and hence, the reaction will not occur. However, if the medium is slightly acidic, the protonation of the carbonyl group will not occur. This in turn will not increase the electron deficiency (or+ve charge) on the carbon atom of the carbonyl group and hence, weak nucleophiles like ammonia derivatives will not be able to react. Hence, the reaction will not occur. Therefore, to carry out such reactions, an optimum value of pH is needed. Hence, pH should be controlled in such reactions. **(1)**

9. (i) **Iodoform test** Given by CH_3CO — or $CH_3CH(OH)$— group containing compounds.
(ii) **Sodium bicarbonate test** Given by — COOH group containing compounds.

(i) **Distinguishing test between ethanal and propanal**

Iodoform test Ethanal because of the presence of CH_3CO— skeleton gives positive iodoform test whereas propanal due to the absence of such a skeleton does not gives such test. **(1)**

$$CH_3CHO + 4NaOH + 3I_2 \longrightarrow CHI_3 + HCO\bar{O}\overset{+}{N}a + 3NaI + 3H_2O$$

Ethanal Or Acetaldehyde; CHI_3 (Yellow ppt.) Iodoform; Sodium formate; Sodium iodide

$$CH_3CH_2CHO + 4NaOH + 3I_2 \longrightarrow \text{No reaction}$$

Propanal

(ii) **Distinguishing test between benzoic acid and phenol** **(1)**

Refer to solution 4 of Topic 2.

10. (i) **Propanal and propanone**

These compounds can be distinguished by using Tollen's test. Propanal being an aldehyde reduces Tollen's reagent to shining silver mirror and propanone being a ketone does not.

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

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[\text{reagent}]{\text{Tollen's}} \text{No silver mirror}$$

(1)

(ii) **Benzaldehyde and benzoic acid**

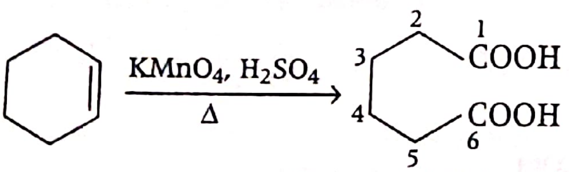
Both can be distinguished by using sodium bicarbonate ($NaHCO_3$) test. Benzoic acid being an acid reacts with $NaHCO_3$ solution to produce brisk effervescence due to evolution of CO_2 gas while benzaldehyde does not.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow C_6H_5CO\bar{O}\overset{+}{N}a + CO_2\uparrow + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + NaHCO_3 \longrightarrow \text{No effervescence}$$

(due to evolution of CO_2 gas) **(1)**

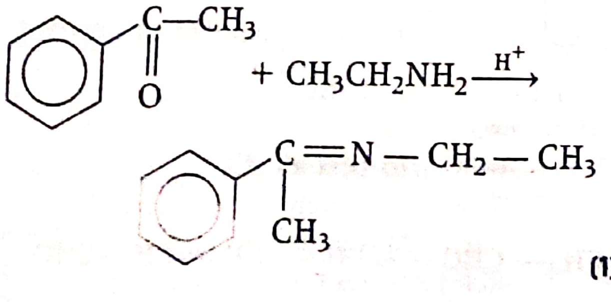
11. (i)



Hexane-1,6-dioic acid

(1)

(ii)



(1)

12. (i) Ethanol reacts with I_2 / NaOH to give yellow ppt. of iodoform but propanol does not react with I_2 / NaOH.

$$C_2H_5OH \xrightarrow{[O]} CH_3CHO$$

$$\underset{\text{Ethanol}}{CH_3CHO} + 3I_2 + 4NaOH \longrightarrow HCO\bar{O}\overset{+}{N}a + \underset{\text{Iodoform}}{CHI_3\downarrow} + 3NaI + 3H_2O$$

$$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} \xrightarrow{I_2 + NaOH} \text{No reaction}$$

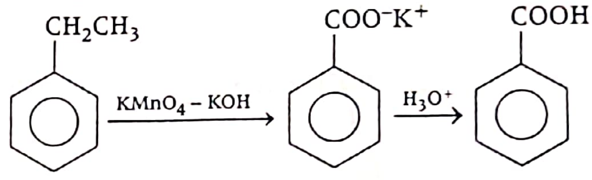
(1)

(ii) Benzoic acid produces brisk effervescence with $NaHCO_3$ solution while ethyl benzoate does not.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow C_6H_5CO\bar{O}\overset{+}{N}a + H_2O + CO_2\uparrow$$

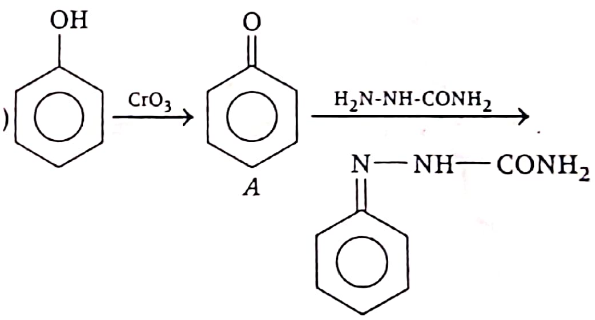
$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + NaHCO_3 \longrightarrow \text{No reaction}$$ **(1)**

13. (i)



A B **(1½)**

(ii)



B **(1½)**

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

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CHO,\ CH_3CH_2CH_2CHO,\ CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

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

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} \xrightarrow{\Delta} RCOO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3\uparrow$$

$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CHO \text{ and } CH_3CH_2CH_2CHO$$

(b) Isomer (B) does not give Tollen's test, but gives positive Iodoform test, thus it must be a ketone with $CH_3\overset{\overset{\displaystyle O}{||}}{C}-$ group.

$$RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3 \quad [X = Cl, Br, I]$$ (1)

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

$$\underset{(C)}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CHO} + 4[H] \xrightarrow{Zn-Hg/conc.\ HCl} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 + H_2O$$

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

$$\underset{(B)}{CH_3CH_2COCH_3} + 4[H] \xrightarrow{Zn-Hg/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3} + H_2O$$

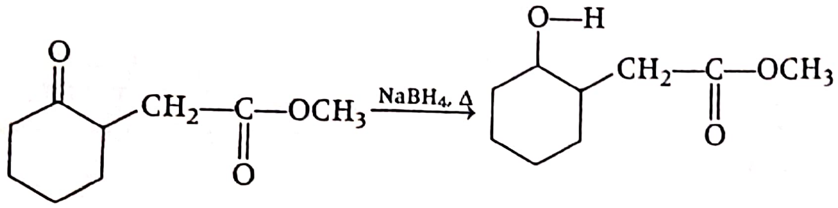
So, the structures of (A), (B), (C) and (D) are :

$$\underset{(A)}{CH_3CH_2CH_2CHO}, \quad \underset{(B)}{CH_3CH_2COCH_3}, \quad \underset{(C)}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H-CHO}, \quad \underset{(D)}{CH_3CH_2CH_2CH_3}$$ (1)

(ii) The isomer (B) is least reactive towards addition of HCN. Since, aldehydes are more reactive towards nucleophilic addition reactions than ketones due to inductive and steric effects. (1)

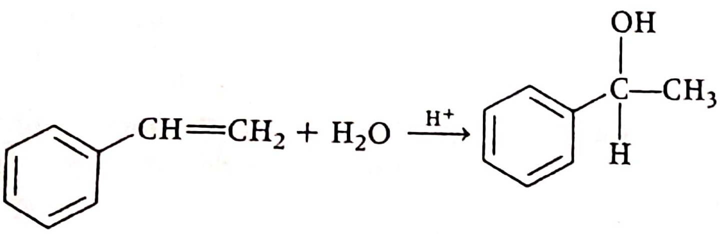
15.

(i)



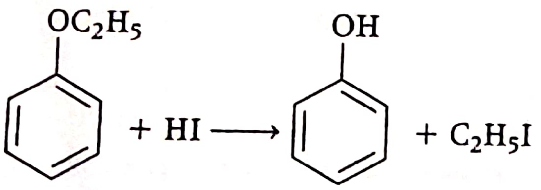
(1)

(ii)



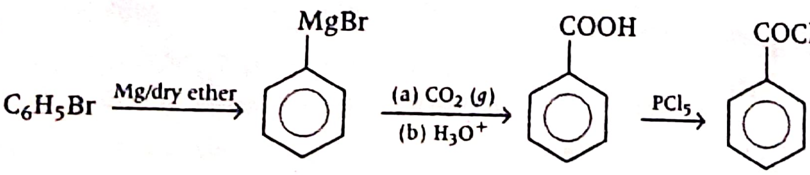
(1)

(iii)



(1)

16. (i)



(A) Phenyl magnesium bromide

(B) Benzoic acid

(C) Benzoyl chloride

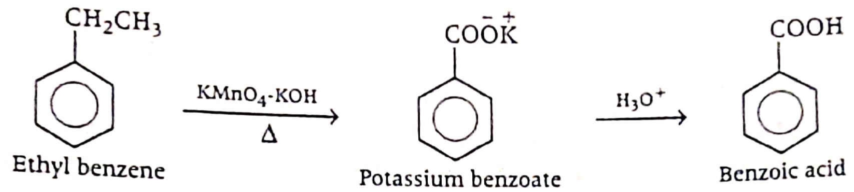
(1½)

(ii) $$CH_3CN \xrightarrow[(ii)\ H_3O^+]{(i)\ SnCl_2/HCl} \underset{\text{Acetaldehyde}}{\underset{(A)}{CH_3CHO}} \xrightarrow{\text{Dil. NaOH}} \underset{\text{3-hydroxy butanal}}{\underset{(B)}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CHO}} \xrightarrow{\Delta} \underset{\text{But-2-enal}}{\underset{(C)}{CH_3-CH=CH-CHO}}$$

(1½)

17. (i) **Benzoic acid to benzaldehyde** Refer to solution 12 of topic 2. (1)

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



(1)

(iii) **Propanone to propene**

$$\underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + NaBH_4 \longrightarrow \underset{\text{Propan-2-ol}}{CH_3\underset{\underset{OH}{|}}{C}HCH_3} \xrightarrow{\text{conc}\cdot H_2SO_4} \underset{\text{Propene}}{CH_2=CHCH_3}$$

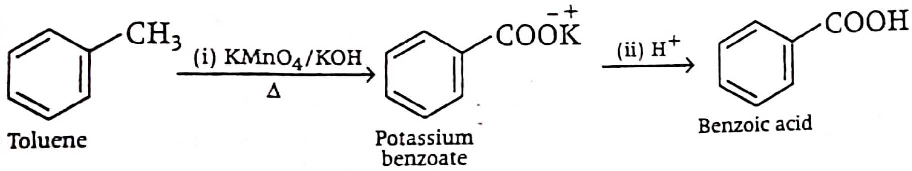
(1)

18. (i)

$$\underset{\text{Propanone}}{(H_3C)_2C=O} \xrightarrow{H_2N-NH_2} \underset{\text{2-propanone hydrazone}}{(H_3C)_2C=N-NH_2} + H_2O$$

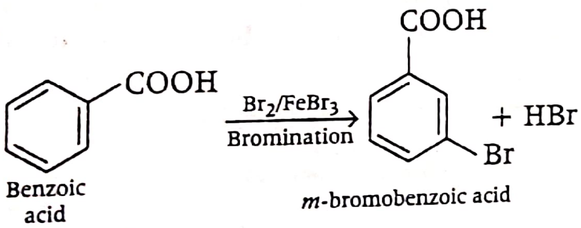
(1)

(ii)



(1)

(iii)



(1)

19. (i)

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{(i)\ NH_2-NH_2} (H_3C)_2C=N-NH_2 \xrightarrow{(ii)\ \text{KOH/ethylene glycol, }\Delta} \underset{\text{Propane}}{(H_3C)_2CH_2}$$

(1)

This is an example of **Wolff-Kishner reduction.**

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} C_6H_5CO\bar{O}Na^+ + \underset{\text{Iodoform}}{CHI_3\downarrow}$ (1)

This is an example of **haloform reaction.**

(iii) $CH_3CO\bar{O}\overset{+}{N}a \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_3-H} + Na_2CO_3$ (1)

This is an example of **decarboxylation.**

20. (i) **Benzoic acid to benzaldehyde** (1)

Refer to solution 12 of Topic 2.

(ii) **Ethyne to ethanal**

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[\text{Dil. }H_2SO_4/HgSO_4]{H_2O} \underset{\text{(Unstable)}}{\overset{\overset{OH}{|}}{C}H=CH_2} \xrightarrow{\text{Tautomerisation}} \underset{\text{Ethanal}}{H-\overset{\overset{O}{\|}}{C}-CH_3}$$

(1)

Acetic acid to methane

$$CH_3COOH \xrightarrow[-H_2O]{NaOH} CH_3CO\bar{O}\overset{+}{N}a \xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$$

Acetic acid — Sodium acetate — Methane (1)

21. Since, the molecular formula of D is CH_2O_2, thus, D is HCOOH (formic acid). D is obtained by the acidification of C, so, C is sodium formate ($HCO\bar{O}\overset{+}{N}a$).

Thus, A must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base) and B must be methyl alcohol as on dehydrogenation with Cu, B gives back A. The reaction involved are as follows:

$$\underset{\text{Formaldehyde}}{\underset{A}{2HCHO}} \xrightarrow[\text{(Cannizzaro reaction)}]{NaOH} \underset{\text{Methanol}}{\underset{B}{CH_3OH}} + \underset{\text{Sodium formate}}{\underset{C}{HCO\bar{O}\overset{+}{N}a}}$$

$B \xrightarrow{\text{Cu (dehydrogenation)}}$ HCHO (Formaldehyde, A)

$C \xrightarrow{\text{Acidification}}$ HCOOH (Formic acid, D) (1)

Thus, A = Formaldehyde (HCHO) (1/2)

B = Methanol (CH_3OH) (1/2)

C = Sodium formate ($HCO\bar{O}\overset{+}{N}a$) (1/2)

D = Formic acid (HCOOH) (1/2)

22. Compound 'A' has characteristic odour that means it can be benzaldehyde, which undergo cannizzaro reaction with NaOH to give alcohol and sodium salt of acid. Compound 'B' can be alcohol as it contain only one oxygen atom which on oxidation gives back compound 'A'. Compound 'C' can be sodium salt of benzoic acid which on heating with sodalime yields aromatic compound 'D', which may be benzene. Reaction involved are given below

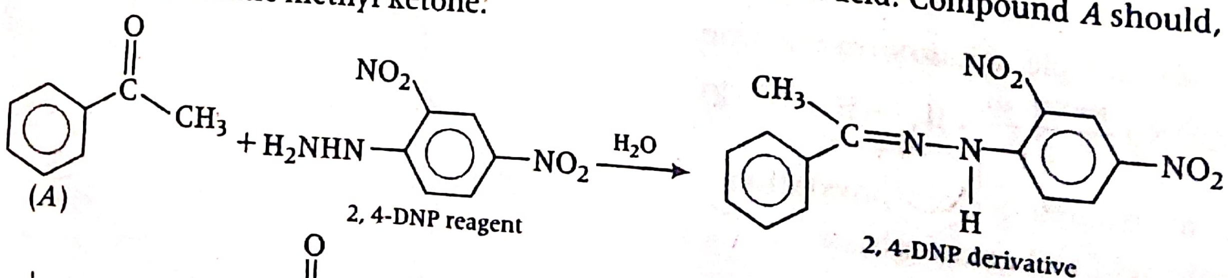
$$\underset{(A)}{C_6H_5CHO} \xrightarrow{NaOH} \underset{\underset{(C_7H_8O)}{(B)}}{C_6H_5CH_2OH} + \underset{\text{(Sodium salt of benzoic acid)}}{\underset{(C)}{C_6H_5CO\bar{O}\overset{+}{N}a}} \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{(Benzene aromatic)}}{\underset{(D)}{C_6H_6 + Na_2CO_3}}$$

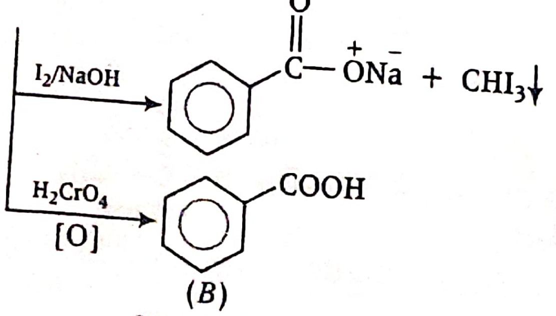
$(B) \xrightarrow{CrO_3} (A)$ (3)

23. Organic compound (A) react with 2, 4-DNP reagent and forms, 2, 4-DNP derivative, therefore it is an aldehyde or a ketone. As A does not reduce Tollen's or fehling reagent. So, it must be a ketone. It also give iodoform test.

Hence, it has $CH_3-\overset{O}{\overset{\|}{C}}-$ group. A form carboxylic acid B on oxidation.

From molecular formula $C_7H_6O_2$ we can say that it should be benzoic acid. Compound A should, therefore, be a monosubstituted aromatic methyl ketone.





(B)

Benzoic acid

24. Given organic compound $C_5H_{10}O$ does not reduce Tollen's reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it is a carbonyl compound. It is also given that it gives positive iodoform test so it should contain $-\overset{O}{\overset{\|}{C}}-CH_3$ group. So It must be a ketone. The possible structure may be

$$\underset{\text{I}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2CH_3} \qquad \underset{\text{II}}{CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3}$$

Further given compound on oxidation gives ethanoic and propanoic acid and which is possible when the compound is I.

$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2\,CH_2\,CH_3 \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(3)

25. Monobasic carboxylic acid = RCOOH. Given that, molar mass of RCOOH = 60 $gmol^{-1}$

i.e. $x + 12 + 16 + 16 + 1 = 60;\ x = 15$

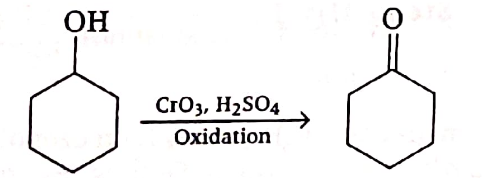
Thus, $R = -CH_3$ (molar mass 15) and the acid is CH_3COOH. Since, the acid is obtained by the oxidation of aldehyde, so B is an aldehyde, i.e. CH_3CHO and A is CH_3CH_2OH as it gives B on oxidation by PCC. C is an alkene as it is formed by subsequent heating of aldehyde (B) with aqueous alkali. Thus, the involved reactions are as follows:

$$\underset{A}{CH_3-CH_2-OH} \xrightarrow{PCC} \underset{B}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{KMnO_4} \underset{\text{(Molecular weight, 60 g mol}^{-1}\text{)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

$$2\underset{B}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[\text{Aldol condensation}]{OH^-} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{\text{Heat}} \underset{C}{CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H}$$

(3)

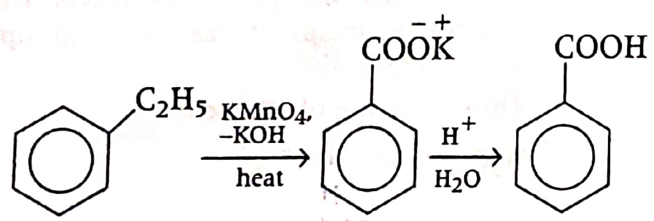
26. (i)



Cyclohexanol Cyclohexan-1-one

(1)

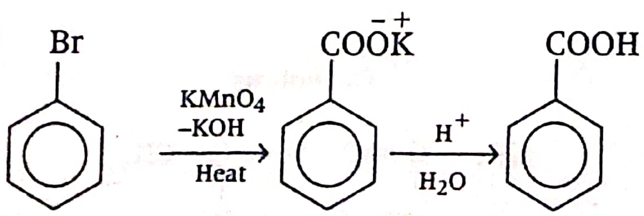
(ii)



Ethyl benzene Potassium benzoate Benzoic acid

(1)

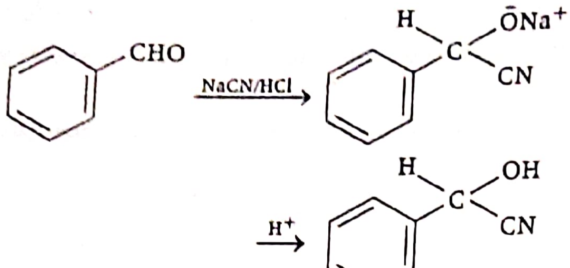
(iii)



Bromobenzene Potassium benzoate Benzoic acid

(1)

27.

(i) 

(1)

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl$

$$\longrightarrow C_6H_5CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2 \quad (1)$$

(iii) $CH_3-\underset{|}{\overset{CH_3}{CH}}-COOH \xrightarrow[\text{(i) } H_2O]{\text{(i) } Br_2/RedP_4}$

$$CH_3-\overset{CH_3}{\underset{Br}{C}}-COOH$$

(1)

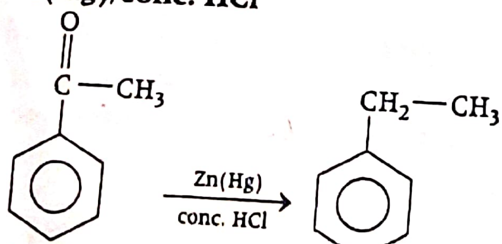
28. (i) **Propanone is treated with dilute $Ba(OH)_2$**

$$2CH_3COCH_3 \underset{\text{Aldol reaction}}{\overset{\text{Dil. } Ba(OH)_2}{\rightleftharpoons}} CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2-CO-CH_3$$

$$\xrightarrow{\Delta} CH_3-\overset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \quad (1)$$

4- methyl pent -3- en-2- one
(Aldol condensation product)

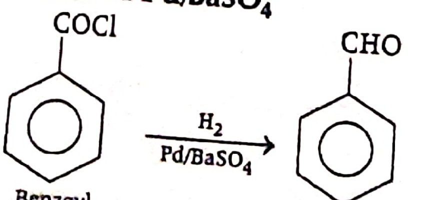
(ii) **Acetophenone is treated with Zn(Hg)/conc. HCl**



Acetophenone   Ethyl benzene

(1)

(iii) **Benzoyl chloride when hydrogenated in presence of $Pd/BaSO_4$**



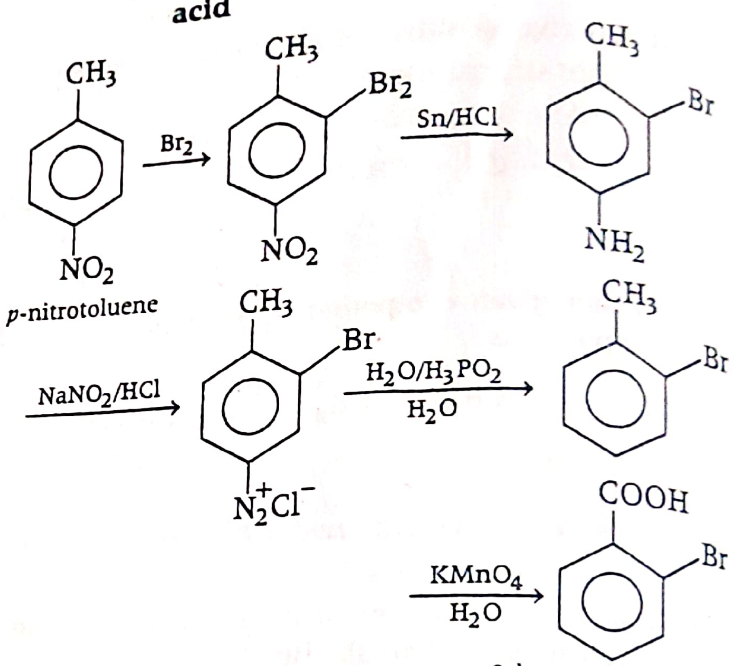
Benzoyl chloride   Benzaldehyde

(1)

This reaction is known as **Rosenmund reduction.**

29. (a)

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



p-nitrotoluene

2-bromobenzoic acid

(1½)

(ii) **Propanoic acid to acetic acid**

Step (I) $CH_3CH_2-COOH + NaOH$

$$\longrightarrow CH_3CH_2COONa + H_2O$$

Step (II) $CH_3-CH_2-COONa$

$$\xrightarrow{NaOH + CaO} C_2H_6 + Na_2CO_3$$

Step (III) $C_2H_6 \xrightarrow[\text{(Oxidation)}]{K_2Cr_2O_7} CH_3COOH$ (Acetic acid)

(1½)

(b) Given alkene $= C_5H_{10}$, which on ozonolysis gives (B) which gives positive Fehling test, means last carbon is bonded with double bond with next C-atom. Also, compound (B) reacts with iodine and NaOH, means it has $-CH_3$ group bonded with —CO-group.

Thus structure of alkene is

$$H_3C-\underset{CH_3}{C}=\underset{H}{C}-CH_3$$

(C_5H_{10})
(A)

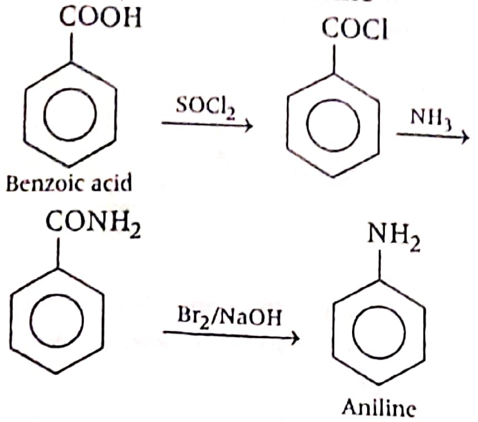
$\downarrow$ Ozonolysis

$$CH_3-\underset{CH_3}{C}=O + O=\underset{H}{C}-CH_3$$

(C) (Acetone)   (B) (Acetaldehyde)

(2)

30. (a) (i) Benzoic acid to aniline



(1)

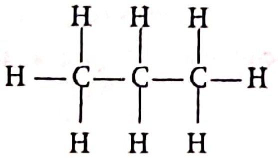
(ii) **Bromoethane to ethanol**

$$\underset{\text{Bromoethane}}{C_2H_5-Br} \xrightarrow{\text{KOH (aq)}} \underset{\text{Ethanol}}{C_2H_5OH}$$ (1)

(b) Structure of major product

(i) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[\text{(b) KOH, glycol or heat}]{\text{(a) } H_2N-NH_2}$ $\underset{\text{Propane}}{CH_3-CH_2-CH_3}$

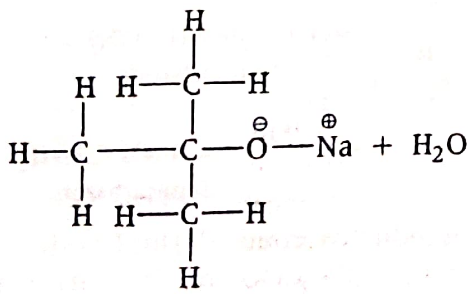
Or,



(1)

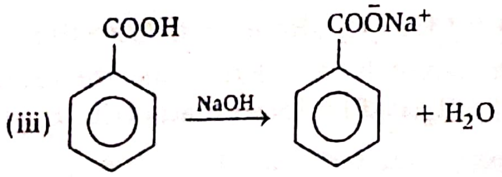
(ii) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO \xrightarrow{\text{Conc. NaOH}}$ $(CH_3)_3CO\bar{O}\overset{+}{Na} + H_2O$

Or

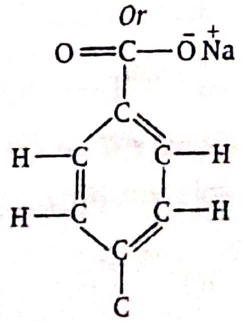


(1)

(iii)



Or



(1)

31. (i) (a) HCHO is more reactive than CH_3—CHO, towards addition of HCN because in HCHO, we have no alkyl group, directly bond to carbonyl $\left(\rangle C=O\right)$ group which offers (+)*I*-effect and decreases the reactivity of carbonyl group, whereas, CH_3—CHO has one alkyl group (—CH_3) directly bonded with carbonyl group. (1)

(b) Strength of acidic nature of a compound is measured by inductive effect (*I*) of the atom or group of atoms present along with —COOH group. (–)*I*-effect increases the acidic nature whereas, (+)*I*-effect decreases the acidic nature.

Also, $pK_a = -\log[K_a]$

i.e., $K_a \propto$ acidic nature of a carboxylic acid.

and $pK_a \propto \frac{1}{K_a}$ i.e.

Higher be the pK_a value of a carboxylic acid, lower is its acidic strength and *vice-versa*. (1)

(c) The carbon atom next to carbonyl group is called α-carbon atom and hydrogens attached to α-carbon atom are called α-hydrogens. Due to strong electron withdrawing effect of carbonyl group. the α-carbon atom becomes electron deficient, which in turn, withdraws electrons from C_α —H bond. As a result, the electron density in C_α—H bond decreases and hence, α-H atom becomes weakly held which can be easily abstracted by strong bases forming enolate ion which are stabilised by resonance.

Thus, strong electron withdrawing effect of carbonyl group and resonance stabilisation of the conjugate base are responsible for the acidity of α-hydrogen atoms of aldehydes and ketones.

(ii) (a) **Ethanal and propanal** Ethanal gives iodoform test whereas propanal (CH_3CH_2CHO) does not.

$$\underset{\text{Ethanal}}{CH_3CHO} + 3NaOI \xrightarrow[\text{Heat}]{NaOH,\ I_2} \underset{\substack{\text{Iodoform} \\ \text{(Yellow ppt.)}}}{CHI_3\downarrow}$$

$+ HCOONa + 2NaOH$ (1)

(b) **Pentan-2-one and pentan-3-one** Pentan-2-one gives iodoform test whereas pentan-3-one ($C_2H_5COC_2H_5$) does not.

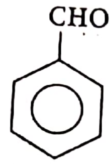
$$CH_3—CO—CH_2—CH_2—CH_3 + 3NaOI$$
Pentan-2-one

$$\xrightarrow[\text{Heat}]{NaOH,\ I_2} \underset{\text{Yellow ppt.}}{CHI_3 \downarrow} + CH_3CH_2CH_2COONa + 2NaOH$$ **(1)**

32. (i) (a) $CH_3—CH_2—COOH \xrightarrow{Cl_2,\ \text{Red phosphorus}} \underset{\text{(Product)}}{CH_3—\underset{\underset{Cl}{|}}{C}H—COOH}$ **(1)**

(b) $C_6H_5COCl \xrightarrow{H_2,\ Pd—BaSO_4} C_6H_5CHO$

or



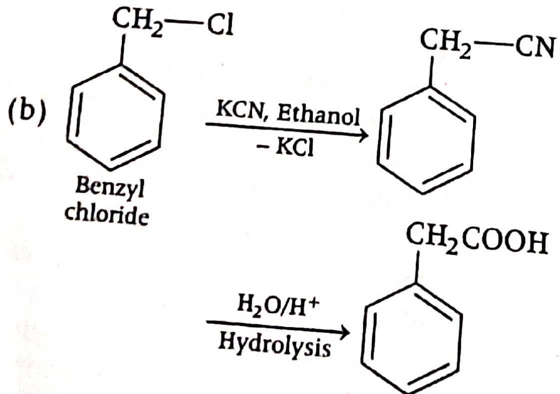
(Product) **(1)**

(c) $2HCHO \xrightarrow{\text{Conc. KOH}} \underset{\text{(Products)}}{H\cdot CO\bar{O}\overset{+}{K} + CH_3—OH}$
(Cannizzaro -reaction) **(1)**

(ii) (a) **Propanone to propene**

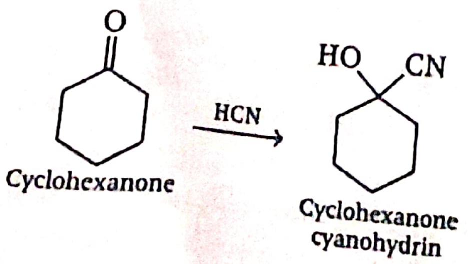
$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[2[H]]{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3\underset{\underset{OH}{|}}{C}HCH_3} \xrightarrow[\text{Heat}]{H_2SO_4\ \text{(Conc.)}} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$ **(1)**

(b)



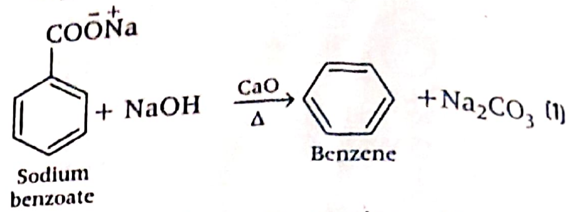
(Phenyl ethanoic acid) **(1)**

33. (i) (a) Cyclohexanone when reacts with hydrogen cyanide (HCN) it form cyclohexanone cyanohydrin



(1)

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



(1)

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

$$\underset{\text{But-2-en-1-nitrile}}{CH_3CH = CH — CN} \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} \underset{\text{But-2-en-1-ol}}{CH_3CH{=} CH— CHO}$$ **(1)**

(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.

$$\underset{\text{Butanal}}{CH_3CH_2CH_2CHO} + \underset{\text{Tollen's reagent}}{2\ [Ag(NH_3)_2]^+} + 3\bar{O}H \xrightarrow{\Delta}$$
$$CH_3CH_2CH_2COO^- + \underset{\text{Silver mirror}}{2Ag \downarrow} + 4NH_3 + 2\ H_2O$$

$$\underset{\text{Butan-2-one}}{CH_3CH_2\overset{\overset{O}{||}}{C}CH_3} \xrightarrow[\text{reagent}]{\text{Tollen's}} \text{No silver mirror}$$ **(1)**

(b) Refer to solution 4 of Topic 2. **(1)**

34. (i) Refer to solution 28 (ii) Topic 1.

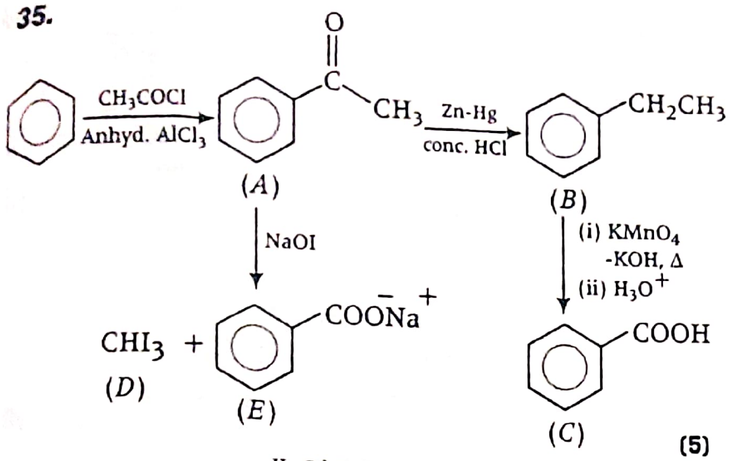
(ii) $$\underset{\text{Ethanol}}{\overset{CH_3}{\underset{H}{>}}C{=}O} + \underset{\text{Semicarbazide}}{H_2N\cdot NH\cdot CONH_2} \longrightarrow \underset{\text{Semicarbazone}}{\overset{CH_3}{\underset{H}{>}}C{=}N\cdot NH\cdot CONH_2}$$ **(1)**

(iii) As inductive effect $(-I)$ for F is stronger than that of Cl, $F.CH_2COO^-$ ion is more stable than of $Cl\cdot CH_2COO^-$ ion. Hence, $F.CH_2COOH$ is stronger acid than of $Cl.CH_2COOH$. Thus, the value of pK_a for $F.CH_2COOH$ is lower than of $Cl.CH_2COOH$.
$\left(\because pK_a \propto \dfrac{1}{\text{acid strength}}\right)$ **(1)**

(iv) $$CH_3—CH = CH —CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3—CH = CH —CH_2CHO$$

(v) Refer to solution 10(i). **(1)**

35.

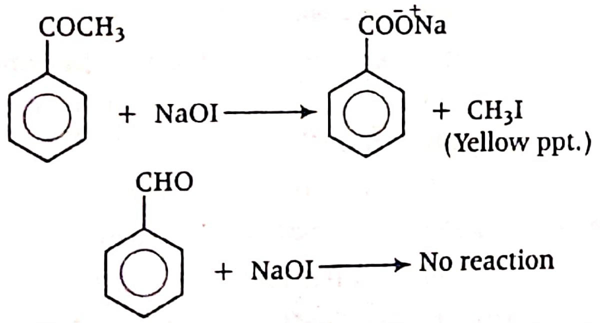


(5)

36. (i) (a) $CH_3COCl \xrightarrow{H_2, Pd\text{-}BaSO_4} \underset{(A)}{CH_3CHO} \xrightarrow{H_2N\text{-}OH} \underset{(B)}{(CH_3)(H)C=NOH}$ (1)

(b) $CH_3MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} \underset{(A)}{CH_3COOH} \xrightarrow{PCl_5} \underset{(B)}{CH_3-\overset{\overset{O}{||}}{C}-Cl}$ (1)

(ii) (a) $C_6H_5COCH_3$ give positive iodoform test whereas C_6H_5CHO does not.



(1)

(b) HCOOH decolourises pink colour of $KMnO_4$ (acidifier) whereas CH_3COOH does not show this test.

$HCOOH + 2KMnO_4 + 3H_2SO_4 \longrightarrow$
$K_2SO_4 + 5CO_2 + 8H_2O + MnSO_4$

$CH_3COOH \xrightarrow{KMnO_4/H^+}$ no discharge of pink colour of $KMnO_4$ solution. (1)

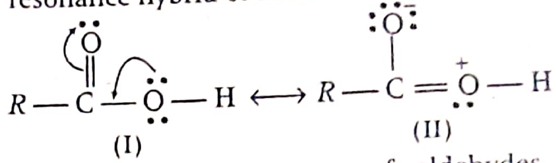
(iii) As carboxylic acid have strongest hydrogen bonding therefore, they have highest boiling points. Next, stronger hydrogen bonding is shown by alcohol. Hence, order of boiling point is as follows.

$CH_3CHO < CH_3CH_2OH < CH_3COOH$. (1)

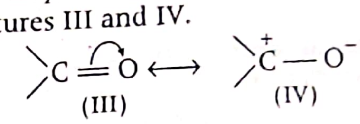
37. (i) Refer to solution 22 of Topic 1. (1)

(ii) Refer to solution 6(i). (1)

(iii) The carboxylic acids may be regarded as resonance hybrid of structures I and II as.



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



Due to contribution of structure IV, the carbonyl carbon in aldehydes and ketones is electrophilic. However, due to contribution of structure II of carboxylic acid, the electrophilic character of carboxyl carbon is reduced, i.e. carbonyl carbon of carboxyl group is less electrophilic than carbonyl carbon in aldehydes and ketones and hence, nucleophilic addition reactions (such as formation of oximes, hydrazones, phenyl hydrazones, semicarbazones and 2, 4-dinitrophenyl hydrazones) does not take place with carboxylic acids. (1)

(iv) $CH_3 \cdot CH_2 \cdot CH = CH-CH_2 \cdot CN \xrightarrow[(ii)\ H_2O]{(i)(i\text{-but})_2AlH}$
$CH_3 \cdot CH_2 \cdot CH = CH \cdot CH_2.CHO$ (1)

(v) Isomer B on heating with NaOH and I_2 form yellow ppt. of iodoform. Hence, contain $-\overset{\overset{}{}}{\underset{\underset{O}{||}}{C}}-CH_3$ group having three carbons in total.

Hence, isomer B is $CH_3-\underset{\underset{O}{||}}{C}-CH_3$

whereas isomer A is $CH_3 \cdot CH_2 \cdot CHO$ (a functional isomer of B).

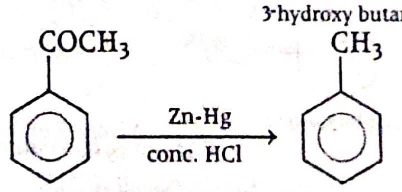
$CH_3-\underset{\underset{O}{||}}{C}-CH_3 + NaOH + I_2 \longrightarrow$
$CH_3CO\overset{-}{O}\overset{+}{N}a + \underset{\text{(Yellow ppt.)}}{CHI_3}$

$CH_3 \cdot CH_2 \cdot CHO + NaOH + I_2 \longrightarrow$ No reaction.

(1)

38. (i) (a) $\underset{\text{Ethanol}}{2CH_3-CHO} \xrightarrow[\text{Cross aldol condensation}]{\text{Dil. NaOH}} \underset{\text{3-hydroxy butanal}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO}$ (1)

(b)



(Clemmensen reduction) (1)

(ii) (a) Refer to solution 39 (ii) (a) Topic 1. (1)

(b) Refer to solution 39 (ii) (b) Topic 1. **(1)**

(c) Refer to solution 12 (ii). **(1)**

39. (i) (a) Refer to solution 42 (ii) (a) Topic 1. **(1)**

(b) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$ **(1)**

(c) $CH_3COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2,\text{ Red P}} \underset{\underset{\text{Cl}}{|}}{CH_2}—COOH$ **(1)**

α-chlorocarboxylic acid

(ii) Phenol and acetic acid

$NaHCO_3$ test When both are reacted with $NaHCO_3$, acetic acid gives brisk effervescence due to liberation of CO_2 gas. But phenol does not give any reaction with $NaHCO_3$.

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3CO\overset{-}{O}\overset{+}{Na} + CO_2 \uparrow + H_2O$$

$$C_6H_5OH + NaHCO_3 \longrightarrow \text{No evolution of } CO_2 \text{ gas.}$$

(1)

(iii) Acetaldehyde and acetone

Tollen's reagent test When both are reacted with Tollen's reagent, aldehyde gives silver mirror while acetone does not. Reaction involved are as follows.

$$CH_3CHO + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]OH} \longrightarrow CH_3CO\overset{-}{O}\overset{+}{N}H_4 + 2Ag \downarrow + H_2O + 3NH_3$$

$$CH_3—\overset{\overset{\text{O}}{||}}{C}—CH_3 + 2\ \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2OH]} \longrightarrow \text{No reaction.}$$

(1)

40. (i) (a) **Aldol** It is a hydroxy ketone or aldehyde. It is formed as a product during aldol condensation reaction.

e.g. $2CH_3—CHO \xrightarrow{\text{Dil. NaOH}} CH_3—\underset{\underset{OH}{|}}{CH}—CH_2—CHO$ **(1)**

3-hydroxybutanal (Aldol)

(b) **Semicarbazone** It is a derivative of imines formed by a condensation reaction between a ketone or aldehyde and semicarbazide.

e.g.

$$\underset{\text{Acetone}}{\overset{CH_3}{\underset{H}{>}}C{=}O} + \underset{\text{Semicarbazide}}{H_2N—NH—\overset{\overset{O}{||}}{C}—NH_2} \xrightarrow{-H_2O} \underset{\text{Semicarbazone}}{CH_3—CH{=}N—NH—\overset{\overset{O}{||}}{C}—NH_2}$$

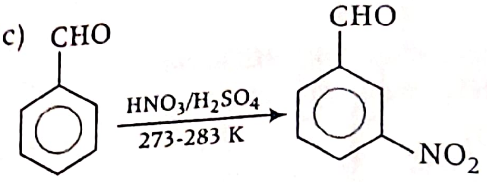
(1)

(ii) (a) $CH_3—\overset{\underset{||}{}}{\underset{\underset{O}{||}}{C}}—Cl + H_2 \xrightarrow[\text{Rosenmund reaction}]{Pd,\ BaSO_4} \underset{\text{Ethanal}}{CH_3CHO} + HCl$

Acetyl chloride **(1)**

(b) Refer to solution 33 (i) (c). **(1)**

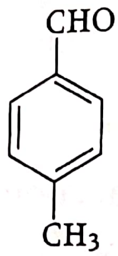
(c)



(1)

41. (i) **Structures of**

(a) *p*-methylbenzaldehyde



(1)

(b) **4-methylpent-3-en-2-one**

$$\underset{1}{CH_3}—\underset{2}{\overset{\overset{O}{||}}{C}}—\underset{3}{CH_2}{=}\underset{4}{\overset{\overset{CH_3}{|}}{C}}—\underset{5}{CH_3}$$

(1)

(ii) (a) **Benzoic acid and ethyl benzoate**

Refer of solution 12 (ii).

(b) **Benzaldehyde and acetophenone** **(1)**

Refer to solution 39 (ii) b of Topic 1. **(1)**

(c) **Phenol and benzoic acid**

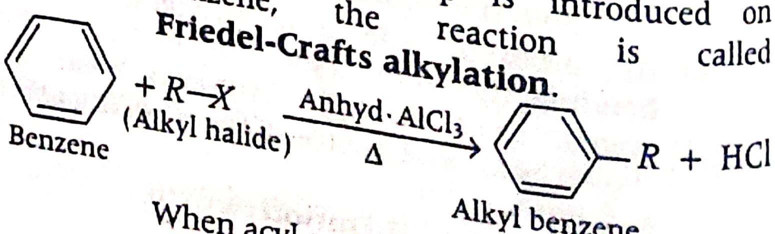
Refer to solution 4 of Topic 2. **(1)**

42. (i) (a) **Decarboxylation reaction**

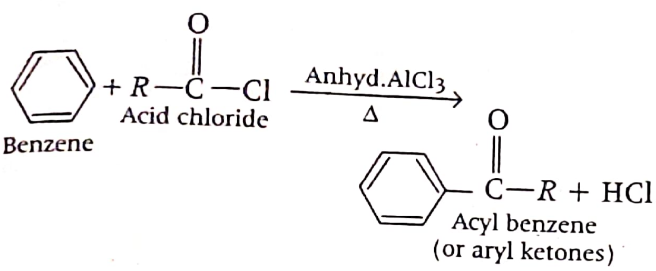
Refer to solution 5 of Topic 2. **(1)**

(b) **Friedel-Crafts reaction** When benzene or substituted benzene is treated with alkyl halide or acid chloride in the presence of anhydrous aluminium chloride, then either an alkyl substituted benzene or acyl benzene is formed. This reaction is known as **Friedel-Crafts reaction.**

When alkyl group is introduced on benzene, the reaction is called **Friedel-Crafts alkylation.**



When acyl group is introduced on benzene, the reaction is called **Friedel- Crafts acylation.**

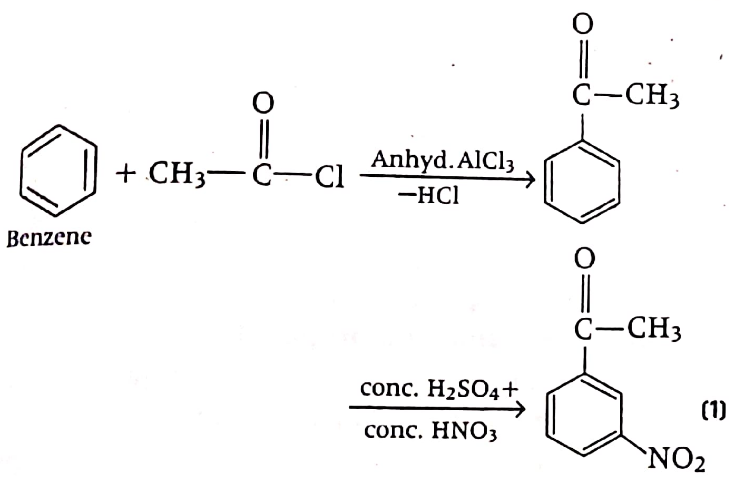


(1)

(ii) (a) **Benzoic acid to benzaldehyde**

Refer to solution 12 of Topic 2. (1)

(b) **Benzene to *m*-nitroacetophenone**



m-nitroacetophenone

(c) **Ethanol to 3-hydroxybutanal**

$$2CH_3—CH_2OH \xrightarrow{PCC} 2CH_3—CHO$$

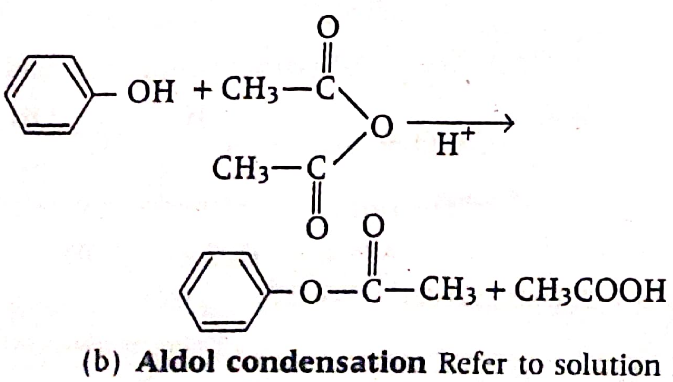
Ethanol, Ethanal

$$\xrightarrow{\text{Dil. NaOH (Aldol-condensation)}} CH_3—\underset{\underset{OH}{|}}{CH}—CH_2—CHO$$

3-hydroxybutanal (1)

43. (i) (a) **Acetylation**

The introduction of acetyl group ($—COCH_3$) into a chemical compound like phenols, alcohols is called **acetylation**.



(1)

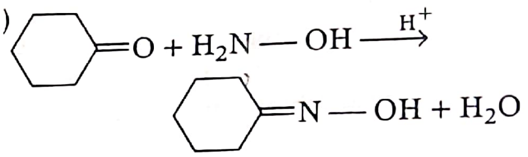
(b) **Aldol condensation** Refer to solution 39 (i) (a) of Topic 1. (1)

(ii) (a) $CH_3—\underset{\underset{O}{||}}{C}—CH_3 \xrightarrow{LiAlH_4} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$ (1)

(b) Refer to solution 40 (ii) (c). (1)

(c) $CH_3COOH \xrightarrow{PCl_5} CH_3\overset{\overset{O}{||}}{C}—Cl + POCl_3 + HCl$ (1)

44. (i) (a)



(1)

(b) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5CO\overset{-}{O}\overset{+}{N}a$

Benzyl alcohol, Sodium benzoate (1)

(c) $CH_3COOH \xrightarrow{Cl_2/P} ClCH_2COOH$

Acetic acid, Monochloroacetic acid (1)

(ii) (a) **Benzaldehyde and benzoic acid**

Refer to solution 10 (ii). (1)

(b) **Propanal and propanone**

Refer to solution 10 (i). (1)

45. (i) (a) This is because of the fact that due to smaller $+I$-effect of one alkyl group ($—CH_3$) in CH_3CHO as compared to larger $+I$-effect of two alkyl $(—CH_3)_2$ groups in CH_3COCH_3, the magnitude of positive charge on the carbonyl carbon is more in CH_3CHO than in CH_3COCH_3. Also the steric effect is more pronounced in case of CH_3COCH_3. (1)

(b) Refer to solution 14 of Topic 2. (1)

(ii) (a) **Wolff-Kishner reduction** Refer to solution 22 of Topic 1. (1)

(b) **Aldol condensation** (1)

Refer to solution 39 (i) (a) of Topic 1.

(c) **Cannizzaro reaction**

Refer to solution 28 (ii) of Topic 1. (1)

46. (i) (a) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$ (1)

Acetaldehyde cyanohydrin

(b) $\overset{H_3C}{\underset{H}{>}}C{=}O + NH_2OH \longrightarrow \overset{H_3C}{\underset{H}{>}}C{=}NOH + H_2O$

Ethanal oxime (1)

(c) $CH_3CHO + CH_3CHO \xrightarrow[\text{Aldol condensation}]{\text{Dil. NaOH}}$

$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO \quad (1)$$

(ii) (a) Refer to solution 4 of Topic 2. (1)

(b) Refer to solution 10 (i). (1)

47. (i) (a) $Cl-CH_2COOH$ is a stronger acid than CH_3COOH. It is because $-Cl$ group exhibits $-I$-effect which makes the carboxylate ion more stable. Higher the stability of carboxylate ion, easier is the removal of proton from the carboxylic acid and stronger is the acid. In CH_3COOH, $-CH_3$ group has $+I$-effect which destabilised it. Hence, CH_3COOH is a weaker acid. (1)

(b) Refer to solution 37 (iii). (1)

(ii) (a) **Rosenmund reduction**

$$\underset{\text{Ethanoyl chloride}}{CH_3-\underset{\underset{O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd,\ BaSO_4} \underset{\text{Ethanal}}{CH_3CHO} + HCl$$

(b) **Cannizzaro reaction** (1)

Refer to solution 28 (ii) of Topic 1.

(iii) $CH_3CH_2-CH_2-CO-CH_3$ gives iodoform test as it contains CH_3CO- group. (1)

48. (i) (a) Refer to solution 45(i)(a). (1)

(b) Refer to solution 31 (i) of Topic 1. (1)

(ii) (a) Refer to solution 47 (ii) (a). (1)

(b) Refer to solution 7 of Topic 2. (1)

(c) Refer to solution 28 (ii) of Topic 1. (1)

49. (i) (1)

(a) $$\overset{1}{C}H_3-\overset{2}{\underset{}{\overset{\overset{O}{\|}}{C}}}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$$

Heptan-2-one

(b) $Ph-\underset{3}{C}H=\underset{2}{C}H-\underset{1}{C}HO$ (1)

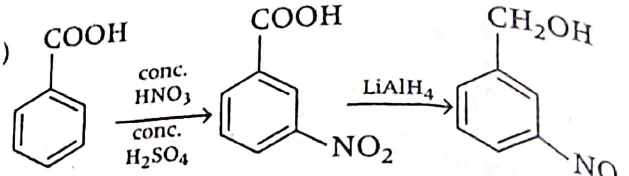
3-phenylprop-2-en-1-al

(ii) (a) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[CrO_3/PCC]{[O]} CH_3CHO$$ (1)

$$\xrightarrow[\text{(Aldol condensation)}]{CH_3CHO+\text{dil. NaOH}} CH_3-CH(OH)-CH_2-CHO \quad (1)$$

3-hydroxy butanal

(b)



Benzoic acid

m-nitrobenzyl alcohol

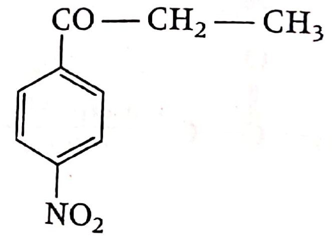
(1)

(c) $$\underset{\text{propanone}}{CH_3COCH_3} \xrightarrow{LiAlH_4} CH_3CH(OH)CH_3 \xrightarrow[443K]{\text{Conc. }H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$$ (1)

50. (i) (a) $\overset{1}{C}H_3-\overset{2}{C}O-\overset{3}{C}H_2-\overset{4}{C}H(Cl)-\overset{5}{C}H_3$ (1)

4-chloropentan-2-one

(b)



p-nitropropiophenone (1)

(ii) (a) **Ethanal and propanal**

Refer to solution 39 (ii) a of Topic 1. (1)

(b) **Phenol and benzoic acid**

Refer to solution 4 of Topic 2. (1)

(c) **Benzaldehyde and acetophenone**

Refer to solution 39 (ii) b of topic 1.

51. (i) (a) $\overset{1}{C}H_3\overset{2}{C}O\overset{3}{C}H_2\overset{4}{C}H(Cl)\overset{5}{C}H_3$ (1)

(b) $\overset{4}{C}H_3\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}HO$ (1)

(ii) (a) $CH_2(Br)COOH$ (1)

(b) CH_3CH_2OH (1)

(c) $CH_3CH_2CH_3$ (1)

52. (i) (a) **Propanone to propan-2-ol**

$$\underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3}$$ (1)

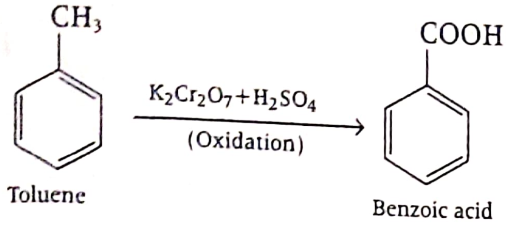
(b) **Ethanal to 2-hydroxypropanoic acid**

$$\underset{\text{Ethanal}}{(H_3C)(H)C=O} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{(H_3C)(H)C(OH)(CN)}$$

$$\xrightarrow[+HCl]{2H_2O} (H_3C)(H)C(OH)(COOH)$$

2-h...

(c) **Toluene to benzoic acid**



(1)

(ii) (a) Refer to solution 5 of Topic 1. (1)

(b) Refer to solution 39 (ii) a of Topic 1. (1)

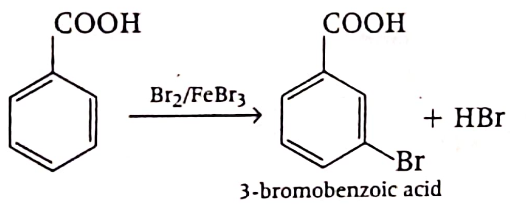
53. (i) (a) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(Clemmensen reduction)}]{\text{Zn-Hg, Conc. HCl}}$ $CH_3CH_2CH_3 + H_2O$ (1)

Acetone — Propane

(b) $CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{(Rosenmund reduction)}]{Pd-BaSO_4}$ $CH_3-\underset{\underset{O}{\|}}{C}-H + HCl$ (1)

Acetyl chloride — Acetaldehyde

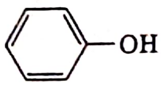
(c)



(1)

(ii) (a) $F-CH_2-COOH$ is a stronger acid than $Cl-CH_2-COOH$ because, higher the $-I$ effect, stronger is the acid. The order of $-I$ effect is $I < Br < Cl < F$. (1)

(b) CH_3COOH is a stronger acid than phenol,



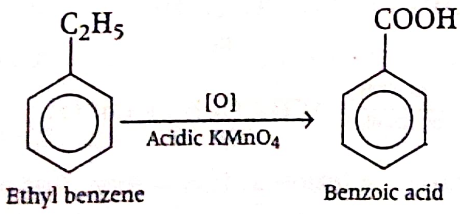
(For explanation, refer to solution 14 of Topic 2). (1)

54. (i) (a) Refer to solution 10 (i). (1)

(b) Refer to solution 39 (ii) b of Topic 1. (1)

(ii) (a) Refer to solution 17 (ii) of Topic 2. (1)

(b)



(2)

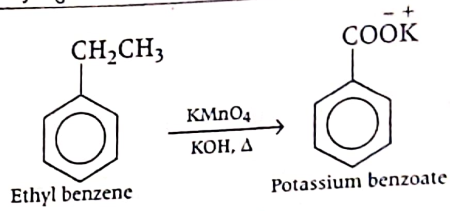
55. (i) (a) **Cannizzaro reaction** Refer to solution 28 (ii) of Topic 1. (1)

(b) **Decarboxylation** Refer to solution 5 of Topic 2. (1)

(ii)

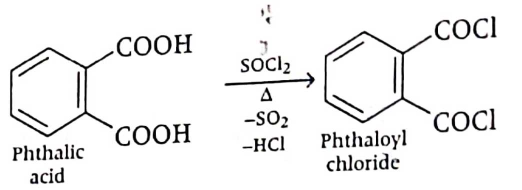
(a) Oxidation, i.e. conversion of alkyl chain directly attached to benzene nucleus into— COOK group. (b) Chlorination, i.e. conversion of —OH of carboxylic acid —COOH into —Cl. (c) Conversion of —$CONH_2$ group into —COOH by H_3O^+.

(a)



(1)

(b)



(1)

(c) $C_6H_5CONH_2 \xrightarrow[\Delta]{H_3O^+} C_6H_5COOH + NH_3$ (1)

56. (i) Refer to solution 28 (ii) of Topic 1. (2)

(ii) (a) Refer to solution 17 (ii) of Topic 2.

(b) Refer to solution 54 (ii) (b). (3)

57.

(a) Sodium bicarbonate test (given by — COOH group containing compounds). (b) Iodoform test (given by CH_3CO— or $CH_3CH(OH)$— group containing compounds).

(i) (a) Refer to solution 12 (ii). (1)

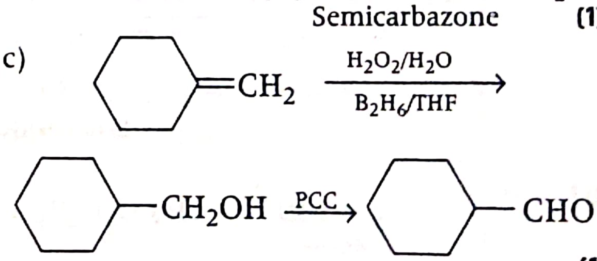
(b) Refer to solution 39 (ii)(b) of Topic 1. (1)

(ii) (a) Refer to solution 55 (ii) (b). (1)

(b) $C_6H_5CHO + H_2NCONHNH_2 \longrightarrow C_6H_5CH = NNHCONH_2$

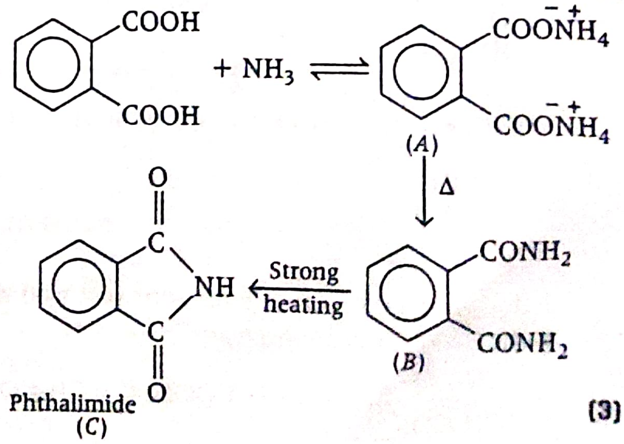
Semicarbazone (1)

(c)

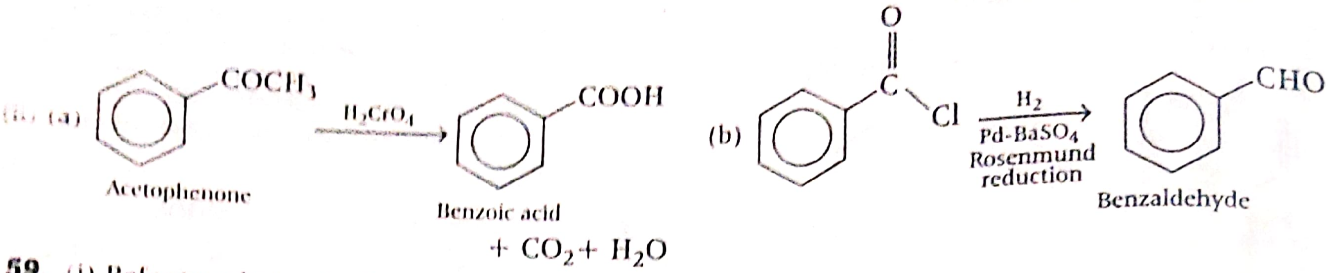


(1)

58. (i)



(3)

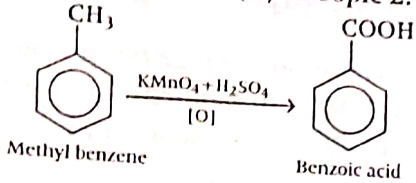
(ii) (a)


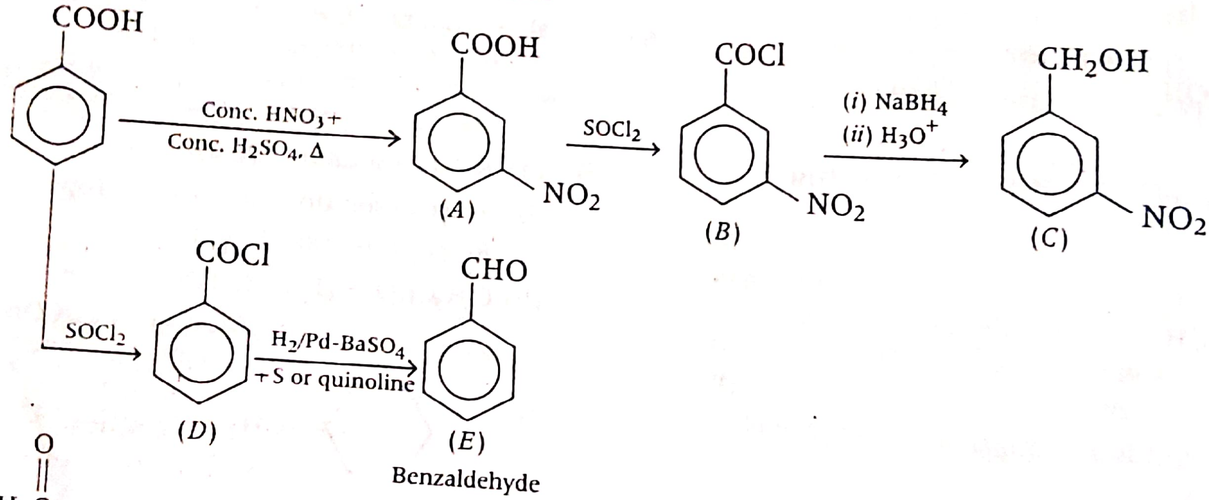
59. (i) Refer to solution 7 of Topic 2. (2)

(ii) (a) CH_3CH_2CN (Ethyl cyanide) $\xrightarrow[\text{Partial hydrolysis}]{\text{conc. HCl}}$ $CH_3CH_2-\underset{\underset{O}{\|}}{C}-NH_2$ (Propanamide) $\xrightarrow{Br_2/KOH}$ (2)

$CH_3CH_2NH_2$ (Ethylamine) $\xrightarrow{HNO_2}$ CH_3CH_2-OH (Ethanol) $\xrightarrow{[O]}$ CH_3COOH (Ethanoic acid) (1)

(b) Refer to solution 17 (ii) of Topic 2.

(c) (1)


60.


(1)

(5 × 1 = 5)

61. $\begin{matrix} CH_3C(=O) \\ CH_3C(=O) \end{matrix}\!\!>O$ (A) $+ C_2H_5OH$ (Ethanol) $\longrightarrow CH_3COOC_2H_5$ (C) (Ethyl ethanoate) $+ CH_3COOH$ (B) (Ethanoic acid)

$CH_3COOC_2H_5$ (C) $+ H_2O \xrightarrow{H^+} CH_3COOH$ (B) $+ CH_3CH_2OH$ (D); CH_3CH_2OH (D) $\xrightarrow{KMnO_4} CH_3COOH$ (B)

$\xrightarrow[\text{Dry distillation}]{Ca(OH)_2} CH_3COCH_3$ (E) $+ CaCO_3$

E does not give Tollen's reagent test and does not reduce Fehling's solution as it is ketone. But it forms a 2, 4-dinitrophenyl hydrazone.

$A = \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O$, $B = CH_3COOH$, $C = CH_3COOC_2H_5$, $D = CH_3CH_2OH$, $E = CH_3COCH_3$

(5 × 1 = 5)