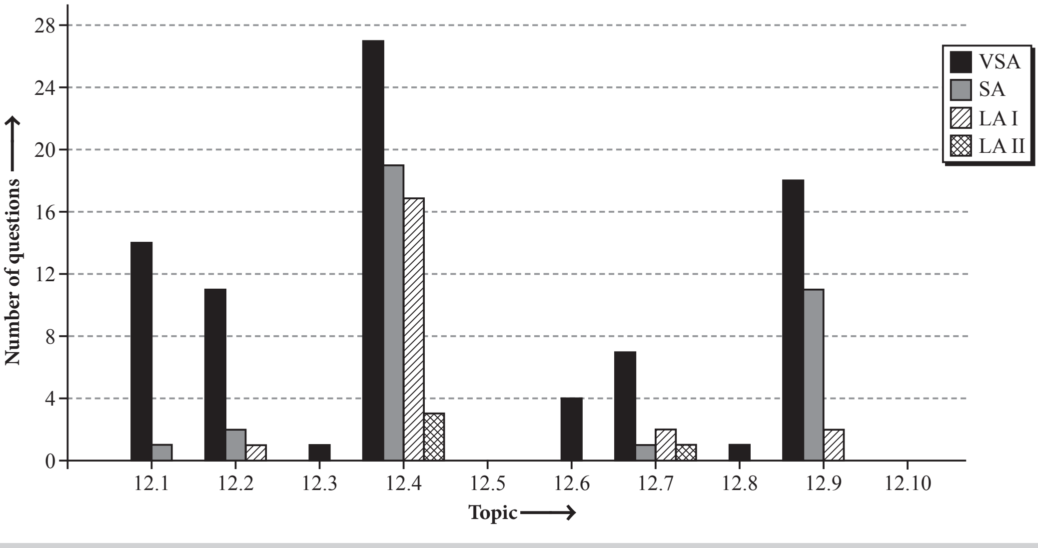
CHAPTER
12

Aldehydes, Ketones and Carboxylic Acids

- 12.1 Nomenclature and Structure of Carbonyl Group
- 12.2 Preparation of Aldehydes and Ketones
- 12.3 Physical Properties
- 12.4 Chemical Reactions
- 12.5 Uses of Aldehydes and Ketones
- 12.6 Nomenclature and Structure of Carboxyl Group
- 12.7 Methods of Preparation of Carboxylic Acids
- 12.8 Physical Properties
- 12.9 Chemical Reactions
- 12.10 Uses of Carboxylic Acids

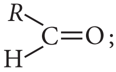
Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)

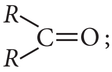


- ⏩ Maximum total weightage is of *Chemical Reactions of Aldehydes and Ketones.*
- ⏩ Maximum VSA type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*
- ⏩ Maximum SA and LA I type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*

QUICK RECAP

ALDEHYDES AND KETONES

- **General formula :** $C_nH_{2n}O$ having $>C{=}O$ group.
- **Aldehydes :**  $\underset{H}{\overset{R}{>}}C{=}O$; where R = H, alkyl or aryl.

- **Ketones :**  $R_2C{=}O$; where R = alkyl or aryl.

Nomenclature : The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.

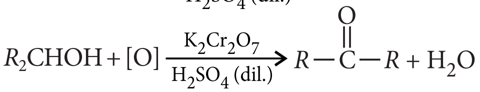
– The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.

Structure : The C-atom of carbonyl group is sp^2 hybridised and forms three σ-bonds and one π-bond with O atom. Carbonyl carbon with three atoms attached to it lie in a same plane with bond angle 120° (trigonal coplanar structure) and π-electron cloud lies above and below of this plane.

Preparation :

- **Oxidation of alcohols :**

$$RCH_2OH + [O] \xrightarrow[H_2SO_4\,(\text{dil.})]{K_2Cr_2O_7} RCHO + H_2O$$



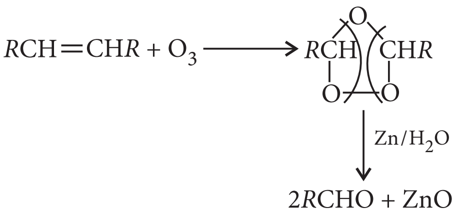
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(\text{dil.})]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$

- **Catalytic dehydrogenation of alcohols :**

$$RCH_2OH \xrightarrow[573\text{ K}]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\text{ K}]{Cu} R_2CO + H_2\uparrow$$

- **Reductive ozonolysis of alkenes :**



- **Rosenmund reduction :**

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\ S} RCHO + HCl$$

- **Reduction of nitriles :**

$$RC{\equiv}N \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-}Bu)_2} RCHO$$

$$RC{\equiv}N \xrightarrow[(ii)\ H_3O^+]{(i)\ R'MgX/\text{dry ether}} RCOR'$$

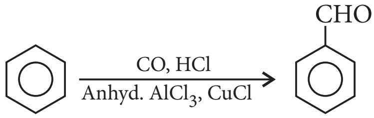
$$RC{\equiv}N \xrightarrow[\substack{\text{Dry ether} \\ (ii)\ H_3O^+}]{(i)\ SnCl_2 + HCl} RCHO + NH_4Cl$$

(Stephen reduction)

- **From esters :**

$$RCOOR \xrightarrow[(ii)\ H_2O]{(i)\ \text{DIBAL-H, 195 K}} RCHO$$

- **Gatterman-Koch reaction :**



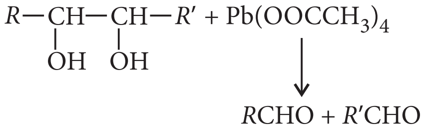
- **Friedel-Crafts acylation :**

- **From alkynes :**

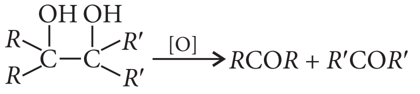
$$-C{\equiv}C- \xrightarrow[HgSO_4,\ 333\text{ K}]{\text{dil. } H_2SO_4} RCHO \text{ or } RCOR$$

$$-C{\equiv}C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\ THF} RCHO \text{ or } RCOR$$

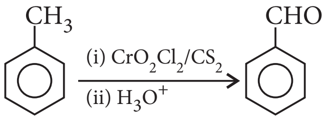
- **Oxidation of 1,2-glycols :**



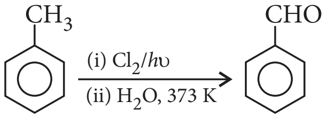
$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO$$



- **Etard reaction :**



- **Side chain chlorination :**



Physical properties :

- **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.

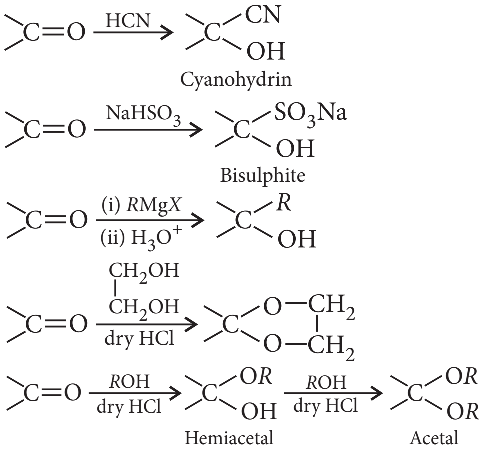
- Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.

▶ **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.

- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
- All carbonyl compounds are fairly soluble in organic solvents.

Chemical properties :

▶ **Nucleophilic addition reactions :**



$$>C=O \xrightarrow{HCN} >C<\begin{matrix}CN\\OH\end{matrix}$$

Cyanohydrin

$$>C=O \xrightarrow{NaHSO_3} >C<\begin{matrix}SO_3Na\\OH\end{matrix}$$

Bisulphite

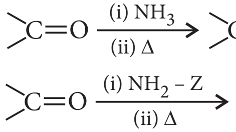
$$>C=O \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } RMgX} >C<\begin{matrix}R\\OH\end{matrix}$$

$$>C=O \xrightarrow[\text{dry HCl}]{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} >C<\begin{matrix}O-CH_2\\|\\O-CH_2\end{matrix}$$

$$>C=O \xrightarrow[\text{dry HCl}]{ROH} >C<\begin{matrix}OR\\OH\end{matrix} \xrightarrow[\text{dry HCl}]{ROH} >C<\begin{matrix}OR\\OR\end{matrix}$$

Hemiacetal Acetal

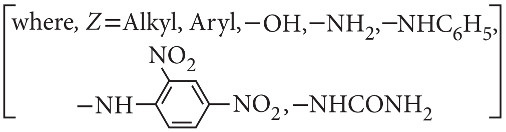
▶ **Nucleophilic addition-elimination reactions :**



$$>C=O \xrightarrow[\text{(ii) }\Delta]{\text{(i) } NH_3} >C=NH$$

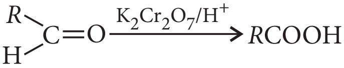
Imine

$$>C=O \xrightarrow[\text{(ii) }\Delta]{\text{(i) } NH_2-Z} >C=N-Z$$

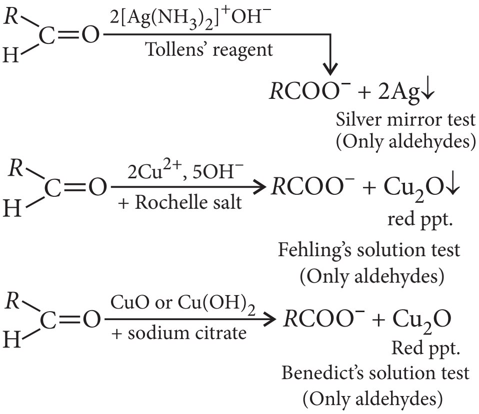


[where, Z=Alkyl, Aryl, $-OH, -NH_2, -NHC_6H_5$, $-NH-C_6H_3(NO_2)-NO_2$, $-NHCONH_2$]

▶ **Oxidation :**



$$\begin{matrix}R\\H\end{matrix}>C=O \xrightarrow{K_2Cr_2O_7/H^+} RCOOH$$



$$\begin{matrix}R\\H\end{matrix}>C=O \xrightarrow[\text{Tollens' reagent}]{2[Ag(NH_3)_2]^+OH^-} RCOO^- + 2Ag\downarrow$$

Silver mirror test
(Only aldehydes)

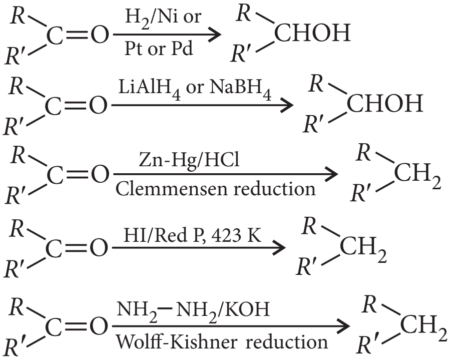
$$\begin{matrix}R\\H\end{matrix}>C=O \xrightarrow[\text{+ Rochelle salt}]{2Cu^{2+},\ 5OH^-} RCOO^- + Cu_2O\downarrow$$

red ppt.
Fehling's solution test
(Only aldehydes)

$$\begin{matrix}R\\H\end{matrix}>C=O \xrightarrow[\text{+ sodium citrate}]{CuO \text{ or } Cu(OH)_2} RCOO^- + Cu_2O$$

Red ppt.
Benedict's solution test
(Only aldehydes)

▶ **Reduction :**



$$\begin{matrix}R\\R'\end{matrix}>C=O \xrightarrow[\text{Pt or Pd}]{H_2/Ni \text{ or}} \begin{matrix}R\\R'\end{matrix}>CHOH$$

$$\begin{matrix}R\\R'\end{matrix}>C=O \xrightarrow{LiAlH_4 \text{ or } NaBH_4} \begin{matrix}R\\R'\end{matrix}>CHOH$$

$$\begin{matrix}R\\R'\end{matrix}>C=O \xrightarrow[\text{Clemmensen reduction}]{Zn\text{-}Hg/HCl} \begin{matrix}R\\R'\end{matrix}>CH_2$$

$$\begin{matrix}R\\R'\end{matrix}>C=O \xrightarrow{HI/\text{Red P, 423 K}} \begin{matrix}R\\R'\end{matrix}>CH_2$$

$$\begin{matrix}R\\R'\end{matrix}>C=O \xrightarrow[\text{Wolff-Kishner reduction}]{NH_2-NH_2/KOH} \begin{matrix}R\\R'\end{matrix}>CH_2$$

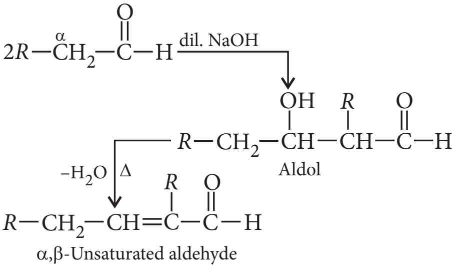
▶ **Haloform reaction :**

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$
$$RCOCH_3 + 3NaOI \longrightarrow RCOONa + CHI_3\downarrow + 2NaOH$$

Iodoform (yellow ppt.)

(Given by compounds having CH_3CO— group or $CH_3CH(OH)$—group).

▶ **Aldol condensation :**



$$2R-\overset{\alpha}{C}H_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil. NaOH}} R-CH_2-\overset{OH}{\overset{|}{C}H}-\overset{R}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H$$

Aldol

$$\xrightarrow{-H_2O,\ \Delta} R-CH_2-CH=\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

α,β-Unsaturated aldehyde

(aldehydes and ketones having at least one α-hydrogen)

- **Intramolecular aldol condensation :** It takes place in diketones and gives rise to cyclic products.
- **Crossed aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if

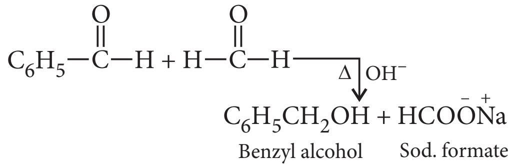
both of them contain α-hydrogen atoms, it gives a mixture of four products.

- **Cannizzaro reaction :**

$$\underset{\text{Formaldehyde}}{HCHO + HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCO\overset{-}{O}\overset{+}{K}}$$

(aldehydes which do not have an α-hydrogen atom)

  - **Crossed Cannizzaro reaction :**



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + H-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\Delta]{OH^-} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCO\overset{-}{O}\overset{+}{Na}}$$

  - **Intramolecular Cannizzaro reaction :** It is given by dialdehydes having no α-hydrogen atoms.

- **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

- **Distinction between aldehydes and ketones :**

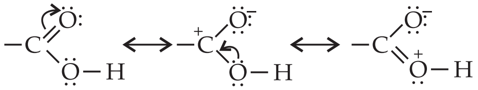
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

CARBOXYLIC ACIDS

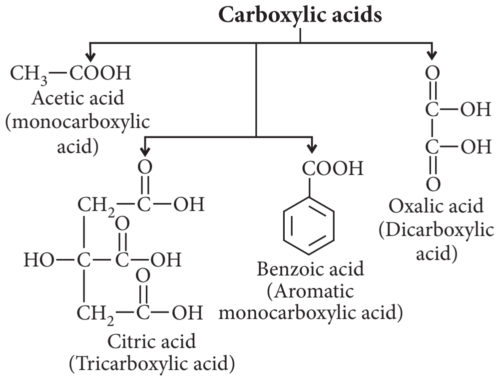
- **General Formula :** $C_nH_{2n}O_2$ having —COOH group.
  *R*COOH where, *R*=H or alkyl or aryl.

- **Nomenclature :** The common names end with the suffix –'*ic acid*' and have been derived from Latin or Greek names of their natural sources.
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –'*e*' in the name of the corresponding alkane with –'*oic* acid'. In numbering the carbon chain, the carboxylic carbon is numbered one.

- **Structure :** In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



- **Classification :** They are classified as mono, di, tri and polycarboxylic acids depending upon the number of carboxyl groups present in a molecule.



- Aliphatic monocarboxylic acids and aliphatic esters are known as *functional isomers*. Some higher aliphatic monocarboxylic acids (C_{12}—C_{18}) are known as *fatty acids* because they occur in natural fats as esters of glycerol, *e.g.*, palmitic acid and stearic acid are obtained on hydrolysis of fats.

- **Preparation :**

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7\ +\ \text{dil. } H_2SO_4]{\text{Oxidation, alk. } KMnO_4,\ H_3O^+ \text{ or } CrO_3\text{–}H_2SO_4} RCOOH$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[K_2Cr_2O_7\ +\ \text{dil. } H_2SO_4 \text{ or Fehling's solution or Tollens' reagent}]{\text{Oxidation}} RCOOH$$

$$\underset{\text{Alkyl Cyanide}}{RCN} \xrightarrow[\text{Mineral acid } HCl,\ H_2SO_4, \text{ etc.}]{\text{Hydrolysis}} RCOOH$$

$$\begin{tikzcd}\underset{\text{Alkyl Cyanide}}{RCN} \arrow[r, "\text{Hydrolysis}", "\text{Alkali NaOH or KOH}"'] & RCOONa \arrow[d, "HCl"] \\ & RCOOH\end{tikzcd}$$

$$\underset{\text{Grignard reagent}}{RMgX} \xrightarrow[\text{dry ether}]{CO_2 \text{ (dry ice)}} RCOOH$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[\Delta]{H_3O^+} RCOOH$$

$$\underset{\text{Acyl halide}}{RCOCl} \xrightarrow[\text{or, (i) } OH^-/H_2O \text{ (ii) } H_3O^+]{H_2O} RCOOH$$

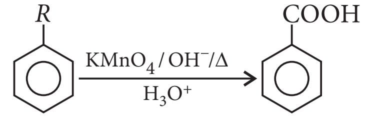
$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow{H_2O} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{H_3O^+,\ \Delta} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{NaOH,\ H_3O^+} RCOOH$$

$$\underset{\text{Alkene}}{RCH{=}CHR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$

$$\underset{\text{Alkyne}}{RC{\equiv}CR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$



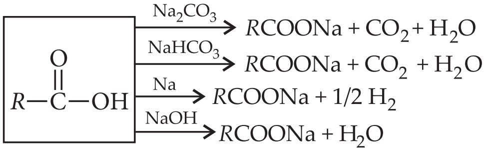
Alkyl benzene

Physical Properties :

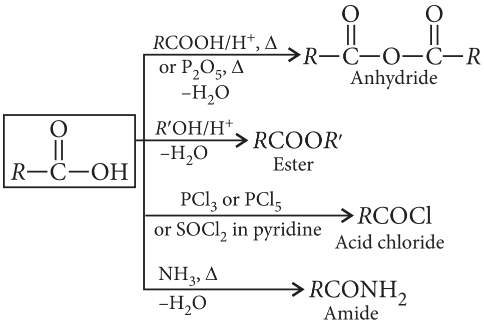
- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
  - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
  - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
  - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.
- **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

Chemical reactions :

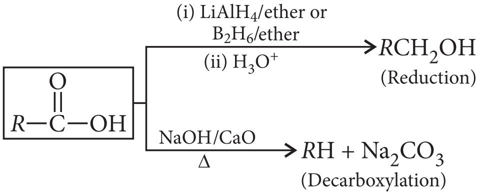
- **Reactions involving cleavage of O—H bond :**



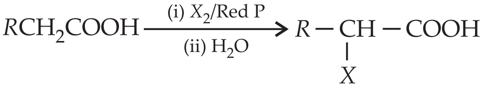
- **Reactions involving cleavage of C—OH bond :**



- **Reactions involving —COOH group :**



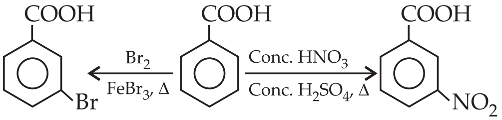
- **Hell-Volhard-Zelinsky reaction :**



$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R-\underset{\displaystyle X}{\underset{|}{CH}}-COOH$$

α-Halocarboxylic acid

- **Ring substitution in aromatic acids :** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a *deactivating* and *meta* directing group.



- **Distinction test between phenol and carboxylic acid :**

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

Previous Years' CBSE Board Questions

12.1 Nomenclature and Structure of Carbonyl Group

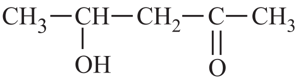
VSA **(1 mark)**

1. Write the structure of 2-methylbutanal. *(1/5, AI 2015)*

2. Draw the structure of 3-methylpentanal. *(Delhi 2015C)*

3. Write the IUPAC name of the following :
CH_3-CH_2-CHO *(AI 2015C)*

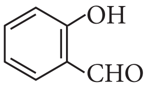
4. Write the IUPAC name of the compound :



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{||}{C}}-CH_3$ *(Delhi 2014)*

5. Write the structure of 4-chloropentan-2-one. *(AI 2014, Delhi 2013)*

6. Write the IUPAC name of the following compound :



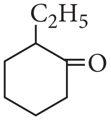
(Foregin 2014)

7. Write the structure of 3-methylbutanal. *(Delhi 2013)*

8. Write the structure of *p*-methylbenzaldehyde molecule. *(Delhi 2013)*

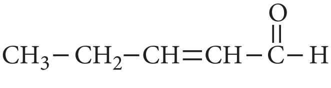
9. Draw the structure of the compound named 4-methylpent-3-en-2-one. *(Delhi 2013C)*

10. Write the IUPAC name of the following :



(AI 2013C)

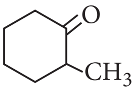
11. Write the IUPAC name of the following :



$CH_3-CH_2-CH=CH-\overset{O}{\overset{||}{C}}-H$ *(AI 2012)*

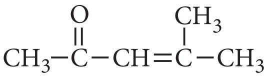
12. Write the IUPAC name of
$Ph-CH=CH-CHO$ *(AI 2012)*

13. Write the IUPAC name of the following :



(AI 2012C)

14. Write the IUPAC name of



$CH_3-\overset{O}{\overset{||}{C}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$ *(AI 2011C)*

SA **(2 marks)**

15. Draw the structures of the following :
(i) *p*-Methylbenzaldehyde
(ii) 4-Methylpent-3-en-2-one
(2/5, AI 2015C)

12.2 Preparation of Aldehydes and Ketones

VSA **(1 mark)**

16. What happens when benzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$? *(1/2, 2020)*

17. How can you convert the following : Benzene to acetophenone? *(1/3, 2020)*

18. Complete the following reaction :

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

(1/3, Delhi 2019)

19. Write chemical equations for the following reaction :
Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$. *(1/3, Delhi 2019, 1/5, 2018C)*

20. Write the equation involved in the following reaction :
Etard reaction. *(1/2, Delhi 2017)*

21. Write the reaction involved in the following :
Stephen reduction. *(1/5, AI 2017)*

22. Write the product in the following reaction :

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

(1/5, AI 2017)

23. Write the product in the following reaction :

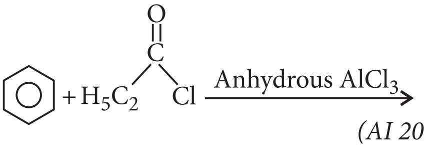
$$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

(1/5, Delhi 2016)

24. How do you convert the following :
Ethyne to ethanal *(1/3, Foregin 2015)*

25. How will you obtain the following :
Benzaldehyde from phenol *(1/5, AI 2013C)*

26. Write the structure of the product formed in the following reaction :



(AI 2012C)

SA (2 marks)

27. Write the major product(s) in the following :

(i) $CH_3—CH=CH—CH_2—CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) DIBAL–H}}$

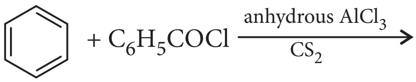
(ii) $CH_3—CH_2—OH \xrightarrow{CrO_3}$ *(2/5, 2020)*

28. Write the equations involved in the following reactions :
(i) Stephen reaction
(ii) Etard reaction *(2/3, Foregin 2015)*

LA I (3 marks)

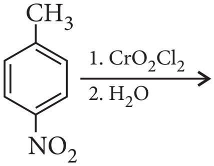
29. Write the structures of the main products of the following reactions :

(i)



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

(iii)



(Delhi 2012)

12.3 Physical Properties

VSA (1 mark)

30. Aldehydes and ketones have lower boiling points than corresponding alcohols. Why? *(AI 2012C)*

12.4 Chemical Reactions

VSA (1 mark)

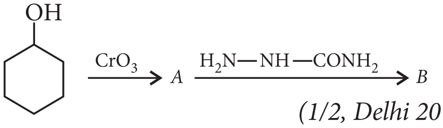
31. Iodoform test is not given by
(a) ethanol (b) ethanal
(c) pentan-2-one (d) pentan-3-one *(2020)*

32. **Assertion (A) :** Reactivity of ketones is more than aldehydes.
Reason (R) : The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

33. What happens when,
propanone is treated with methyl magnesium iodide and then hydrolysed? *(1/2, 2020)*

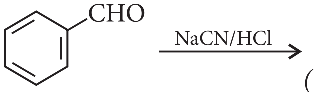
34. How can you convert the following : Acetone to propene ? *(1/3, 2020)*

35. Write structures of compounds *A* and *B* in the following reaction :



(1/2, Delhi 2019)

36. Complete the following reaction :



(1/3, Delhi 2019)

37. How do you convert the following :
Ethanal to propanone *(1/2, 2018)*

38. Give simple chemical tests to distinguish between the following pair of compounds :
Ethanal and propanal
(1/5, 2018C, Delhi 2013, Delhi 2012C)

39. Write the equation involved in the following reaction :
Wolff–Kishner reduction *(1/2, Delhi 2017)*

40. Do the following conversion in not more than two steps:
Propanone to propene *(1/3, Delhi 2017)*

41. Give chemical tests to distinguish between the following pairs of compunds :
Benzaldehyde and acetophenone.
(1/5, AI 2017C, 1/5, Delhi 2015C, AI 2012C)

42. Write the structure of *A* and *B* in the following reaction :

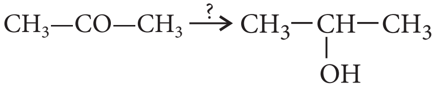
$$CH_3COCl \xrightarrow{H_2,\ Pd-BaSO_4} A \xrightarrow{H_2N-OH} B$$

(1/5, AI 2016)

43. Distinguish between the following :
C_6H_5—$COCH_3$ and C_6H_5—CHO
(1/2, AI 2016, 1/5, AI 2015)

44. Give a simple chemical test to distinguish between the following pair of compounds :
CH_3CH_2CHO and $CH_3CH_2COCH_3$
(1/2, AI 2016, 1/5, AI 2015)

45. Name the reagent used in the following reaction :



$$CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

(Delhi 2015, 1/2, Foreign 2015)

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

(i) Benzaldehyde and benzoic acid

(ii) Propanal and propanone.

(1/5, Delhi 2014)

47. Account for the following :

CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. *(Delhi 2014)*

48. Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and propanone *(1/5, AI 2014)*

49. Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and butan-2-one
(1/5, Foreign 2014)

50. How will you convert the following :
Ethanal to 2-hydroxy propanoic acid
(1/5, AI 2013)

51. Give reason :

pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds. *(1/5, Delhi 2013C)*

52. Give reason :
Aldehydes are more reactive than ketones towards nucleophilic reagents.
(1/5, AI 2013C)

53. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions : ethanal, propanal, propanone, butanone. *(Delhi 2012)*

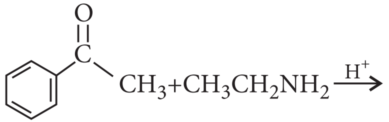
54. Give chemical tests to distinguish between Benzophenone and acetophenone
(1/5, Delhi 2012)

55. Arrange the following compounds in an increasing order of their property as indicated :
Acetaldehyde, acetone, methyl *tert*-butyl ketone (reactivity towards HCN)
(1/5, AI 2012)

56. Predict the organic product of the following reaction :

(1/2, AI 2011C)

57. Predict the product of the following reaction :



(1/5, AI 2011C)

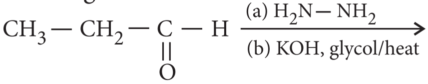
SA (2 marks)

58. Write chemical equations for the following reactions :

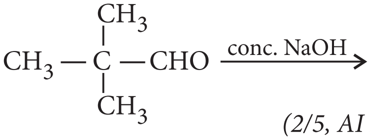
(i) Propanone is treated with dilute $Ba(OH)_2$.

(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl *(2/3, Delhi 2019)*

59. Write the structure of major product(s) in the following:

(i) 

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

(ii) 

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CHO \xrightarrow{\text{conc. NaOH}}$$

(2/5, AI 2019)

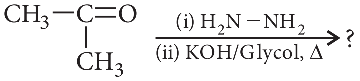
60. (a) Write the product in the following reaction :

(b) Give simple chemical test to distinguish between the following pair of compounds :
Butanal and Butan-2-one
(2/5, AI 2017)

61. Write the equations involved in the following reactions :

(i) Clemmensen reduction
(ii) Cannizzaro reaction *(Delhi 2017)*

62. Predict the products of the following reactions :

(i) 

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

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

(2/3, Delhi 2015)

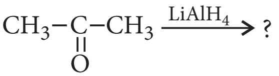
63. A compound '*A*' of molecular formula C_2H_3OCl undergoes a series of reactions as shown below. Write the structure of *A*, *B*, *C* and *D* in the following reactions :

$$(C_2H_3OCl)A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow{\text{dil. NaOH}} C \xrightarrow{\text{Heat}} D$$

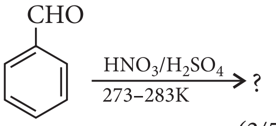
(AI 2015)

64. Describe the following reactions :
(i) Acetylation
(ii) Aldol condensation *(2/5, Delhi 2015C)*

65. Write the main product in the following equations :

(i) 

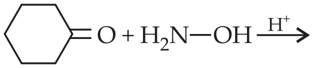
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$$

(ii) 

$$\xrightarrow[273-283K]{HNO_3/H_2SO_4} ?$$

(2/5, Delhi 2015C)

66. Draw the structure of the following derivatives :
(i) Propanone oxime
(ii) Semicarbazone of the CH_3CHO *(2/5, AI 2015C)*

67. (i) 

$$=O + H_2N-OH \xrightarrow{H^+}$$

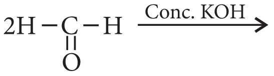
(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow$

(2/5, Delhi 2014)

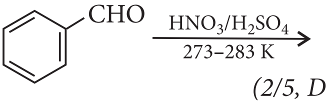
68. Account for the following :
(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.
(ii) There are two $-NH_2$ groups in semicarbazide ($H_2NNHCONH_2$). However, only one is involved in the formation of semicarbazone. *(2/5, Foregin 2014)*

69. Write the chemical equation to illustrate each of the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro reaction *(2/5, Foregin 2014)*

70. Complete the following reactions :

(i) 

$$2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}}$$

(ii) 

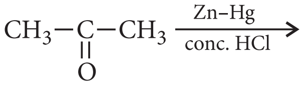
$$\xrightarrow[273-283\text{ K}]{HNO_3/H_2SO_4}$$

(2/5, Delhi 2013)

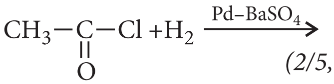
71. How will you convert the following :
(i) Propanone to Propan-2-ol
(ii) Ethanal to 2-hydroxypropanoic acid *(2/5, AI 2013)*

72. Give simple chemical test to distinguish between :
(a) Pentan-2-one and pentan-3-one
(b) Ethanal and propanal *(2/5, AI 2013)*

73. Write the products of the following reactions :

(i) 

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{conc. HCl}]{Zn-Hg}$$

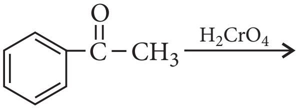
(ii) 

$$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd-BaSO_4}$$

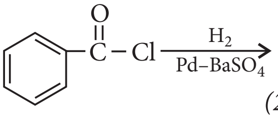
(2/5, AI 2013)

74. Give chemical tests to distinguish between
(i) Propanal and propanone
(ii) Benzaldehyde and acetophenone *(2/5, AI 2012)*

75. Predict the products of the following reactions :

(i) 

$$\xrightarrow{H_2CrO_4}$$

(ii) 

$$\xrightarrow[Pd-BaSO_4]{H_2}$$

(2/5, AI 2011C)

76. An organic compound *A*, having the formula, C_3H_8O, on treatment with copper 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 structure of *A*, *B* and *C*. *(2/5, Delhi 2011C)*

LA I (3 marks)

77. Write the products formed when $(CH_3)_3C-CHO$ reacts with the following reagents :

(i) CH_3COCH_3 in the presence of dilute NaOH
(ii) HCN
(iii) Conc. NaOH *(2020)*

78. (a) How can you distinguish between propanal and propanone?
(b) Draw structures of the following derivatives :
(i) Cyanohydrin of cyclobutanone
(ii) Hemiacetal of ethanal *(3/5, 2020)*

79. An alkene *A* with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, *B* and *C*. Compound *B* gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound *C* does not give Fehling solution test but forms iodoform. Identify the compounds *A*, *B* and *C*. *(3/5, AI 2019)*

80. (*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollens' test whereas isomer (*B*) does not give Tollens' test but gives positive iodoform test. Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give the same product (*D*).
(a) Write the structures of (*A*), (*B*), (*C*) and (*D*).
(b) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN? *(2018)*

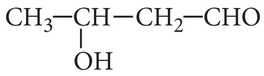
81. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.
(b) Draw the structure of the semicarbazone of ethanal.
(c) How can you distinguish between propanal and propanone? *(3/5, Delhi 2016)*

82. (a) Write the chemical reaction involved in Wolff-Kishner reduction.
(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.

$C_6H_5COCH_3$, CH_3-CHO, CH_3COCH_3

(c) *A* and *B* are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer *B* forms yellow precipitate of iodoform whereas isomer *A* does not form any precipitate. Write the formulae of *A* and *B*. *(3/5, AI 2016)*

83. Write the structures of the main products when acetone ($CH_3-CO-CH_3$) reacts with the following reagents :
(i) Zn – Hg/conc. HCl
(ii) $H_2N-NHCONH_2/H^+$
(iii) CH_3MgBr and then H_3O^+ *(3/5, AI 2015)*

84. How will you convert ethanal into the following compounds? Give the chemical equations involved.
(i) CH_3-CH_3
(ii) 
$CH_3-\underset{\substack{|\\ OH}}{CH}-CH_2-CHO$
(iii) CH_3CH_2OH *(3/5, Delhi 2015C)*

85. Write the chemical equations to illustrate the following name reactions :
(i) Wolff–Kishner reduction
(ii) Aldol condensation
(iii) Cannizzaro reaction *(3/5, Delhi 2014)*

86. Write the products formed when CH_3CHO reacts with the following reagents :
(i) HCN (ii) H_2N-OH
(iii) CH_3CHO in the presence of dilute NaOH *(3/5, AI 2014)*

87. (a) Write the chemical equations to illustrate the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro reaction
(b) Out of $CH_3CH_2-CO-CH_2-CH_3$ and $CH_3CH_2-CH_2-CO-CH_3$, which gives iodoform test? *(3/5, AI 2014)*

88. Write the products formed when ethanal reacts with the following reagents :
(i) CH_3MgBr and then H_3O^+
(ii) Zn-Hg/conc. HCl
(iii) C_6H_5CHO in the presence of dilute NaOH *(3/5, Foregin 2014)*

89. How will you bring about the following conversions?
(i) Propanone to propane
(ii) Benzoyl chloride to benzaldehyde
(iii) Ethanal to but-2-enal *(3/5, Delhi 2013)*

90. An organic compound (*A*) which has characteristic odour, on treatment with NaOH forms two compounds (*B*) and (*C*). Compound (*B*) has the molecular formula C_7H_8O which on oxidation with CrO_3 gives back compound (*A*). Compound (*C*) is the sodium salt of the acid. Compound (*C*) when heated with soda lime yields an aromatic hydrocarbon (*D*). Deduce the structures of (*A*), (*B*), (*C*) and (*D*). Write chemical equations for all reactions taking place.

(3/5, AI 2013C, 2012C)

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

(3/5, AI 2012, 2012C)

92. An organic compound (*A*) with molecular formula C_8H_8O forms an orange red precipitate with 2, 4-DNP reagent and gives yellow precipitate on heating with I_2 and NaOH. It neither reduces Tollens' reagent nor Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (*B*) having molecular formula $C_7H_6O_2$. Identify the compounds (*A*) and (*B*) and explain the reactions involved.

(3/5, Delhi 2012C)

93. An organic compound with molecular formula $C_5H_{10}O$ does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Identify the compound and write all chemical equations for the reactions.

(3/5, AI 2012C)

LA II (5 marks)

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

Identify (*A*), (*B*) and (*C*) and write their structures. Write the reactions of compound (*A*) with (i) $NaOH/I_2$ and (ii) $NaBH_4$.

(b) Give reason :

(i) Oxidation of propanal is easier than propanone.

(ii) α-Hydrogen of aldehydes and ketones is acidic in nature. *(2020)*

95. (a) Give a plausible explanation for each one of the following :

(i) There are two $-NH_2$ groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones.

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

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

(Delhi 2012)

96. (a) Identify *A*, *B* and *C* in the following sequence of reactions :

$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgCl} A \xrightarrow{\text{conc. } H_2SO_4} B \xrightarrow{\text{HBr + Peroxide}} C$$

(b) Predict the structures of the products formed when benzaldehyde is treated with

(i) conc. NaOH

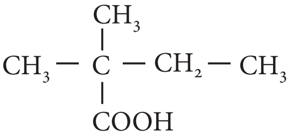
(ii) HNO_3/H_2SO_4 (at 273– 383 K)

(Delhi 2011C)

12.6 Nomenclature and Structure of Carboxyl Group

VSA (1 mark)

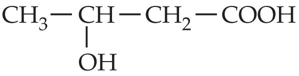
97. What is the correct IUPAC name of the given compound?



$$CH_3-\underset{COOH}{\overset{CH_3}{C}}-CH_2-CH_3$$

(a) 2,2-Dimethylbutanoic acid
(b) 2-Carboxyl-2-methylbutane
(c) 2-Ethyl-2-methylpropanoic acid
(d) 3-Methylbutanecarboxylic acid *(2020)*

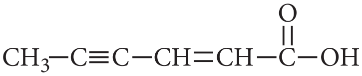
98. Write the IUPAC name of the compound :



$$CH_3-\underset{OH}{CH}-CH_2-COOH$$

(Delhi 2014)

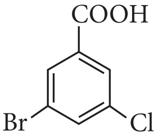
99. Write the IUPAC name of the following :



$$CH_3-C\equiv C-CH=CH-\overset{O}{\overset{\|}{C}}-OH$$

(Delhi 2011C)

100. Write the IUPAC name of

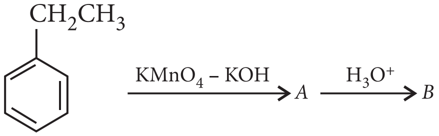


(AI 2011C)

12.7 Methods of Preparation of Carboxylic Acids

VSA (1 mark)

101. Write structures of compounds *A* and *B* in each of the following reaction.



(1/2, Delhi 2019)

102. How do you convert the following :
Toluene to benzoic acid? *(1/2, 2018)*

103. Do the following conversion in not more than two steps:
Ethyl benzene to benzoic acid
(1/3, Delhi 2017)

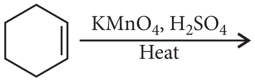
104. Name the reagent used in the following reaction :

$$C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$$

(1/2, Delhi 2015)

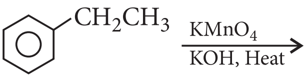
105. How will you carry out the following conversions?
(i) Acetylene to acetic acid
(1/5, Delhi 2013C)

106. Predict the product of the following reaction :



(1/5, AI 2011C)

107. Predict the organic product of the following reaction :



(1/3, AI 2011C)

SA (2 marks)

108. Write a suitable chemical equation to complete each of the following transformations :
(i) Butan-1-ol to butanoic acid
(ii) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid *(2/5, AI 2012)*

LA I (3 marks)

109. Two moles of organic compound '*A*' on treatment with a strong base gives two compound '*B*' and '*C*'. Compound '*B*' on dehydrogenation with Cu gives '*A*' while acidification of '*C*' yields carboxylic acid '*D*' with molecular formula of CH_2O_2. Identify the compounds *A*, *B*, *C* and *D* and write all chemical reactions involved.

(3/5, Delhi 2013C)

110. How are the following conversions carried out?
(i) Ethyl cyanide to ethanoic acid.
(ii) Butan-1-ol to butanoic acid.
(iii) Benzoic acid to *m*-bromobenzoic acid.
(Delhi 2012)

LA II (5 marks)

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

$$\begin{tikzcd}
C_6H_6 \arrow[r, "CH_3COCl"', "\text{Anhyd. }AlCl_3"] & A \arrow[r, "\text{Zn–Hg/conc.HCl}"] \arrow[d, "NaOI"] & B \arrow[d, "\text{(ii) }H_3O^+", "\text{(i) }KMnO_4-KOH, \Delta"'] \\
 & D+E & C
\end{tikzcd}$$

(Delhi 2016)

12.8 Physical Properties

VSA (1 mark)

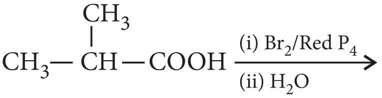
112. Arrange the following in the increasing order of their boiling points.
CH_3CHO, CH_3COOH, CH_3CH_2OH
(1/5, AI 2016, 2015)

12.9 Chemical Reactions

VSA (1 mark)

113. Assertion (A) : Benzoic acid does not undergo Friedal-Crafts reaction.
Reason (R) : The carboxyl group is activating and undergo electrophilic substitution reaction.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

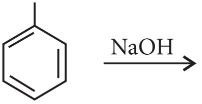
114. Complete the following reaction :



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\text{Red } P_4}$$

(1/3, Delhi 2019)

115. Write the structure of major product(s) in the following:



(1/5, AI 2019)

116. Carry out the following conversions: Propanoic acid to acetic acid. *(1/5, AI 2019)*

117. Do the following conversion in not more than two steps:
Benzoic acid to benzaldehyde.
(1/3, Delhi 2017, 1/5 Delhi 2015C)

118. Why carboxylic acid does not give reactions of carbonyl group?
(1/5, AI 2017C, 1/5, AI 2016)

119. Give simple chemical tests to distinguish between the following pairs of compounds :
Benzoic acid and ethyl benzoate
(1/5, AI 2017C, 1/3, Foreign 2014)

120. Distinguish between
CH_3COOH and $HCOOH$ *(1/2, AI 2016)*

121. Predict the products of the following reaction :

$CH_3COONa \xrightarrow[\Delta]{NaOH/CaO}$? *(1/3, Delhi 2015)*

122. Name the reagent used in the following reaction :

$CH_3-COOH \xrightarrow{?} CH_3-COCl$
(1/2, Foreign 2015)

123. Write the main product in the following equation :

$CH_3-COOH \xrightarrow{PCl_5}$ *(1/5, Delhi 2015C)*

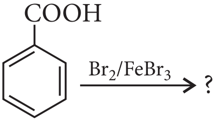
124. Describe the following giving chemical equation :
Decarboxylation reaction
(1/5, Delhi 2015C, 2012)

125. Account for the following :
Carboxylic acids do not give reactions of carbonyl group. *(1/5, AI 2014)*

126. Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and phenol
(1/5, AI 2014, Delhi 2013C, 2012, 2012C)

127. Write the chemical equation to illustrate the following name reaction :
Hell-Volhard-Zelinsky reaction
(1/5, Foregin 2014, Delhi 2012)

128. Write the products of the following reaction :



(1/5, AI 2013)

129. Give reasons :
Chloroacetic acid is stronger than acetic acid. *(1/5, Delhi 2013C)*

130. How will you carry out the following conversion :
Toluene to *m*-nitrobenzoic acid
(1/5, Delhi 2013C)

SA (2 marks)

131. Account for the following :

(a) Aromatic carboxylic acids do not undergo Friedel–Crafts reaction.

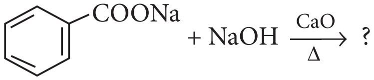
(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. *(2018)*

132. Write the reactions involved in the following :

(i) Hell—Volhard—Zelinsky reaction

(ii) Decarboxylation reaction *(Delhi 2017)*

133. (a) Write the product in the following reaction :



(b) Give simple chemical test to distinguish between the following pair of compounds: Benzoic acid and phenol *(2/5, AI 2017)*

134. How will you convert the following in not more than two steps :

(i) Acetophenone to benzoic acid

(ii) Ethanoic acid to 2-hydroxyethanoic acid *(2/5, AI 2017)*

135. (a) Write the product of the following reaction :

$$CH_3COOH \xrightarrow{Cl_2/P}$$

(b) Give simple chemical test to distinguish between the following pair of compounds :

Benzaldehyde and benzoic acid

(2/5, Delhi 2014)

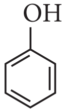
136. Account for the following :

Cl—CH_2COOH is a stronger acid than CH_3COOH. *(2/5, AI 2014)*

137. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons. *(2/5, Delhi 2013)*

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

(i) F—CH_2—COOH or Cl—CH_2—COOH

(ii) 

or CH_3COOH *(2/5, AI 2013)*

139. Give reasons :

(i) Electrophilic substitution in benzoic acid takes place at *meta*-position.

(ii) Carboxylic acids do not give the characteristic reactions of carbonyl group. *(2/5, AI 2013C, Delhi 2012C)*

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

(i) Benzoic acid, 3,4-dinitrobenzoic acid, 4-methoxybenzoic acid (acid strength)

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

(2/5, AI 2012)

141. Write the mechanism of esterification of carboxylic acids. *(2/5, Delhi 2012C)*

LA I (3 marks)

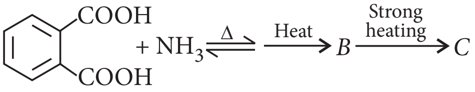
142. Write the structures of compounds *A*, *B* and *C* in each of the following reactions :

(i)
$$\begin{tikzcd} C_6H_5Br \arrow[r, "\text{Mg/dry ether}"] & A \arrow[r, "(a)\ CO_{2(g)}", "(b)\ H_3O^+"'] & B \arrow[d, "PCl_5"] \\ & & C \end{tikzcd}$$

(ii)
$$\begin{tikzcd} CH_3CN \arrow[r, "(a)\ SnCl_2/HCl", "(b)\ H_3O^+"'] & A \arrow[r, "\text{dil. NaOH}"] & B \arrow[d, "\Delta"] \\ & & C \end{tikzcd}$$

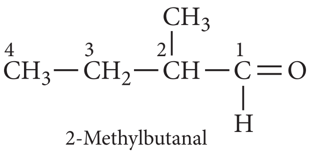
(Delhi 2017)

143. Identify *B* and *C* in the following sequence of reaction :



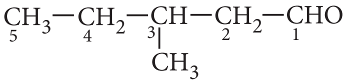
(3/5, AI 2011C)

Detailed Solutions

1. 

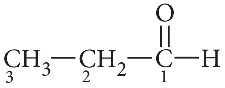
$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(CH_3)-\overset{1}{C}H=O$$

2-Methylbutanal

2. 

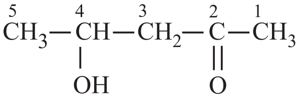
$$\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{3}{C}H(CH_3)-\underset{2}{C}H_2-\underset{1}{C}HO$$

3-Methylpentanal

3. 

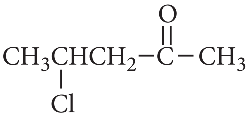
$$\underset{3}{C}H_3-\underset{2}{C}H_2-\underset{1}{C}(=O)-H$$

1-Propanal

4. 

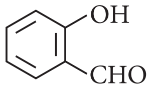
$$\overset{5}{C}H_3-\overset{4}{C}H(OH)-\overset{3}{C}H_2-\overset{2}{C}(=O)-\overset{1}{C}H_3$$

4-Hydroxypentan-2-one

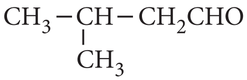
5. 

$$CH_3CH(Cl)CH_2-C(=O)-CH_3$$

4-Chloropentan-2-one

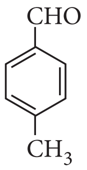
6. 

2-Hydroxybenzaldehyde

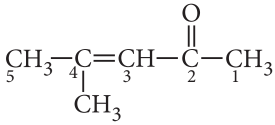
7. 

$$CH_3-CH(CH_3)-CH_2CHO$$

3-Methylbutanal

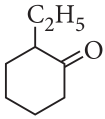
8. 

p-Methylbenzaldehyde

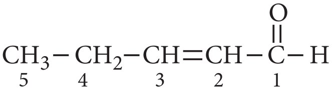
9. 

$$\underset{5}{C}H_3-\underset{4}{C}(CH_3)=\underset{3}{C}H-\underset{2}{C}(=O)-\underset{1}{C}H_3$$

4-Methylpent-3-en-2-one

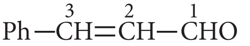
10. 

2-Ethylcyclohexanone

11. 

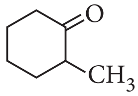
$$\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{3}{C}H=\underset{2}{C}H-\underset{1}{C}(=O)-H$$

Pent-2-enal

12. 

$$Ph-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}HO$$

3-Phenylprop-2-enal

13. 

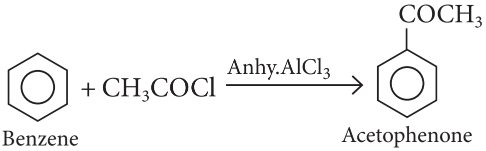
2-Methylcyclohexanone

14. *Refer to answer 9.*

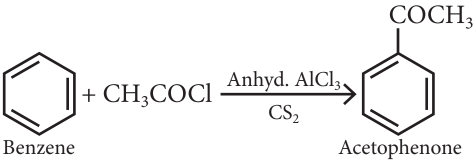
15. (i) *Refer to answer 8.*

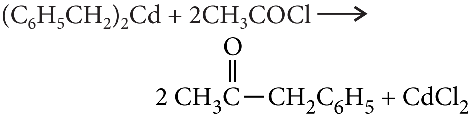
(ii) *Refer to answer 9.*

16.

(b) 

17.

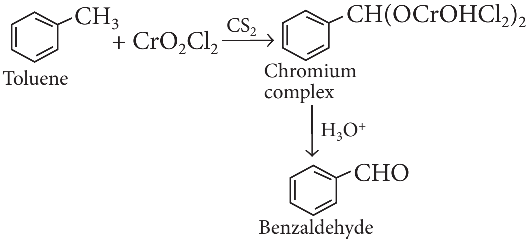


18. 

$$(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2\ CH_3C(=O)-CH_2C_6H_5 + CdCl_2$$

19. $C_6H_5COCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5CHO$ Benzaldehyde

20. **Etard reaction :**



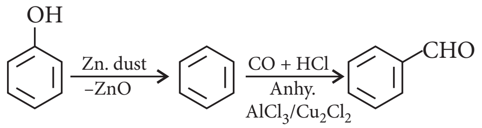
21. Stephen reduction :

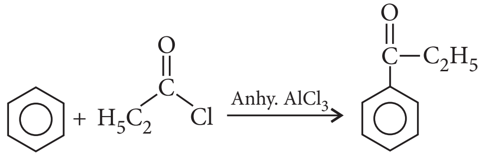
$$R\text{—CN} + SnCl_2 + HCl \xrightarrow{\text{Dry ether}} R-CH{=}NH \xrightarrow{H_3O^+} R-CHO$$

22. $$CH_3-CH{=}CH-CN \xrightarrow{\text{(a) DIBAL–H}} CH_3\text{—}CH{=}CH\text{—}CH{=}NH \xrightarrow{\text{(b) }H_2O} CH_3\text{—}CH{=}CH\text{—}CHO$$

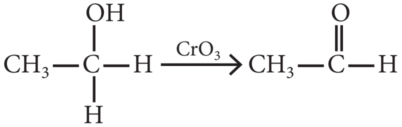
23. $$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) }H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$$

24. $$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[HgSO_4]{\text{dil. }H_2SO_4} \underset{\text{Ethanal}}{CH_3-CHO}$$

25. 

26. 

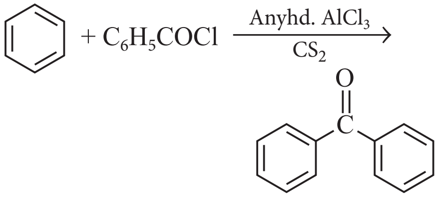
27. (i) *Refer to answer 23.*

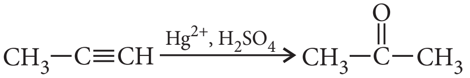
(ii) 

$$CH_3-\underset{H}{\overset{OH}{C}}-H \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-H$$

28. (i) *Refer to answer 21.*

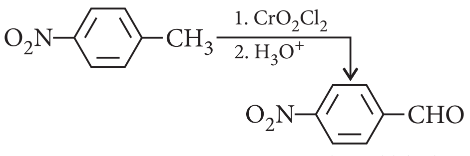
(ii) *Refer to answer 20.*

29. (i) 

(ii) 

$$CH_3-C\equiv CH \xrightarrow{Hg^{2+}, H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Propanone

(iii) 

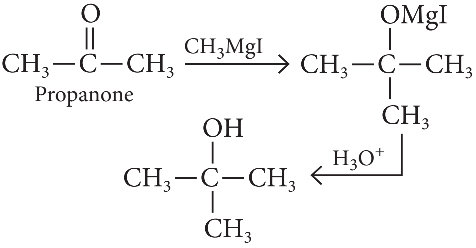
p-Nitrobenzaldehyde

30. The boiling points of aldehydes and ketones are lower than that of corresponding alcohols and acids due to absence of intermolecular H–bonding in aldehydes and ketones.

31. (d) : Iodoform test is given by the compound containing $CH_3\text{—}\underset{O}{\underset{\|}{C}}\text{—}$ or $CH_3\text{—}\underset{OH}{\underset{|}{CH}}\text{—}$ group thus it cannot be given by pentan-3-one, *i.e.*, $CH_3\text{—}CH_2\text{—}\underset{O}{\underset{\|}{C}}\text{—}CH_2\text{—}CH_3$.

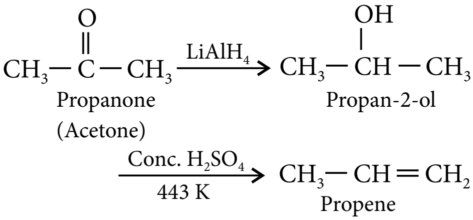
32. (d) : Reactivity of ketones is less than aldehydes.

33.

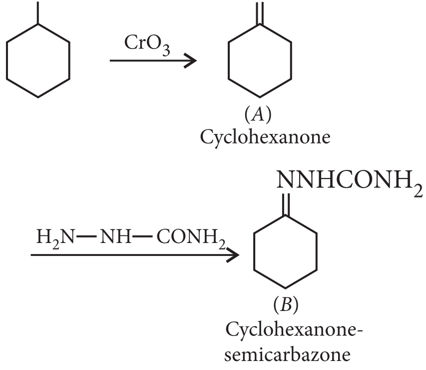


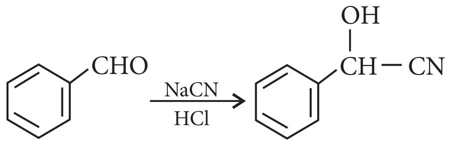
$$\underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{CH_3MgI} CH_3-\underset{CH_3}{\overset{OMgI}{C}}-CH_3 \xrightarrow{H_3O^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

2-Methylpropan-2-ol

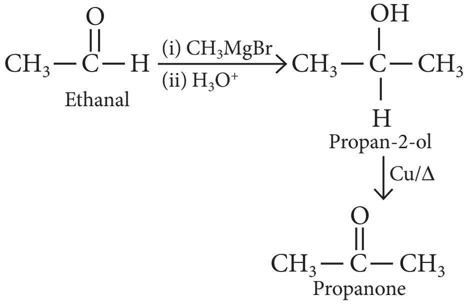
34. 

$$\underset{\substack{\text{Propanone}\\\text{(Acetone)}}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{CH}-CH_3} \xrightarrow[443\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

35. (c) : 

36. 

37.

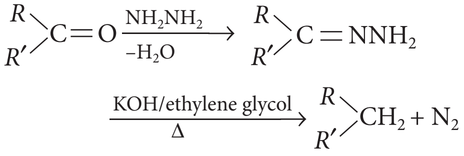


$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3} \xrightarrow{Cu/\Delta} \underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

38. Ethanal and propanal can be distinguished by iodoform test.

Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution whereas propanol will not give iodoform test.

39. Wolff-Kishner reduction :



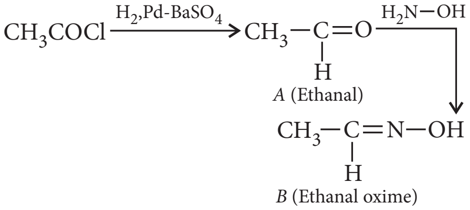
$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O \xrightarrow[-H_2O]{NH_2NH_2} \begin{matrix}R\\R'\end{matrix}\!\!>C=NNH_2 \xrightarrow[\Delta]{\text{KOH/ethylene glycol}} \begin{matrix}R\\R'\end{matrix}\!\!>CH_2 + N_2$$

40. *Refer to answer 34.*

41. Benzaldehyde and acetophenone can be distinguished by Tollens' test.

Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' test.

42.



$$CH_3COCl \xrightarrow{H_2,Pd\text{-}BaSO_4} \underset{A \text{ (Ethanal)}}{CH_3-\underset{\underset{H}{|}}{C}=O} \xrightarrow{H_2N-OH} \underset{B \text{ (Ethanal oxime)}}{CH_3-\underset{\underset{H}{|}}{C}=N-OH}$$

43. *Refer to answer 41.*

44. Propanal and butan-2-one can be distinguished by their reactions with Tollens' reagent.

Propanal will form the silver mirror, but butan-2-one does not react.

45. Lithium aluminium hydride ($LiAlH_4$).

46. (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

Benzoic acid will give effervescence with $NaHCO_3$ but benzaldehyde will not react.

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

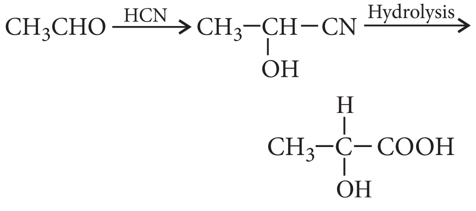
Propanal will form the silver mirror, but propanone does not react.

47. It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to carbonyl carbon.

48. *Refer to answer 46(ii).*

49. *Refer to answer 44.*

50.

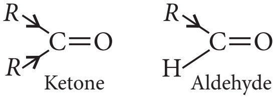


$$CH_3CHO \xrightarrow{HCN} CH_3-\underset{\underset{OH}{|}}{C}H-CN \xrightarrow{\text{Hydrolysis}} \underset{\text{2- Hydroxypropanoic acid}}{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-COOH}$$

51. In strongly acidic medium, ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH^- will attack carbonyl group.

Therefore, pH of the reaction should be carefully controlled.

52. Ketones are less reactive than aldehydes towards nucleophilic addition reactions because the two electron releasing alkyl groups decrease the magnitude of positive charge on carbonyl carbon and make it less susceptible to nucleophilic attack.

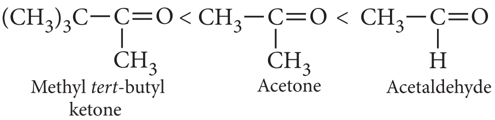


The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

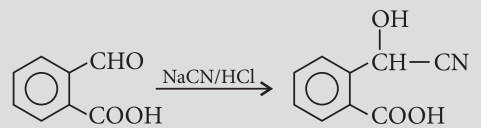
53. Butanone < propanone < propanal < ethanal.

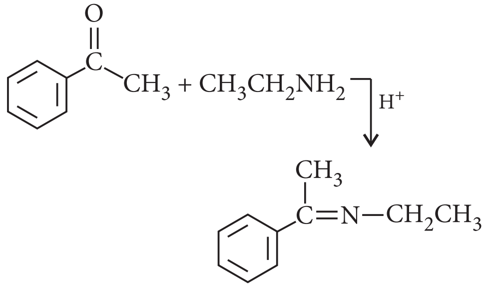
54. Acetophenone and benzophenone can be distinguished by iodoform test.

Acetophenone will give yellow precipitate of iodoform, but benzophenone will not react.

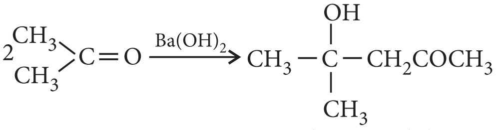
55. 
$(CH_3)_3C-\underset{CH_3}{\underset{|}{C}}=O < CH_3-\underset{CH_3}{\underset{|}{C}}=O < CH_3-\underset{H}{\underset{|}{C}}=O$

Methyl *tert*-butyl ketone · Acetone · Acetaldehyde

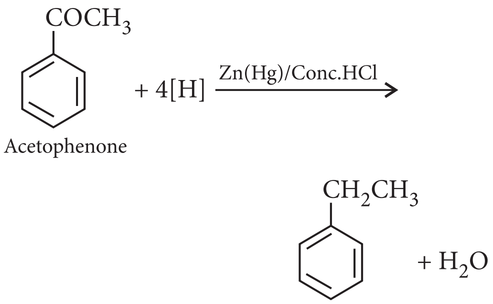
56. 

57. 

58.

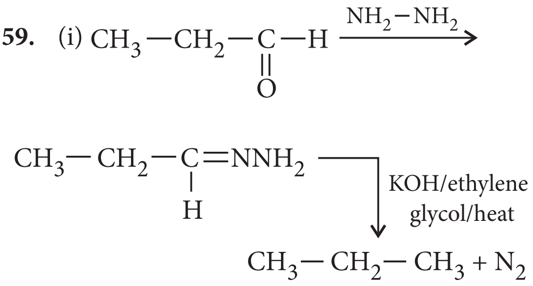
(i) 
$2\,{}^{CH_3}_{CH_3}{>}C=O \xrightarrow{Ba(OH)_2} CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2COCH_3$

4-Hydroxy-4-methyl-pentane-2-one

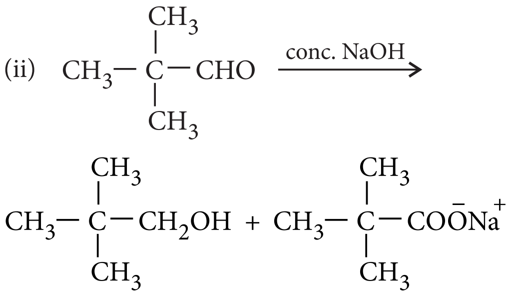
(ii) 

Acetophenone

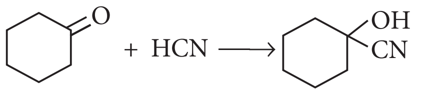
Ethylbenzene

59. (i) 
$CH_3-CH_2-\underset{O}{\underset{||}{C}}-H \xrightarrow{NH_2-NH_2} CH_3-CH_2-\underset{H}{\underset{|}{C}}=NNH_2 \xrightarrow{KOH/ethylene\ glycol/heat} CH_3-CH_2-CH_3+N_2$

(Wolff-Kishner reduction)

(ii) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CHO \xrightarrow{conc.\ NaOH} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH + CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CO\bar{O}\overset{+}{Na}$

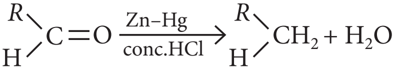
(Cannizzaro reaction)

60. (a) 

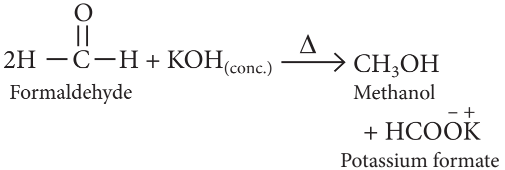
Cyclohexanone · Cyclohexane cyanohydrin

(b) Butanal respond to Fehling test and silver mirror test but butan-2-one does not respond.

61. (i) **Clemmensen reduction :**

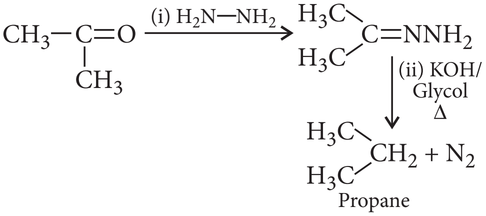


(ii) **Cannizzaro reaction :**


$2H-\overset{O}{\overset{||}{C}}-H + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCO\bar{O}\overset{+}{K}$

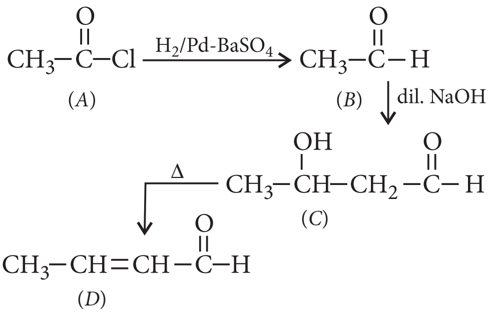
Formaldehyde · Methanol · Potassium formate

62. (i)

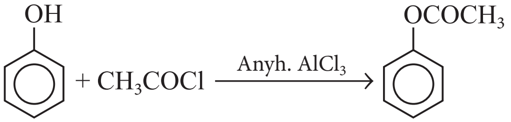


Propane

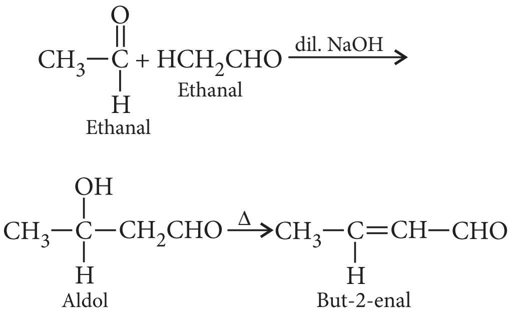
(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} CHI_3\downarrow$ Iodoform $+ C_6H_5CO\bar{O}\overset{+}{Na}$

63. 
$CH_3-\overset{O}{\overset{||}{C}}-Cl \; (A) \xrightarrow{H_2/Pd\text{-}BaSO_4} CH_3-\overset{O}{\overset{||}{C}}-H \; (B) \xrightarrow{dil.\ NaOH} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-H \; (C) \xrightarrow{\Delta} CH_3-CH=CH-\overset{O}{\overset{||}{C}}-H \; (D)$

64. (i) **Acetylation :** Introduction of acetyl group $\left(-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3\right)$ in alcohols, phenols or amines is called acetylation.



(ii) **Aldol condensation :** Two molecules of an aldehyde or ketones having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating give α,β-unsaturated aldehyde or ketone.



$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + HCH_2CHO \xrightarrow{\text{dil. NaOH}}$$

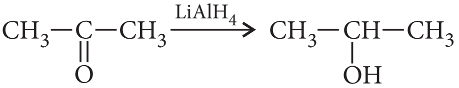
Ethanal Ethanal

$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2CHO \xrightarrow{\Delta} CH_3-\underset{\underset{\displaystyle H}{|}}{C}=CH-CHO$$

Aldol But-2-enal

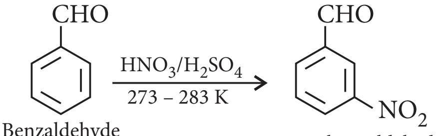
65.

(i)



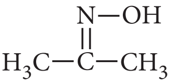
$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

(ii)



Benzaldehyde *m*-Nitrobenzaldehyde

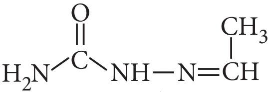
66. (i)



$$H_3C-\overset{\overset{\displaystyle N-OH}{\|}}{C}-CH_3$$

2-propanone oxime

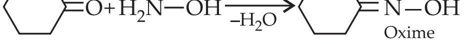
(ii)



Semicarbazone

67.

(i)



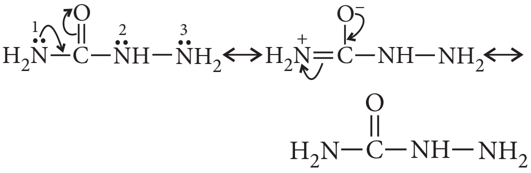
Oxime

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

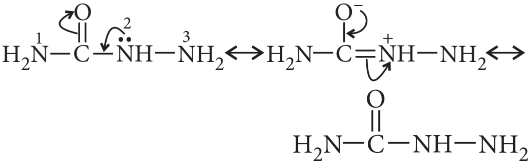
$C_6H_5COONa + C_6H_5CH_2OH$

68. (i) *Refer to answer 47.*

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.



$$H_2\ddot{N}-\overset{\overset{O}{\|}}{C}-\ddot{N}H-\ddot{N}H_2 \leftrightarrow H_2\overset{+}{N}=\overset{\overset{O^-}{|}}{C}-NH-NH_2 \leftrightarrow H_2N-\overset{\overset{O}{\|}}{C}-NH-NH_2$$



$$H_2N-\overset{\overset{O}{\|}}{C}-\ddot{N}H-NH_2 \leftrightarrow H_2N-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H-NH_2 \leftrightarrow H_2N-\overset{\overset{O}{\|}}{C}-NH-NH_2$$

Lone pairs of N-1 and N-2 are involved in conjugation with $>C=O$ group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

69. (i) **Rosenmund's reaction :**

$$CH_3COCl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4,\ S} CH_3CHO + HCl$$

Ethanoyl chloride Ethanal
(Acetyl chloride) (Acetaldehyde)

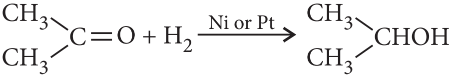
(ii) *Refer to answer 61(ii).*

70. (i) *Refer to answer 61(ii).*

(ii) *Refer to answer 65(ii).*

71.

(i)



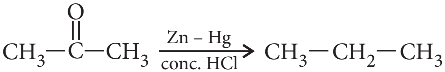
Propanone Propan-2-ol

(ii) *Refer to answer 50.*

72.

(a) NaOI	 $CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$ Pentan-3-one ⟶ No reaction	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_2CH_3$ Pentan-2-one gives iodoform test.
(b) NaOI	CH_3CHO Ethanal gives iodoform test.	$CH_3CH_2CHO \longrightarrow$ Propanal No reaction

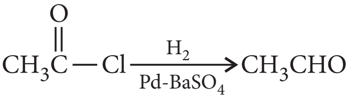
73. (i)



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{conc. HCl}]{\text{Zn – Hg}} CH_3-CH_2-CH_3$$

Acetone Propane

(ii)

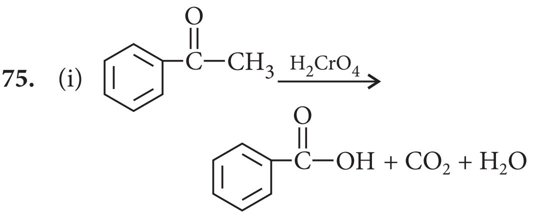


$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\text{Pd-BaSO}_4]{H_2} CH_3CHO$$

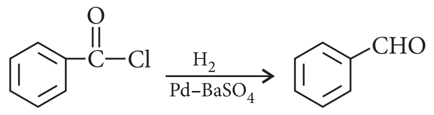
74. (i) *Refer to answer 46(ii).*

(ii) *Refer to answer 41.*

75. (i)

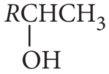


(ii)



Benzoyl chloride Benzaldehyde

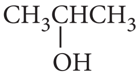
76. Compound *B* gives positive iodoform test, it means it contains —$COCH_3$ (methyl ketone) group *i.e.*, it is a ketone. Moreover, *B* is obtained by the oxidation of *A*, thus *A* must be a 2° alcohol. (As only 2° alcohol give ketones on oxidation with Cu at 573 K. Hence, the structure of compound *A* is



$R\underset{|\atop OH}{C}HCH_3$

Comparing with the given molecular formula gives $R = CH_3$.

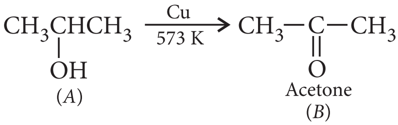
Thus, compound *A* is



$CH_3\underset{|\atop OH}{C}HCH_3$

(Propan-2-ol)

The reaction is as follows :



$$CH_3\underset{\underset{(A)}{OH}}{\underset{|}{C}}HCH_3 \xrightarrow[573\text{ K}]{Cu} \underset{\text{Acetone }(B)}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3}$$

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

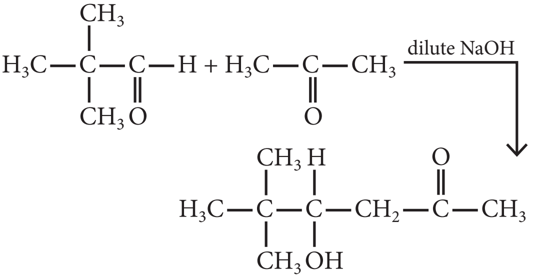
$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3COONa + 3NaI + \underset{\underset{(C)}{\text{Iodoform}}}{CHI_3}\downarrow + 3H_2O$$

Thus, $A = CH_3CH(OH)CH_3$

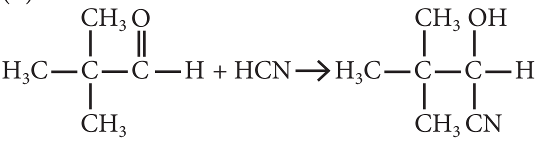
$B = CH_3COCH_3$

$C = CHI_3$

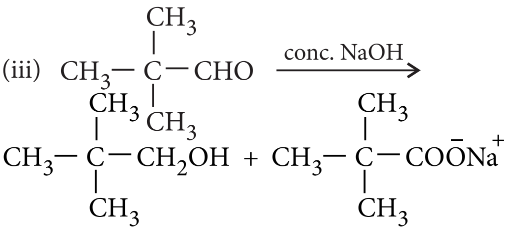
77. (i)



(ii)



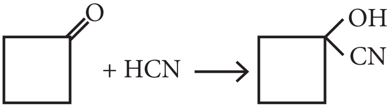
(iii)



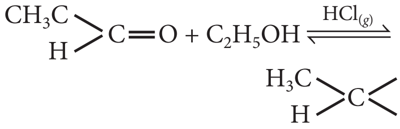
(Cannizzaro reaction)

78. (a) *Refer to answer 46(ii).*

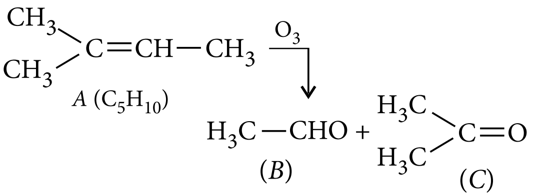
(b) (i)



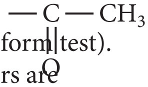
(ii)



79. As compound *B* gives positive Fehling's test so it is an aldehyde and as it gives positive iodoform test so it is acetaldehyde. Compound *C* does not give Fehling's solution test. So it is a ketone which could be acetone because acetone gives positive iodoform test.



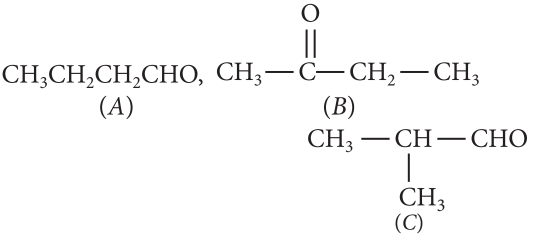
80. (a) As (*A*) and (*C*) give positive Tollens' test thus these two should be aldehyde while (*B*) should be a ketone (does not give Tollens' test) with



$-\underset{\underset{O}{\|}}{C}-CH_3$

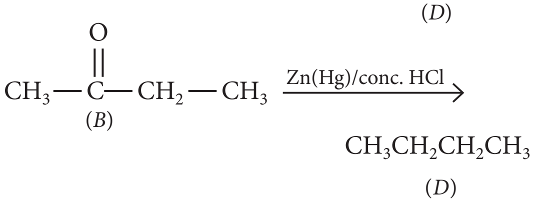
group (as it gives positve iodoform test).

Three isomers are



$$\underset{(A)}{CH_3CH_2CH_2CHO},\quad \underset{(B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3}\quad \underset{(C)}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO}$$

$$\underset{(A)}{CH_3CH_2CH_2CHO} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

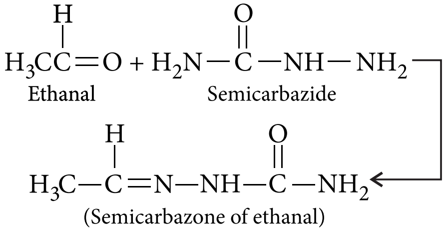


$$\underset{(B)}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

(b) Out of (*A*), (*B*) and (*C*) isomers, (*B*) is least reactive towards addition of HCN.

81. (a) *Refer to answer 61(ii).*

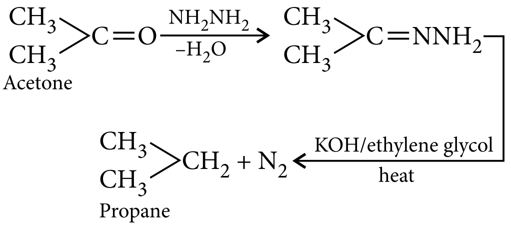
(b)



$$\underset{\text{Ethanal}}{H_3C\overset{H}{\overset{|}{C}}=O} + \underset{\text{Semicarbazide}}{H_2N-\overset{O}{\overset{||}{C}}-NH-NH_2} \longrightarrow \underset{\text{(Semicarbazone of ethanal)}}{H_3C-\overset{H}{\overset{|}{C}}=N-NH-\overset{O}{\overset{||}{C}}-NH_2}$$

(c) *Refer to answer 46(ii).*

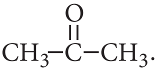
82. (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



(b) Increasing order of reactivity towards nucleophilic addition reaction :

$$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$$

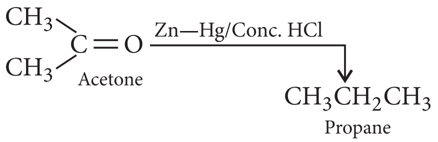
(c) Formula of compounds *A* and *B* = C_3H_6O
B forms yellow precipitate of iodoform. Hence, *B* must contain $—COCH_3$ group. Therefore,



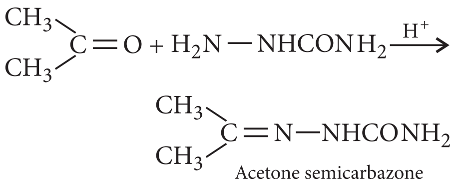
compound '*B*' must be $CH_3-\overset{O}{\overset{||}{C}}-CH_3$.

A does not give iodoform test and it is functional isomer of *B* thus, it may be CH_3CH_2CHO.

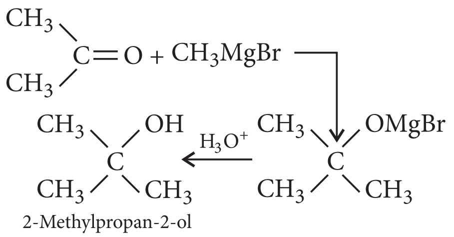
83. (i)



(ii)

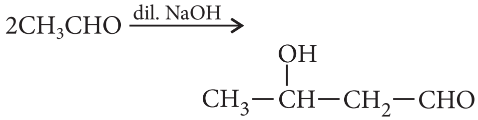


(iii)



84. (i) $CH_3CHO \xrightarrow{Zn-Hg/conc.\ HCl} CH_3—CH_3$

(ii)



$$2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$$

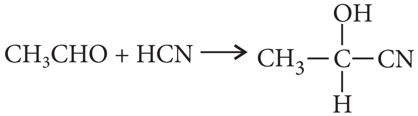
(iii) $CH_3CHO \xrightarrow{H_2/Ni} CH_3—CH_2—OH$

85. (i) *Refer to answer 82(a).*

(ii) *Refer to answer 64(ii).*

(iii) *Refer to answer 61(ii).*

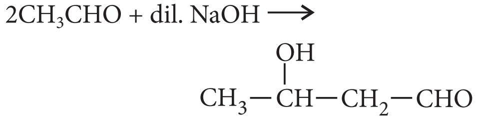
86. (i)



$$CH_3CHO + HCN \longrightarrow CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CN$$

(ii) $CH_3CHO + H_2NOH \longrightarrow CH_3—CH=N—OH$

(iii)



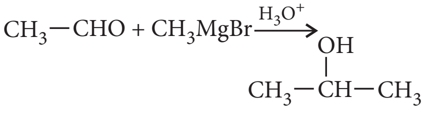
$$2CH_3CHO + dil.\ NaOH \longrightarrow CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$$

87. (a) (i) *Refer to answer 69(i).*

(ii) *Refer to answer 61(ii).*

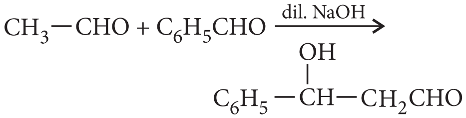
(b) $CH_3CH_2CH_2—CO—CH_3$ will give iodoform test because it contains acetyl group.

88. (i)

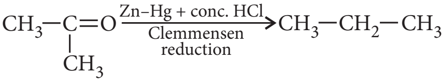


$$CH_3-CHO + CH_3MgBr \xrightarrow{H_3O^+} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$$

(ii) $CH_3CHO \xrightarrow[Conc.\ HCl]{Zn-Hg} CH_3-CH_3$

(iii) 

$$CH_3-CHO + C_6H_5CHO \xrightarrow{\text{dil. NaOH}} C_6H_5-\overset{OH}{\overset{|}{C}H}-CH_2CHO$$

89. (i) 

$$CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow[\text{Clemmensen reduction}]{\text{Zn–Hg + conc. HCl}} CH_3-CH_2-CH_3$$

(ii) *Refer to answer 75(ii).*

(iii) *Refer to answer 64(ii).*

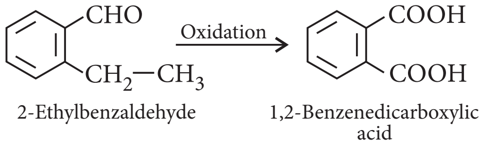
90. Benzaldehyde has a characteristic odour. Reaction of '*A*' with NaOH appears to be Cannizzaro reaction which gives '*B*' (benzyl alcohol) and '*C*' (Sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime gives benzene (*D*).

$$\underset{\text{'}A\text{'}}{C_6H_5CHO} \xrightarrow{NaOH} \underset{\substack{\text{'}B\text{'}\\(C_7H_8O)}}{C_6H_5CH_2OH} + \underset{\substack{\text{'}C\text{'}\\\text{(Sodium salt of}\\\text{benzoic acid)}}}{C_6H_5COONa}$$

$$\underset{\text{'}B\text{'}}{C_6H_5CH_2OH} \xrightarrow{CrO_3} \underset{\text{'}A\text{'}}{C_6H_5CHO}$$

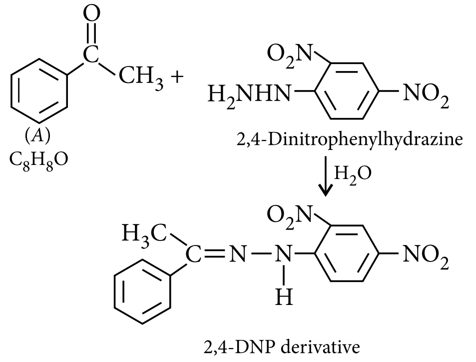
$$\underset{\text{'}C\text{'}}{C_6H_5COONa} \xrightarrow[\Delta]{NaOH/CaO} \underset{\substack{\text{'}D\text{'}\\\text{(Benzene)}\\\text{(Aromatic)}}}{C_6H_6} + Na_2CO_3$$

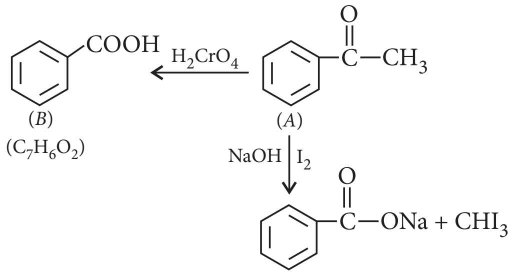
91. The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α-hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid which shows that there are two carbon residues on benzene ring. Since the molecular formula is $C_9H_{10}O$, it fits into the structure, 2-ethylbenzaldehyde.



92. (*A*) forms, 2, 4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (*A*) must be a ketone. (*A*) responds to iodoform test.

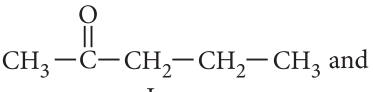
Compound (*B*), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (*B*) indicates that it should be benzoic acid and compound (*A*) should, therefore, be a mono-substituted aromatic methyl ketone.





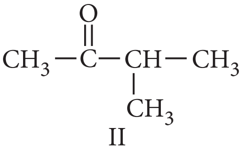
93. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should contain $-\overset{O}{\overset{\|}{C}}-CH_3$ group.

On the basis of this information, two possible structures are written as under :



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$$ and

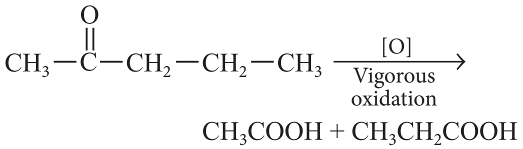
I



$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}H}-CH_3$$

II

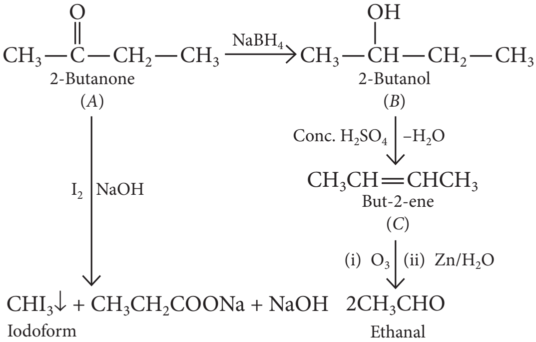
On oxidation, this compound gives ethanoic and propanoic acids which confirm its structure to be I.



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3 \xrightarrow[\text{Vigorous oxidation}]{[O]} CH_3COOH + CH_3CH_2COOH$$

94. (a) As (*A*) forms 2, 4-DNP derivative, hence it is an aldehyde or ketone. Since it does not reduce Tollens' reagent, hence it is a ketone (*A*). As it gives iodoform reaction, hence it is a methyl ketone, *i.e.*, contains $CH_3-\overset{\overset{O}{||}}{C}-$ group.

Therefore, (*A*) must be $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$ *i.e.*, 2-butanone.



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow{NaBH_4} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CH_3$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow{I_2/NaOH} CHI_3\downarrow + CH_3CH_2COONa + NaOH$$

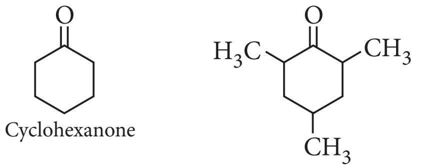
$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CH_3 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CH_3CH=CHCH_3 \xrightarrow{(i)\ O_3\ (ii)\ Zn/H_2O} 2CH_3CHO$$

(b) (i) Unlike aldehydes, ketones do not contain any hydrogen atom attached to $\rangle C=O$ group and hence they cannot be oxidised without the cleavage of some carbon-carbon bonds. Thus oxidation of propanal is easier than propanone.

(ii) Due to –*I* effect of the carbonyl group of aldehydes and ketones, it withdraw electrons from the adjacent carbon-carbon bond. This makes α-carbon electron deficient. The α-carbon in turn, withdraws electrons from the $C_\alpha-H$ bonds. As a result, the electron density in $C_\alpha-H$ bond decreases. Hence the α-hydrogens are weakly held and can be easily abstracted by strong bases giving enolate anions which are stabilised by resonance.

95. (a) (i) *Refer to answer 68(ii).*

(ii) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN^-) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,4,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



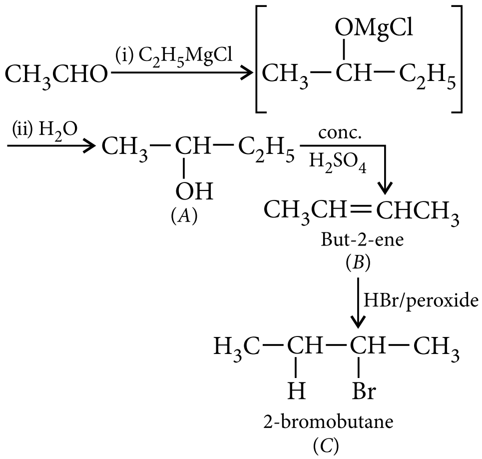
Cyclohexanone

2,4,6-Trimethylcyclohexanone

(b) *Refer to answer 91.*

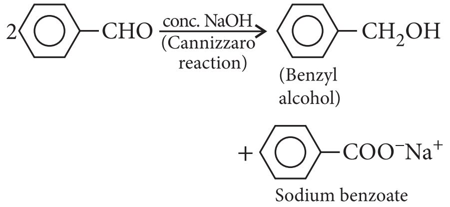
96.

(a)



$$CH_3CHO \xrightarrow{(i)\ C_2H_5MgCl} \left[CH_3-\overset{\overset{OMgCl}{|}}{C}H-C_2H_5\right] \xrightarrow{(ii)\ H_2O} \underset{(A)}{CH_3-\underset{OH}{\underset{|}{C}H}-C_2H_5} \xrightarrow[H_2SO_4]{\text{conc.}} \underset{(B)}{\underset{\text{But-2-ene}}{CH_3CH=CHCH_3}} \xrightarrow{HBr/peroxide} \underset{(C)}{\underset{\text{2-bromobutane}}{H_3C-\underset{H}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3}}}$$

(b) (i)

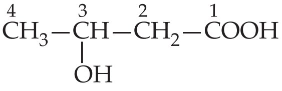


$$2\,C_6H_5CHO \xrightarrow[\text{(Cannizzaro reaction)}]{\text{conc. NaOH}} \underset{\text{(Benzyl alcohol)}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COO^-Na^+}$$

(ii) *Refer to answer 65(ii).*

97. **(a)**

98.



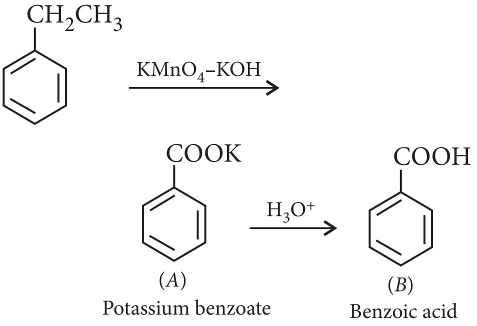
$$\overset{4}{C}H_3-\overset{3}{\underset{OH}{\underset{|}{C}H}}-\overset{2}{C}H_2-\overset{1}{C}OOH$$

3-Hydroxybutan-1-oic acid

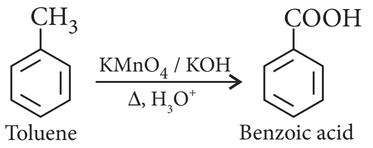
99. Hex-2-en-4-yn-oic acid

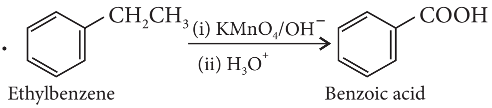
100. 3-Bromo-5-chlorobenzoic acid

101.

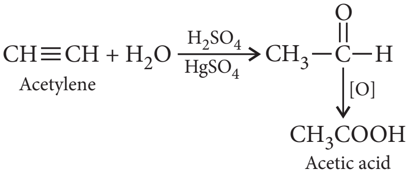


$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4-KOH} \underset{(A)}{C_6H_5COOK} \xrightarrow{H_3O^+} \underset{(B)}{C_6H_5COOH}$$

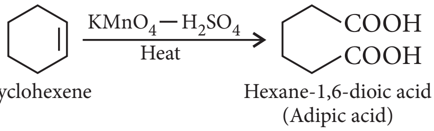
102. 

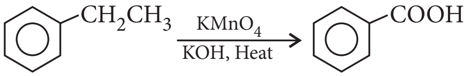
103. 

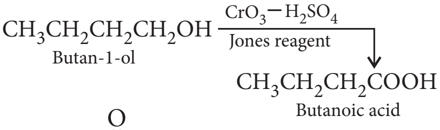
104. Alkaline potassium permanganate ($KMnO_4$, KOH)

105. 

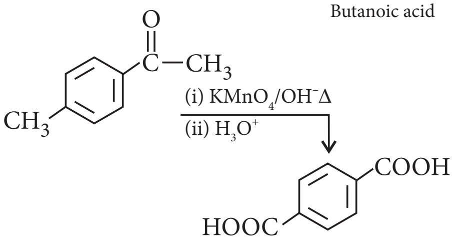
$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

106. 

107. 

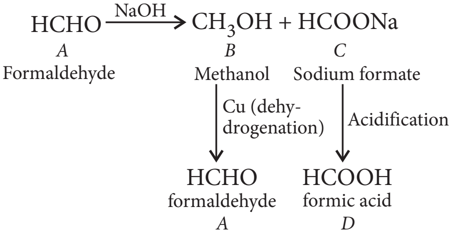
108. (i) 

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Jones reagent}]{CrO_3-H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(ii) 

109. 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 (HCOONa).

Thus, *A* must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



$$\underset{\substack{A\\\text{Formaldehyde}}}{HCHO} \xrightarrow{NaOH} \underset{\substack{B\\\text{Methanol}}}{CH_3OH} + \underset{\substack{C\\\text{Sodium formate}}}{HCOONa}$$

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{\text{Cu (dehydrogenation)}} \underset{\substack{\text{formaldehyde}\\A}}{HCHO} \qquad \underset{\text{Sodium formate}}{HCOONa} \xrightarrow{\text{Acidification}} \underset{\substack{\text{formic acid}\\D}}{HCOOH}$$

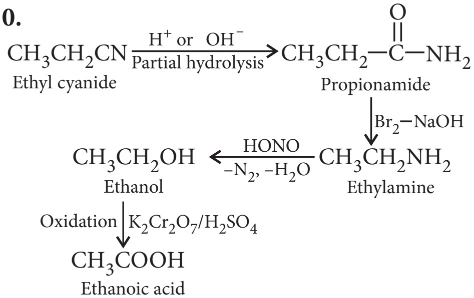
Thus, *A* = Formaldehyde (HCHO)

B = Methanol (CH_3OH)

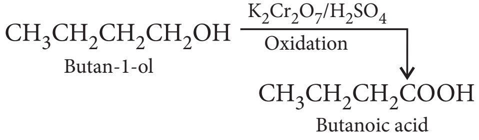
C = Sodium formate (HCOONa)

D = Formic acid (HCOOH)

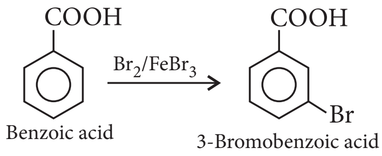
110.

(i) 

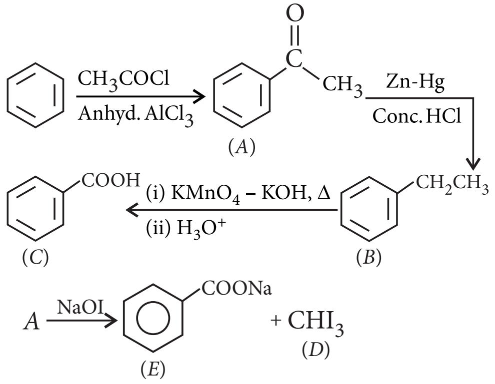
$$\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{H^+ \text{ or } OH^-} \underset{\text{Propionamide}}{CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} \xrightarrow{Br_2-NaOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{Oxidation}} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(ii) 

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(iii) 

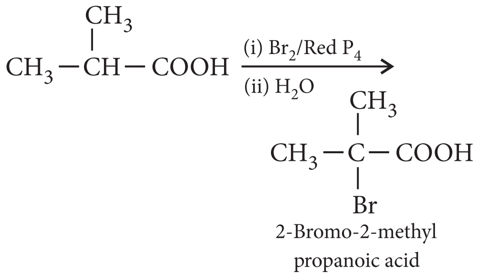
111.



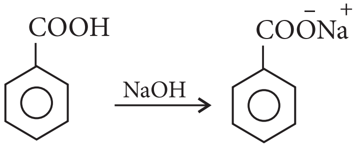
112. Increasing order of boiling point :

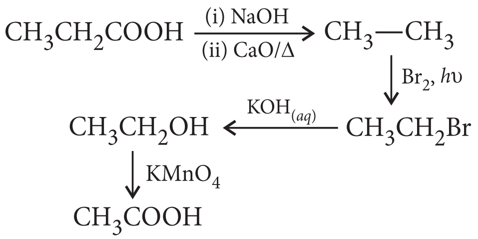
$CH_3—CHO < C_2H_5OH < CH_3—COOH$

113. **(c) :** Due to presence of electron withdrawing group (—COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

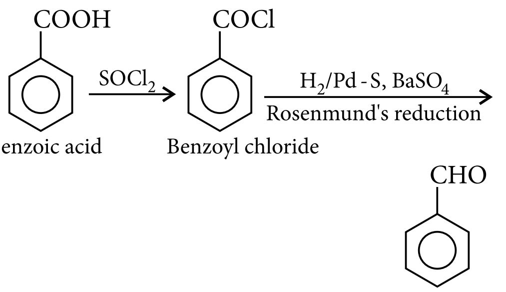
114. 

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\text{Red } P_4} \underset{\text{2-Bromo-2-methyl propanoic acid}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-COOH}$$

115. 

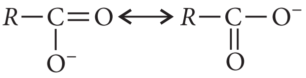
116. 

$$\begin{tikzcd}
& CH_3CH_2COOH \arrow[r, "(i)\ NaOH", "(ii)\ CaO/\Delta"'] & CH_3{-}CH_3 \arrow[d, "Br_2,\ h\upsilon"] \\
CH_3CH_2OH \arrow[d, "KMnO_4"] & & CH_3CH_2Br \arrow[ll, "KOH_{(aq)}"'] \\
CH_3COOH & &
\end{tikzcd}$$

117. 

Benzoic acid Benzoyl chloride Benzaldehyde

118. The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :



$$\underset{\displaystyle O^-}{R-\underset{|}{C}=O} \longleftrightarrow R-\underset{\underset{\displaystyle O}{||}}{C}-O^-$$

119. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.

120. Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \xrightarrow{\text{Warm}} \underset{\text{Silver mirror}}{2Ag} + CO_2 + 2NH_3 + 2NH_4OH$$

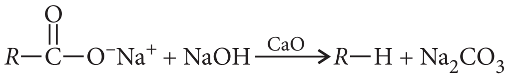
Acetic acid does not give this test.

121. $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

122. $CH_3{-}COOH \xrightarrow{PCl_5} CH_3{-}COCl + POCl_3 + HCl$

123. *Refer to answer 122.*

124. Decarboxylation : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.



$$R-\overset{\overset{\displaystyle O}{||}}{C}-O^-Na^+ + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

125. *Refer to answer 118.*

126. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

127. Hell-Volhard-Zelinsky reaction : Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

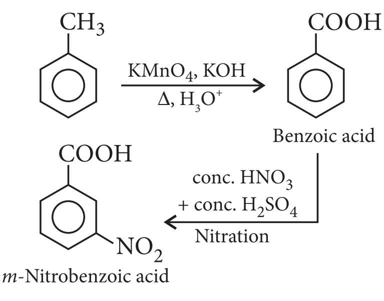
$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2{-}COOH} + HCl$$

$$ClCH_2{-}COOH + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} + HCl$$

$$Cl_2CHCOOH + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH} + HCl$$

128. *Refer to answer 110(iii).*

129. Chloroacetic acid has lower pK_a value than acetic acid; 'Cl' in chloroacetic acid shows $-I$ effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. Hence, chloroacetic acid is stronger than acetic acid.

130. 

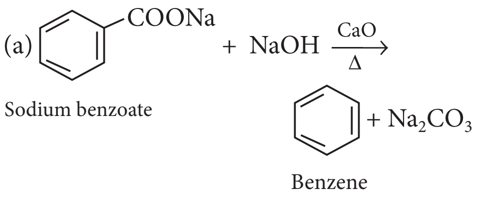
131. (a) Due to presence of electron withdrawing group (— COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

(b) Due to presence of strong electron withdrawing group (—NO_2), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, pK_a value is lower.

132. (i) *Refer to answer 127.*

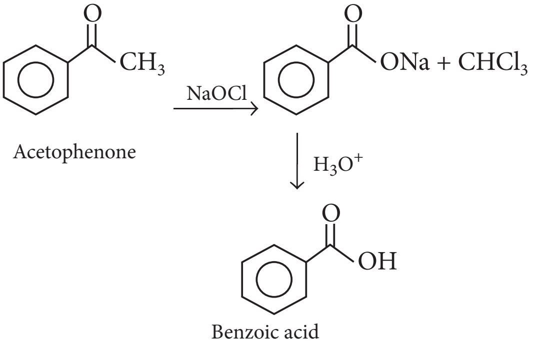
(ii) *Refer to answer 124.*

133. (a)



(b) *Refer to answer 126.*

134. (i) Acetophenone to benzoic acid :

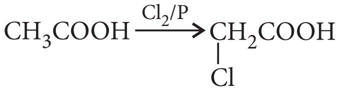


(ii) Ethanoic acid to 2-hydroxyethanoic acid.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O]{Cl_2/\text{Red P}} \underset{\text{2-Chloroethanoic acid}}{Cl{-}CH_2{-}COOH}$$

$$\xrightarrow{NaOH} \underset{\text{2-Hydroxyethanoic acid}}{HO{-}CH_2{-}COOH}$$

135. (a)



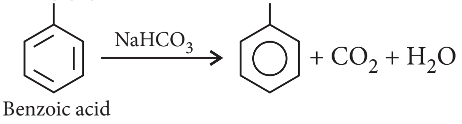
$$CH_3COOH \xrightarrow{Cl_2/P} \underset{\displaystyle Cl}{\underset{|}{CH_2}}COOH$$

(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$
$$C_6H_5COO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

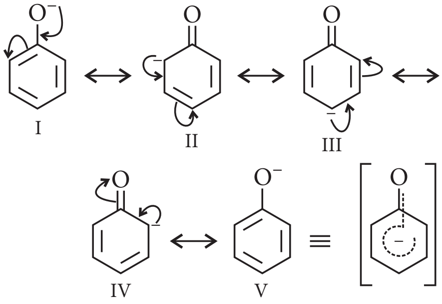
Benzoic acid does not give this test.

Benzoic acid reacts with sodium bicarbonate to liberate CO_2.

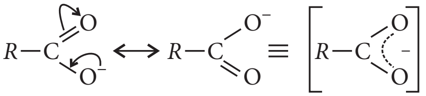


136. *Refer to answer 129.*

137. Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonating structures.

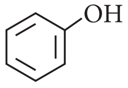


(i) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

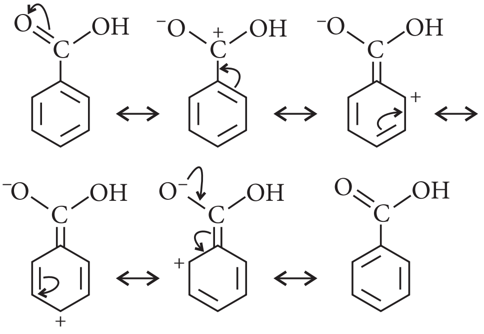
(ii) The negative charge rests on the electronegative O atom in carboxylate ion. The presence of negative charge on an electronegative atom makes the ion more stable. For the same reason $RCOO^-$ is more stable than the phenoxide ion where the carbon has negative charge on it. For the above two reasons carboxylate ion is more stable and hence carboxylic acid has higher acidity than phenol.

138. (i) $F{-}CH_2COOH > Cl{-}CH_2COOH$

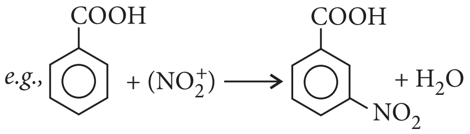
(ii) CH_3COOH is stronger than



139. (i) Electrophilic substitution in benzoic acid takes place at *meta*-position. Due to resonance in benzoic acid, there is high electron density at *meta*-position. Therefore, electrophilic substitution in benzoic acid takes place at *meta*-position.



e.g.,



(ii) *Refer to answer 118.*

140. (i) The overall acid strength increases in the order.

4-Methoxybenzoic acid < benzoic acid < 3,4-dinitrobenzoic acid.

(ii) We know that + *I*-effect decreases while –*I*-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order :

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

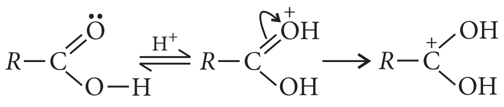
141. Esterification : Carboxylic acids react with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas as catalyst and give ester.

$$R\text{—COOH} + R'\text{OH} \rightleftharpoons R\text{—COO}R' + H_2O$$

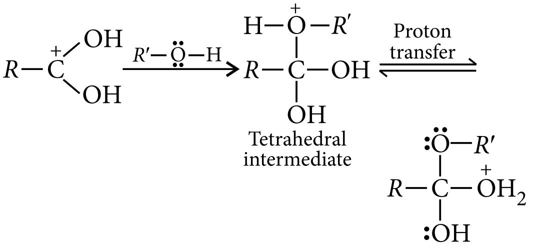
$$\text{e.g., } \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

Mechanism of esterification : It is a nucleophilic acyl substitution.

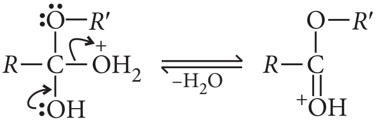
(a) Protonation of carboxyl oxygen :



(b) Nucleophilic addition of alcohol :

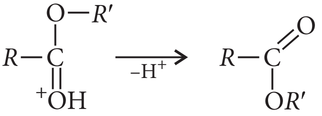


(c) Elimination of water molecule :



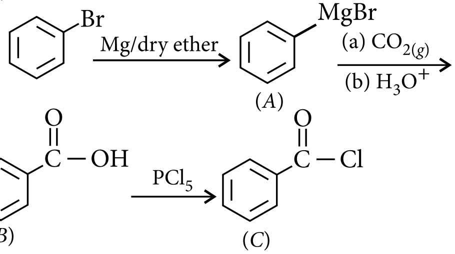
Protonated ester

(d) Protonated ester loses a proton to give ester :

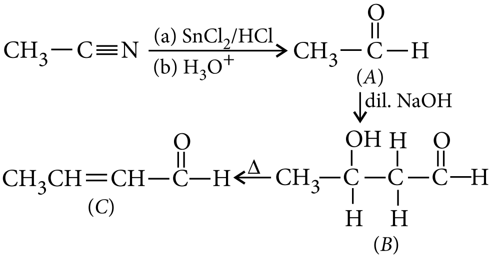


Ester

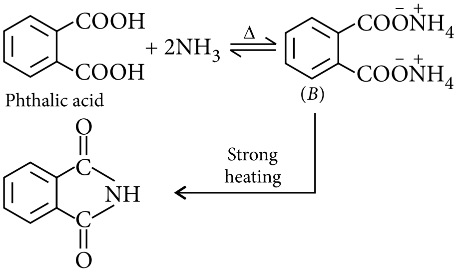
142. (i)



(ii)



143.



Phthalimide
(*C*)