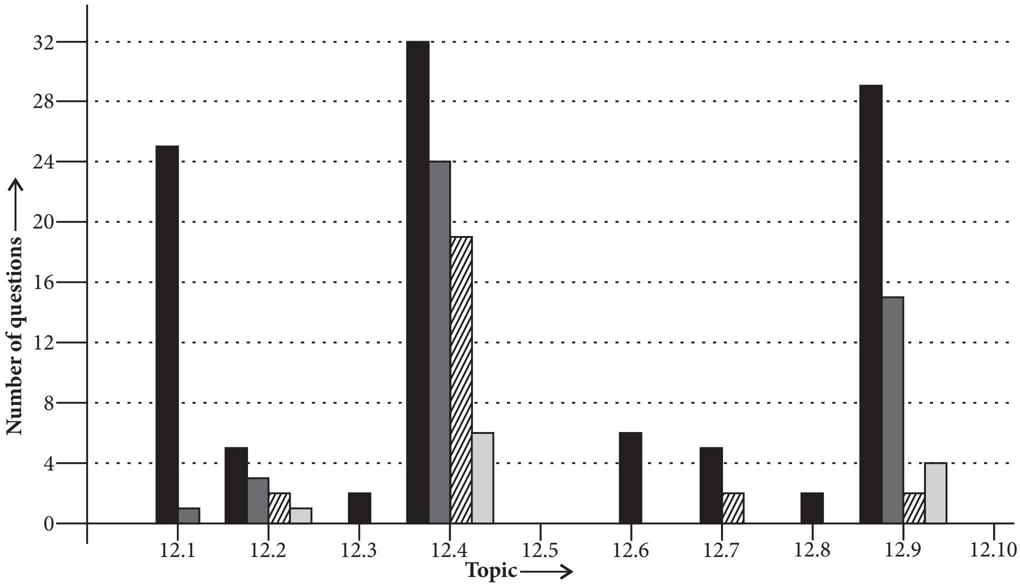
12

Aldehydes, Ketones and Carboxylic Acids

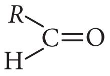
Topicwise Analysis of Last 10 Years' CBSE Board Questions

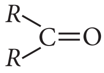


- Maximum total weightage is of *Chemical Reactions of Aldehydes and Ketones.*
- Maximum VSA type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*
- Maximum SA I and SA II type questions were asked from *Chemical Reactions of Aldehydes and Ketones.*

QUICK RECAP

ALDEHYDES AND KETONES

- **General formula :** $C_nH_{2n}O$ having $>C=O$ group.
- **Aldehydes :** 
$\begin{matrix}R\\H\end{matrix}\!>C=O$ 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.

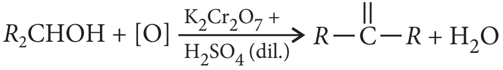
- The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.

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 :**

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



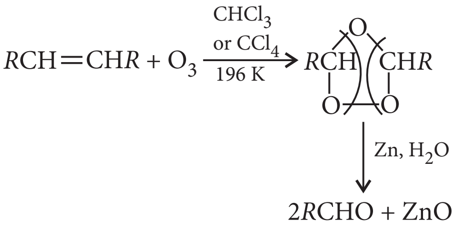
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(\text{dil.})]{K_2Cr_2O_7\,+} R{-}\overset{\overset{O}{\|}}{C}{-}R + H_2O$$

- **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 :**



$$RCH{=}CHR + O_3 \xrightarrow[196\text{ K}]{CHCl_3\text{ or }CCl_4} \text{ozonide} \xrightarrow{Zn,\,H_2O} 2RCHO + ZnO$$

- **Rosenmund reduction :**

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

- **Reduction of nitriles :**

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

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

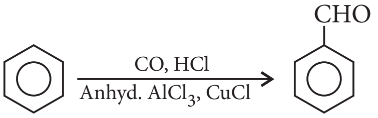
$$RC{\equiv}N \xrightarrow[(ii)\ \text{Ether}\ (iii)\ H_2O]{(i)\ SnCl_2 + HCl} RCHO + NH_4Cl$$

(Stephen reduction)

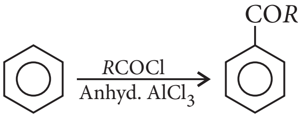
- **From esters :**

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

- **Gatterman-Koch reaction :**



- **Friedel-Crafts acylation :**

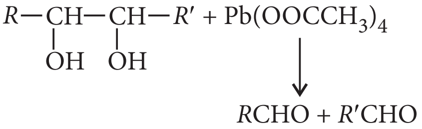


- **From alkynes :**

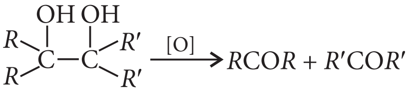
$$-C{\equiv}C- \xrightarrow[HgSO_4,\,333\text{ K}]{\text{dil. }H_2SO_4} RCHO\text{ or }RCOR$$

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

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

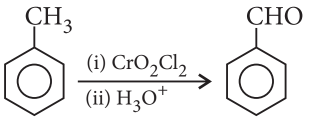


$$R{-}\underset{OH}{CH}{-}\underset{OH}{CH}{-}R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO$$

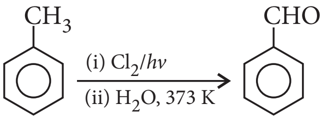


$$R_2C(OH){-}C(OH)R'_2 \xrightarrow{[O]} RCOR + R'COR'$$

- **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.

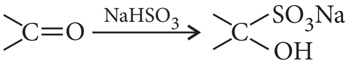
- **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - All carbonyl compounds are fairly soluble in organic solvents.

Chemical properties :

- **Nucleophilic addition reactions :**

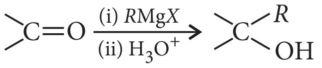
$$>C=O \xrightarrow{HCN} >C(CN)(OH)$$

Cyanohydrin

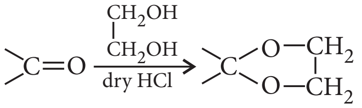


$$>C=O \xrightarrow{NaHSO_3} >C(SO_3Na)(OH)$$

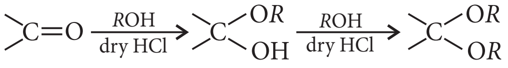
Bisulphite



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



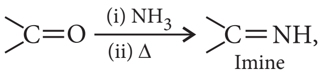
$$>C=O \xrightarrow[\text{dry HCl}]{CH_2OH-CH_2OH} >C<(O-CH_2)(O-CH_2)$$



$$>C=O \xrightarrow[\text{dry HCl}]{ROH} >C(OR)(OH) \xrightarrow[\text{dry HCl}]{ROH} >C(OR)(OR)$$

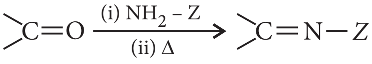
Hemiacetal Acetal

- **Nucleophilic addition-elimination reactions :**

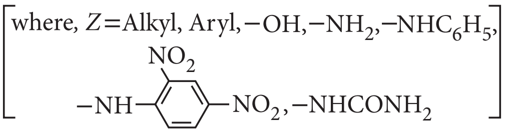


$$>C=O \xrightarrow[\text{(ii) } \Delta]{\text{(i) } NH_3} >C=NH,$$

Imine

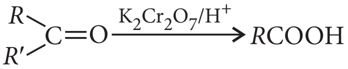


$$>C=O \xrightarrow[\text{(ii) } \Delta]{\text{(i) } NH_2-Z} >C=N-Z$$

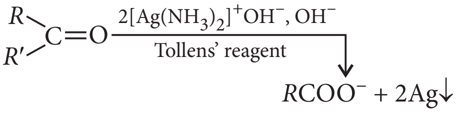


[where, Z=Alkyl, Aryl, $-OH$, $-NH_2$, $-NHC_6H_5$, $-NH-C_6H_3(NO_2)-NO_2$, $-NHCONH_2$]

- **Oxidation :**

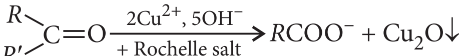


$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow{K_2Cr_2O_7/H^+} RCOOH$$



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

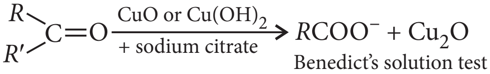
Silver mirror test
(Only aldehydes)



$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow[\text{+ Rochelle salt}]{2Cu^{2+},\ 5OH^-} RCOO^- + Cu_2O\downarrow$$

red ppt.

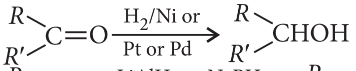
Fehling's solution test
(Only aldehydes)



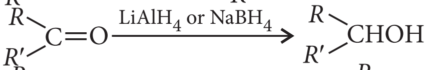
$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow[\text{+ sodium citrate}]{CuO \text{ or } Cu(OH)_2} RCOO^- + Cu_2O$$

Benedict's solution test
(Only aldehydes)

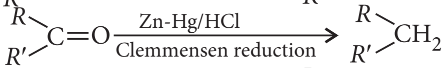
- **Reduction :**



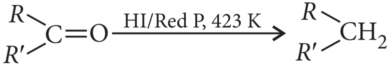
$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow[\text{Pt or Pd}]{H_2/Ni \text{ or}} \underset{R'}{\overset{R}{>}}CHOH$$



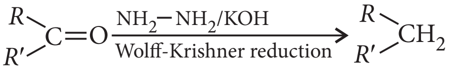
$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow{LiAlH_4 \text{ or } NaBH_4} \underset{R'}{\overset{R}{>}}CHOH$$



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



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



$$\underset{R'}{\overset{R}{>}}C=O \xrightarrow[\text{Wolff-Krishner reduction}]{NH_2-NH_2/KOH} \underset{R'}{\overset{R}{>}}CH_2$$

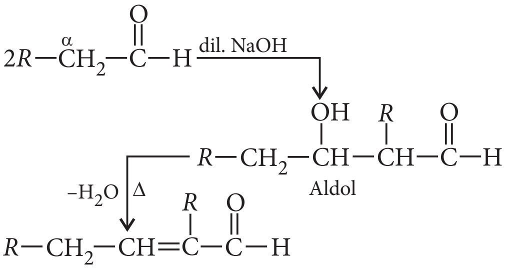
- **Haloform reaction :**

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

$$RCOCH_3 + 3NaOI \longrightarrow RCOONa + \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$$

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

- **Aldol condensation :**



$$2R-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil. NaOH}} \underset{\text{Aldol}}{R-CH_2-\overset{OH}{\overset{|}{CH}}-\overset{R}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[\Delta]{-H_2O} R-CH_2-CH=\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

α,β-Unsaturated aldehyde

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

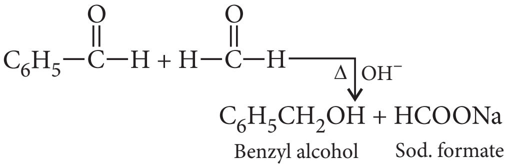
  - **Intramolecular aldol condensation :** It takes place in diketones and gives rise to cyclic products.
  - **Crossed aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if both of them contain α-hydrogen atoms, it gives a mixture of four products.

- **Cannizzaro reaction :**

$$\underset{\text{Formaldehyde}}{HCHO + HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOOK}$$

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

  - **Crossed Cannizzaro reaction :**



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

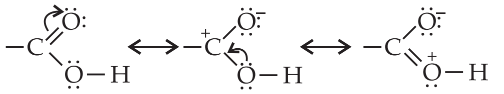
  - **Intramolecular Cannizzaro reaction :** It is given by dialdehydes having no α-hydrogen atoms.

- **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 :**

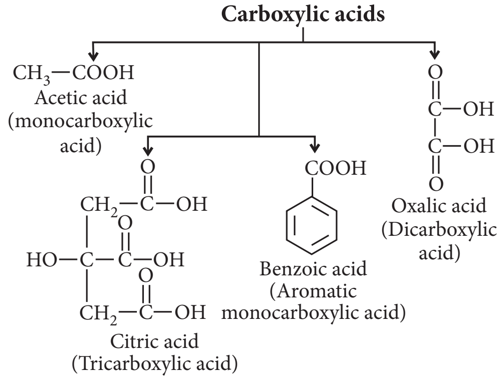
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-Dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow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

CARBOXYLIC ACIDS

- **General Formula :** $C_nH_{2n}O_2$ having —COOH group.
  RCOOH 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 :**

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

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

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

$$\underset{\text{Alkyl Cyanide}}{RCN} \xrightarrow[\text{Alkali NaOH or KOH}]{\text{Hydrolysis}} RCOONa \xrightarrow{HCl} RCOOH$$

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

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

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

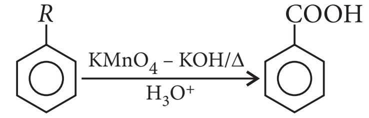
$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow{H_2O} RCOOH$$

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

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

$$\underset{\text{Alkene}}{RCH{=}CHR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} 2RCOOH$$

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



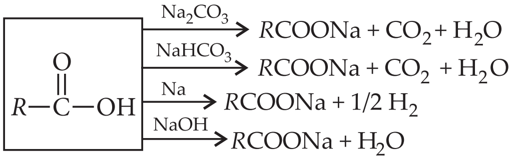
Alkyl benzene

Physical Properties :

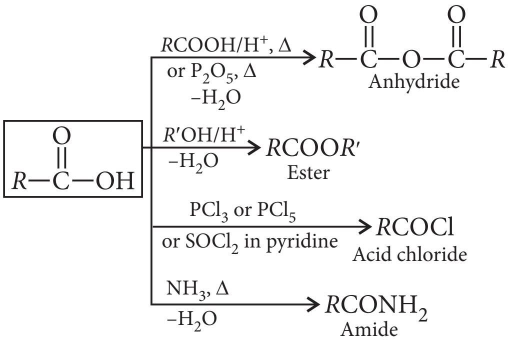
- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Solubility :** 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 :

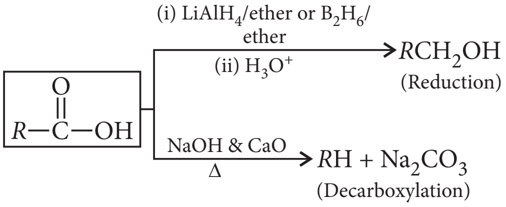
- **Reactions involving cleavage of O—H bond :**



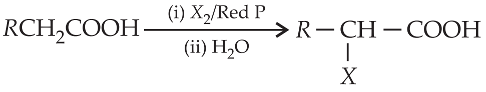
- **Reactions involving cleavage of C—OH bond :**



- **Reactions involving —COOH group :**



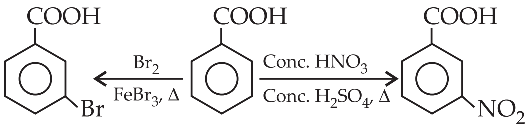
- **Hell-Volhard-Zelinsky reaction :**



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

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

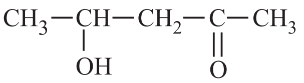
VSA **(1 mark)**

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)*

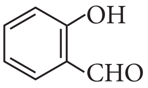
4. Write the IUPAC name of the compound :



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

5. Write the structure of 4-chloropentan-2-one. *(AI 2014, 2008, Delhi 2013)*

6. Write the IUPAC name of the following compound :



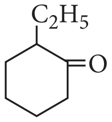
(Foregin 2014)

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

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

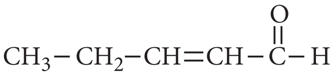
9. Draw the structure of the compound named 4-methylpent-3-en-2-one. *(Delhi 2013C)*

10. Write the IUPAC name of the following :



(AI 2013C)

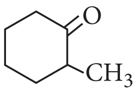
11. Write the IUPAC name of the following :



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

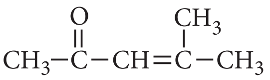
12. Write the IUPAC name of
$Ph-CH=CH-CHO$ *(AI 2012)*

13. Write the IUPAC name of the following :



(AI 2012C)

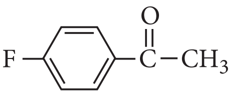
14. Write the IUPAC name of



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

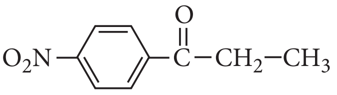
15. Draw the structural formula of 1-phenyl Propan-1-one molecule. *(Delhi 2010)*

16. Write the IUPAC name of the compound :



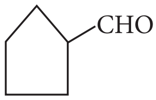
(Delhi 2010C)

17. Write the IUPAC name of the compound :



(Delhi 2010C)

18. Write the IUPAC name of the following compound :

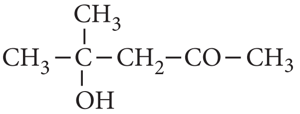


(AI 2010C)

19. Write the structure of 3-oxopentanal. *(Delhi 2009)*

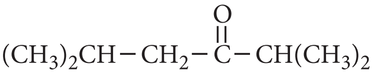
20. Write the structural formula of 1-phenylpentan-1-one. *(AI 2009)*

21. Write the IUPAC name of the following :



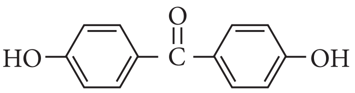
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CO-CH_3$ *(Delhi 2009C)*

22. Write the IUPAC name of the following compound



$(CH_3)_2CH-CH_2-\overset{O}{\overset{||}{C}}-CH(CH_3)_2$ *(AI 2009C)*

23. Write the IUPAC name of the following :



(Delhi 2008C)

SA I **(2 marks)**

24. 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)

25. 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)

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

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

28. How is following obtained?
Benzaldehyde from toluene. *(1/5, Delhi 2009)*

29. How would you convert :
Ethanol to acetone. *(1/5, AI 2007)*

SA I (2 marks)

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

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

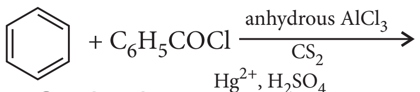
(2/5, AI 2016)

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

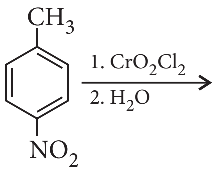
32. An organic compound *A*, having the formula, C_3H_8O, on treatment with copper at 573 K, gives *B*. *B* does not reduce Fehling's solution but gives a yellow precipitate of the compound *C* with I_2/NaOH. Deduce the structure of *A*, *B* and *C*.
(2/5, Delhi 2011C)

SA II (3 marks)

33. 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)

34. How will you bring about the following conversions?
(i) Ethanol to acetone
(ii) Benzene to acetophenone
(iii) Benzoic acid to benzaldehyde
(3/5, Delhi 2008)

LA (5 marks)

35. Identify *A*, *B*, *C*, *D* and *E* in following sequence of reactions :

$$A \xrightarrow{Cl_2} CHCl_3 \xrightarrow{NaOH} B \xrightarrow{C_6H_5COCl} C \xrightarrow{C_6H_6/AlCl_3} D + E$$

(Delhi 2009C)

12.3 Physical Properties

VSA (1 mark)

36. Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why?
(AI 2012C)

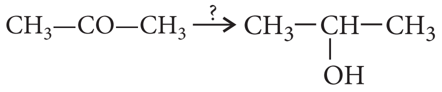
37. How would you account for the following :
The boiling points of aldehydes and ketones are lower than of the corresponding acids.
(1/5, Delhi 2008)

12.4 Chemical Reactions

VSA (1 mark)

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

39. Name the reagents used in the following reactions :

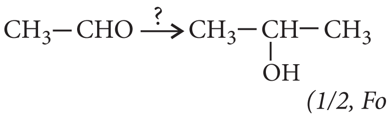
(i) 

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

(Delhi 2015)

40. 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)

41. Name the reagents used in the following reactions :



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

(1/2, Foregin 2015)

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

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

44. 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, AI 2009)

45. Account for the following :
CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. *(Delhi 2014)*

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

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

48. Give simple chemical tests to distinguish between the following pair of compounds :
Ethanal and Propanal
(1/5, Delhi 2013, Delhi 2012C, AI 2009)

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

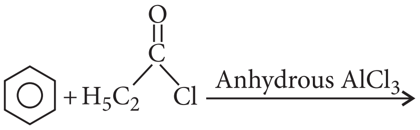
50. Give reason :
Aldehydes are more reactive than ketones towards nucleophilic reagents. *(1/5, AI 2013C)*

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

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

53. 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)*

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

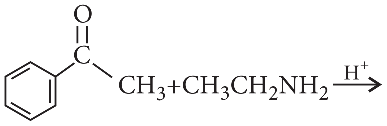


(AI 2012C)

55. Predict the organic product of the following reactions :

(1/2, AI 2011C)

56. Predict the products of the following reactions:



(1/5, AI 2011C)

57. What is Tollens' reagent? Write one usefulness of this reagent. *(AI 2010)*

58. Describe how the following conversions can be brought about :
Cyclohexanol to cyclohexan 1-one
(1/5, AI 2010)

59. Illustrate the following name reaction :
Wolff–Kishner reduction reaction
(1/5, AI 2010)

60. Write chemical equations to illustrate the following name bearing reaction :
Cannizzaro's reaction. *(1/5, AI 2009)*

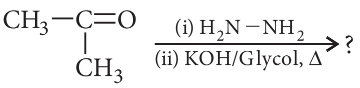
61. State chemical tests to distinguish between the following pairs of compounds :
Propanal and propanone
(1/5, AI 2008, Delhi 2007)

62. Write Cannizzaro reaction giving an example.
(AI 2008C)

SA I (2 marks)

63. Predict the products of the following reactions :

(i)



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

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$
(2/3, Delhi 2015)

64. 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 :

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

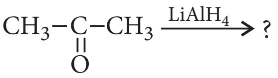
(AI 2015)

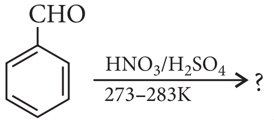
65. Describe the following reactions :

(i) Acetylation

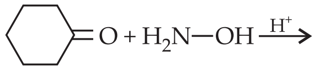
(ii) Aldol condensation *(2/5, Delhi 2015C)*

66. Write the main product in the following equations :

(i) 
$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$

(ii) 

(2/5, Delhi 2015C)

67. (i) 

(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.

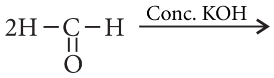
(ii) There are two $-NH_2$ groups in semicarbazide($H_2NNHCONH_2$). However, only one is involved in the formation of semicarbazone. *(2/5, Foregin 2014)*

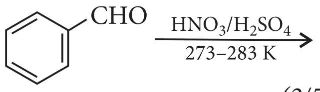
69. Write the chemical equation to illustrate each of the following name reactions :

(i) Rosenmund reduction

(ii) Cannizzaro reaction *(2/5, Foregin 2014)*

70. Complete the following reactions :

(i) 
$2H-\underset{\underset{O}{\parallel}}{C}-H \xrightarrow{\text{Conc. KOH}}$

(ii) 

(2/5, Delhi 2013)

71. How will you convert the following :

(i) Propanone to Propan-2-ol

(ii) Ethanal to 2-hydroxy propanoic acid

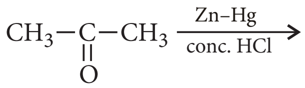
(2/5, AI 2013)

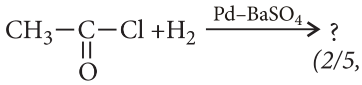
72. Give simple chemical test to distinguish between :

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

(ii) 
$CH_3-\underset{\underset{O}{\parallel}}{C}-Cl + H_2 \xrightarrow{Pd-BaSO_4} ?$

(2/5, AI 2013)

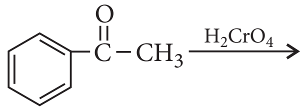
74. Give chemical tests to distinguish between

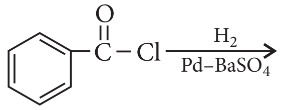
(i) Propanal and propanone

(ii) Benzaldehyde and acetophenone

(2/5, AI 2012)

75. Predict the products of the following reactions :

(i) 

(ii)  *(2/5, AI 2011C)*

76. Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone. *(2/5, Delhi 2010)*

77. How will you bring about the following conversions?

(i) Ethanal to but-2-enal

(ii) Propanone to propene *(2/5, Delhi 2010)*

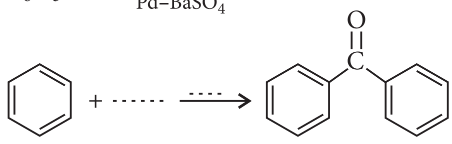
78. Illustrate the following name reactions giving a chemical equations in each case :

(i) Clemmensen reaction

(ii) Cannizzaro's reaction *(AI 2010)*

79. Complete each synthesis by giving the missing material, reagent or products:

(i) $C_6H_5COCl \xrightarrow[Pd-BaSO_4]{H_2} \cdots\cdots$

(ii) 

(2/5, Delhi 2009)

80. How will you bring about the following conversions :

(i) Ethanol to 3-hydroxybutanal

(ii) Benzaldehyde to Benzophenone

(2/5, AI 2009)

81. How would you bring about the following conversions :
(i) Propanone to Propene
(ii) Bromobenzene to 1-phenylethanol
(2/5, AI 2009)

82. How would you account for the following
(i) Aldehydes are more reactive than ketones toward nucleophiles.
(ii) The aldehydes and ketones undergo a number of addition reactions.
(2/5, Delhi 2008)

83. Give chemical tests to distinguish between :
(i) Acetaldehyde and benzaldehyde
(ii) Propanone and propanal. *(2/5, Delhi 2008)*

84. Give a chemical equation for each, illustrate the following processes :
(i) Cannizzaro reaction
(ii) Acetylation *(2/5, AI 2008)*

85. Write the chemical tests to distinguish between the following pairs of compounds :
(i) Acetophenone and Benzophenone
(ii) Ethanal and Propanal *(2/5, AI 2008)*

86. Write one chemical equation for each to illustrate the following reactions :
(i) Rosenmund's reduction
(ii) Cannizzaro reaction *(AI 2007)*

SA II (3 marks)

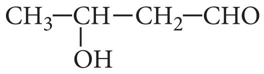
87. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.
(b) Draw the structure of the semicarbazone of ethanal.
(c) How can you distinguish between propanal and propanone? *(3/5, Delhi 2016)*

88. (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_2H_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)*

89. 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)*

90. How will you convert ethanal into the following compounds? Give the chemical equations involved.
(i) $CH_3—CH_3$
(ii)

$CH_3—\underset{OH}{\underset{|}{C}H}—CH_2—CHO$
(iii) CH_3CH_2OH *(3/5, Delhi 2015C)*

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

92. 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)

93. (a) Write the chemical equations to illustrate the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro's 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)*

94. 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)

95. 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)*

96. 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)*

97. An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Identify the compound. *(3/5, AI 2012, 2012C)*

98. 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)*

99. 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)*

100. An organic compound *A* has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid *B* and an alcohol *C*. Oxidation of *C* with chromic acid also produced *B*. *C* on dehydration reaction gives but-1-ene. Write equations for the reactions involved. *(3/5, AI 2009)*

101. An organic compound contains 69.77% carbon, 11.63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It 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 enthanoic and propanoic acids. Deduce the possible structure of the organic compound.

(3/5, AI 2009, 2008, Delhi 2008)

LA (5 marks)

102. (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 cyanohydrins 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 Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzene-di-carboxylic acid. Identify the compound. *(Delhi 2012)*

103. (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

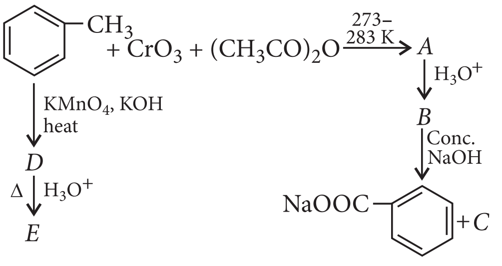
(i) conc. NaOH

(ii) HNO_3/H_2SO_4 (at 273– 383 K)

(Delhi 2011C)

104. A ketone $A(C_4H_8O)$, which undergoes a haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives a compound C which forms monozonide *D*. *D* on hydrolysis in presence of zinc dust gives only acetaldehyde *E*. Identify *A*, *B*, *C*, *D* and *E*. Write the reactions involved. *(Delhi 2010C)*

105. Identify *A* and *E* in the following series of reactions :



(AI 2010C)

106. (a) Illustrate the following name reactions by giving example :

(i) Cannizzaro's reaction

(ii) Clemmensen reduction

(b) An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen.

The molecular mass of the compound is 86. It does not reduce Tollens' reagent but form an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives enthanoic and propanoic acids. Derive the possible structure of compound *A*. *(Delhi 2009)*

107. An organic compound $A(C_3H_6O)$ is resistant to oxidation but forms compound $B(C_3H_8O)$ on reduction. *B* reacts with HBr to form the compound *C*. *C* with Mg forms Grignard reagent *D* which reacts with *A* to form a product which on hydrolysis gives *E*. Identify *A* and *E*. *(AI 2008C)*

12.6 Nomenclature and Structure of Carboxyl Group

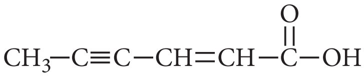
VSA (1 mark)

108. Write the IUPAC name of the compound :

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

(Delhi 2014, Delhi 200C)

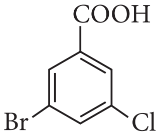
109. Write the IUPAC name of the following :



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

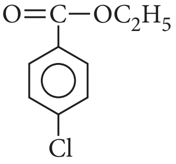
(Delhi 2011C, Delhi 2009)

110. Write the IUPAC name of



(AI 2011C)

111. Write the IUPAC name of the following compound:



(AI 2009)

12.7 Methods of Preparation of Carboxylic Acids

VSA (1 mark)

112. Name the reagents used in the following reaction :

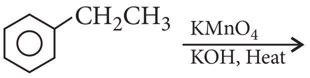
$C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

(1/2, Delhi 2015)

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

114. How will you obtain the following :
Benzoic acid from Aniline *(1/5, AI 2013C)*

115. Predict the organic products of the following reaction :



(1/3, AI 2011C)

116. How is the following obtained?
Benzoic acid from ethyl benzene. *(1/5, Delhi 2009)*

SA II (3 marks)

117. 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)*

118. How are the following conversions carried out :
(i) Ethylcyanide to ethanoic acid
(ii) Butan-1-o1 to butanoic acid
(iii) Methylbenzene to benzoic acid
Write Chemical equations for the involved reactions. *(AI 2010)*

12.8 Physical Properties

VSA (1 mark)

119. 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)

120. 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)

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

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

123. Predict the products of the following reaction :

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

124. Name the reagent used in the following reaction :

$CH_3—COOH \xrightarrow{?} CH_3—COCl$

(1/2, Foreign 2015)

125. Write the main product in the following equation :

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

126. Describe the following giving chemical equation :

De-carboxylation reaction

(1/5, Delhi 2015C, 2012, 2008)

127. How will you bring about the following conversion?

Benzoic acid to Benzaldehyde

(1/5, Delhi 2015C)

128. Account for the following :

Carboxylic acids do not give reactions of carbnyl group. *(1/5, AI 2014)*

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

Benzoic acid and Phenol

(1/5, AI 2014, Delhi 2013C, 2012, 2012C, 2010, 1/5 AI 2009)

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

Benzoic acid and Ethyl benzoate

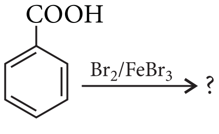
(1/3, Foregin 2014, 1/5 AI 2009)

131. Write the chemical equation to illustrate the following name reaction :

Hell-Volhard-Zelinsky reaction

(1/5, Foregin 2014, Delhi 2012, AI2010)

132. Write the products of the following reaction :



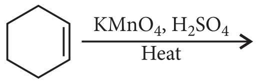
(1/5, AI 2013)

133. Give reasons :

Chloroacetic acid is stronger than acetic acid.

(1/5, Delhi 2013C)

134. Predict the products of the following reaction :



(1/5, AI 2011C)

135. Arrange the following compounds in increasing order of their acid strengths

$(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ *(Delhi 2008)*

136. How are the following conversions carried out

Acetic acid to methylamine. *(1/5, Delhi 2007)*

137. Write one chemical equation for each to illustrate the following reaction :

Fischer esterification. *(AI 2007)*

138. How would you convert :

Benzoic acid to benzamide. *(1/5, AI 2007)*

SA I (2 marks)

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

$CH_3COOH \xrightarrow{Cl_2/P}$

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

Benzaldehyde and benzoic acid

(2/5, Delhi 2014)

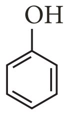
140. Account for the following :

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

141. 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)*

142. 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)*

143. How will you carry out the following conversions?

(i) Acetylene to Acetic acid

(ii) Toluene to *m*-nitrobenzoic acid

(2/5, Delhi 2013C)

144. 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)

145. 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)*

146. 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)*

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

148. Describe how the following conversions can be brought about :

(i) Ethylbenzene to benzoic acid

(ii) Bromobenzene to benzoic acid *(2/5, AI 2010)*

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

(i) Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid. 4-Methoxybenzoic acid (acid strength)

(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength) *(2/5, AI 2009)*

150. State reasons for the following :

(i) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.

(ii) Ethanoic acid is a weaker acid than benzoic acid. *(Delhi 2008)*

151. (a) Giving a chemical equation for the following process :
Decarboxylation

(b) State chemical tests to distinguish between the following pairs of compounds :
Phenol and Benzoic acid *(AI 2008)*

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

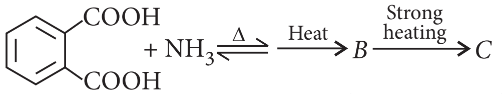
(i) Methyl acetate and ethyl acetate.

(ii) Benzaldehyde and benzoic acid. *(Delhi 2007)*

SA II (3 marks)

153. 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)*

154. Identify, *A*, *B* and *C* in the following sequence of reactions :



(3/5, AI 2011C)

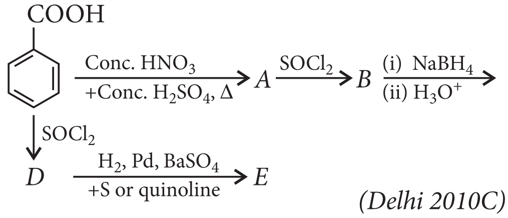
LA (5 marks)

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

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

(Delhi 2016)

156. Identify *A* to *E* in the following reactions :

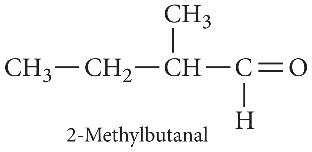


(Delhi 2010C)

157. An organic compound (*A*) on treatment with ethyl alcohol gives a carboxylic acid (*B*) and compound (*C*). Hydrolysis of (*C*) under acidified conditions gives (*B*) and (*D*). Oxidation of (*D*) with $KMnO_4$ also gives (*B*). (*B*) on heating with $Ca(OH)_2$ gives (*E*) having molecular formula C_3H_6O. (E) does not give Tollen's test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify (*A*), (*B*), (*C*), (*D*) and (*E*). *(AI 2010C)*

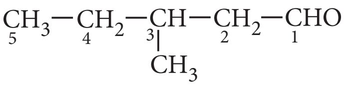
158. An organic compound (*A*) on treatment with acetic acid in the presence of sulphuric acid produces an ester (*B*). (*A*) on mild oxidation gives (*C*). (*C*) with 50% KOH followed by acidification with dilute HCl generates (*A*) and (*D*). (*D*) with PCl_5 followed by reaction with ammonia gives (*E*). (*E*) on dehydration produces hydrocyanic acid. Identify the compounds *A*, *B*, *C*, *D* and *E*. *(Delhi 2009C)*

Detailed Solutions

1. 

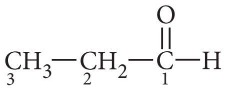
$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{H}{|}}{C}=O$$

2-Methylbutanal

2. 

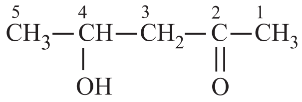
$$\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{\substack{3|\\CH_3}}{C}H-\underset{2}{C}H_2-\underset{1}{C}HO$$

3-Methylpentanal

3. 

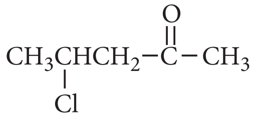
$$\underset{3}{C}H_3-\underset{2}{C}H_2-\underset{1}{\overset{\overset{O}{||}}{C}}-H$$

1-propanal

4. 

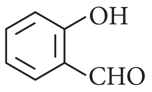
$$\overset{5}{C}H_3-\underset{\underset{OH}{|}}{\overset{4}{C}H}-\overset{3}{C}H_2-\underset{\underset{O}{||}}{\overset{2}{C}}-\overset{1}{C}H_3$$

4-Hydroxypentan-2-one

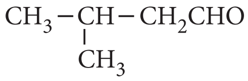
5. 

$$CH_3\underset{\underset{Cl}{|}}{C}HCH_2-\overset{\overset{O}{||}}{C}-CH_3$$

4-Chloropentan-2-one

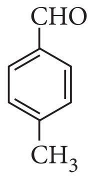
6. 

2-Hydroxybenzaldehyde

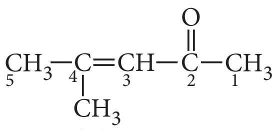
7. 

$$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2CHO$$

3-methylbutanal

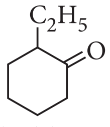
8. 

p-methylbenzaldehyde

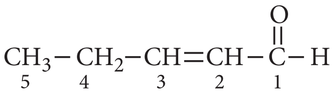
9. 

$$\underset{5}{C}H_3-\underset{\substack{4|\\CH_3}}{C}=\underset{3}{C}H-\underset{2}{\overset{\overset{O}{||}}{C}}-\underset{1}{C}H_3$$

4-methylpent-3-en-2-one

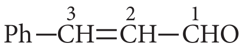
10. 

2-Ethylcyclohexanone

11. 

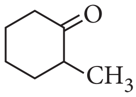
$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{\overset{O}{||}}{C}}-H$$

Pent-2-enal

12. 

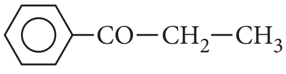
$$Ph-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}HO$$

3-Phenylprop-2-enal

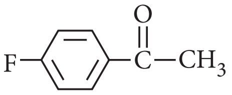
13. 

2-methylcyclohexanone

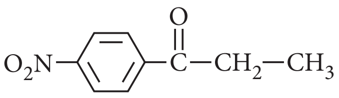
14. *Refer to answer 9.*

15. 

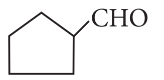
1-phenylpropan-1-one

16. 

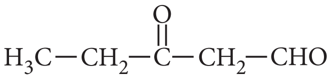
4-Fluoroacetophenone

17. 

1-(4-nitrophenyl)propan-1-one

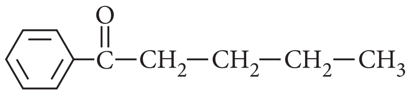
18. 

Cyclopentanecarbaldehyde

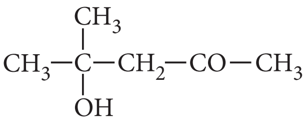
19. 

$$H_3C-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CHO$$

3-oxopentanal

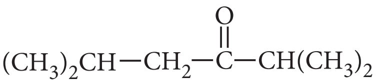
20. 

1-phenylpentan-1-one

21. 

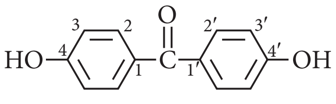
$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CO-CH_3$$

4-Hydroxy-4-Methylpentan-2-one

22. 

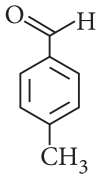
$$(CH_3)_2CH-CH_2-\overset{\overset{O}{||}}{C}-CH(CH_3)_2$$

2,5-dimethylhexan-3-one

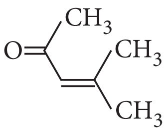
23. 

4,4′-dihydroxybenzophenone

24. (i) *p*-Methylbenzaldehyde :

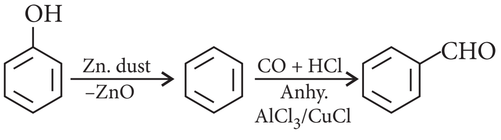


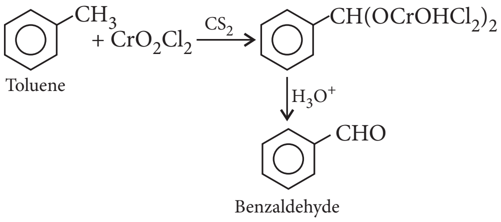
(ii) 4-Methylpent-3-en-2-one :



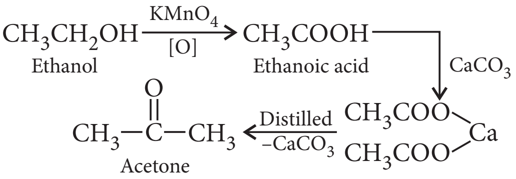
25. $CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) }H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

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

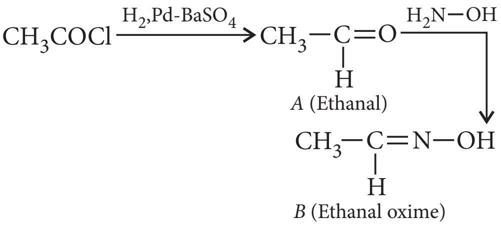
27. 

28. 

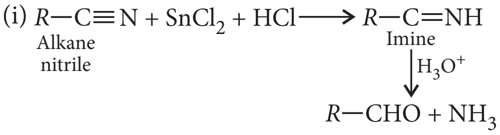
29. Ethanol to acetone :



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{[O]}]{KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{CaCO_3} \begin{matrix}CH_3COO\\ CH_3COO\end{matrix}\!>\!Ca \xrightarrow[-CaCO_3]{\text{Distilled}} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

30. 

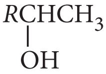
$$CH_3COCl \xrightarrow{H_2,Pd\text{-}BaSO_4} \underset{A\text{ (Ethanal)}}{CH_3-\underset{\underset{H}{|}}{C}=O} \xrightarrow{H_2N-OH} \underset{B\text{ (Ethanal oxime)}}{CH_3-\underset{\underset{H}{|}}{C}=N-OH}$$

31. (i) 

$$\underset{\text{Alkane nitrile}}{R-C\equiv N} + SnCl_2 + HCl \longrightarrow \underset{\text{Imine}}{R-C=NH} \xrightarrow{H_3O^+} R-CHO + NH_3$$

(ii) *Refer to answer 28.*

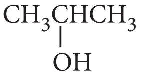
32. Compound *B* gives positive iodoform test, it means it contains —$COCH_3$ (methyl ketone) group *i.e.*, it is a ketone. Moreover, *B* is obtained by the oxidation of *A*, thus *A* must be a 2° alcohol. (As only 2° alcohol give ketones on oxidation with Cu at 573 K. Hence, the structure of compound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



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

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

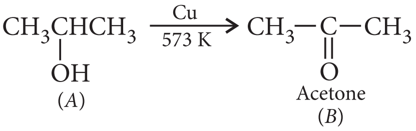
Thus, compound *A* is



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

(Propan-2-ol)

The reaction are as follows :



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

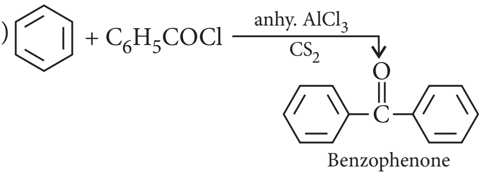
$\text{Acetone} \xrightarrow[\text{solution}]{\text{Fehling}} \text{No reaction}$

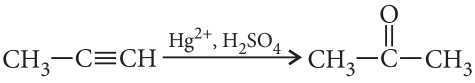
$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3COONa + 3NaI + \underset{\substack{\text{Iodoform}\\(C)}}{CHI_3\downarrow} + 3H_2O$$

Thus, $A = CH_3CH(OH)CH_3$

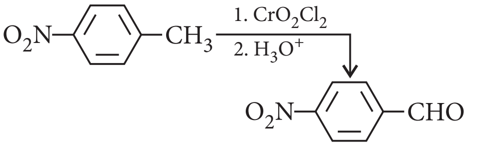
$B = CH_3COCH_3$

$C = CHI_3$

33. (i) 

(ii) 

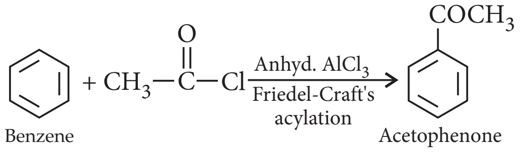
$$CH_3-C\equiv CH \xrightarrow{Hg^{2+}, H_2SO_4} \underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

(iii) 

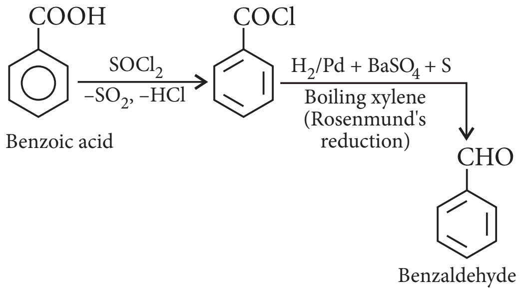
p-Nitrobenzaldehyde

34. (i) *Refer to answer 29.*

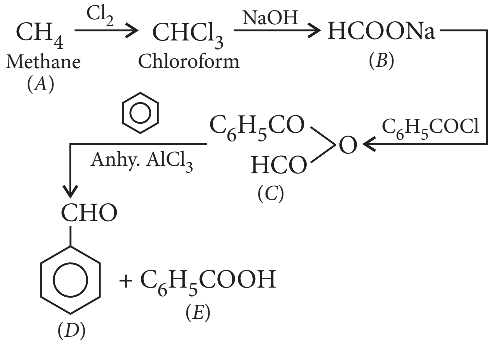
(ii) Benzene to acetophenone.



(iii) Benzoic acid to benzaldehyde.



35.



36. 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.

37. *Refer to answer 36.*

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

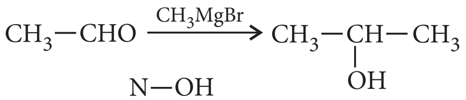
Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' Test.

39. (i) Lithium aluminium hydride ($LiAlH_4$).

40. Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

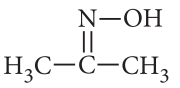
Propanal will form the silver mirror, but propanone does not react.

41.



$$CH_3-CHO \xrightarrow{CH_3MgBr} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

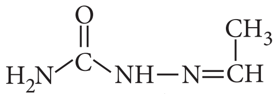
42. (i)



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

2-propanone oxime

(ii)



Semicarbazone

43. *Refer to answer 38.*

44. (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.

45. 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.

46. *Refer to answer 45(ii).*

47. Propanal and Butan-2-one can be distinguised by their reactions with tollen's reagent. Propanal will form the silver mirror, but Butan-2-one does not react.

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

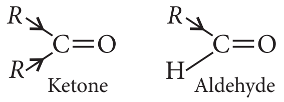
Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution.

49. 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 a reaction should be carefully controlled.

50. 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.



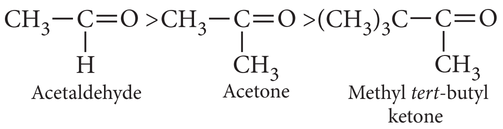
The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

51. Butanone < propanone < propanal < ethanal.

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

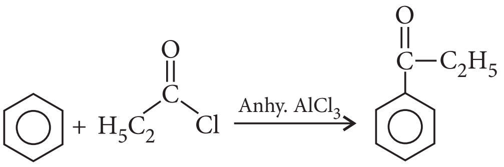
Acetophenone will give the yellow precipitate of iodoform, but benzophenone will not react.

53.

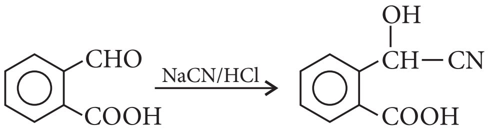


$$\underset{\text{Acetaldehyde}}{CH_3-\underset{H}{C}=O} > \underset{\text{Acetone}}{CH_3-\underset{CH_3}{C}=O} > \underset{\text{Methyl } tert\text{-butyl ketone}}{(CH_3)_3C-\underset{CH_3}{C}=O}$$

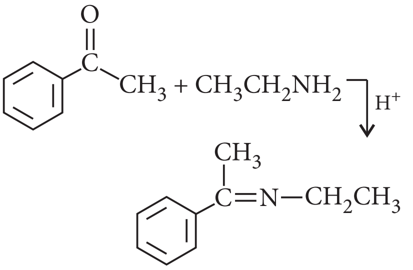
54.



55.



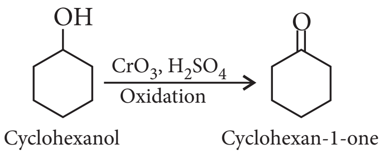
56.



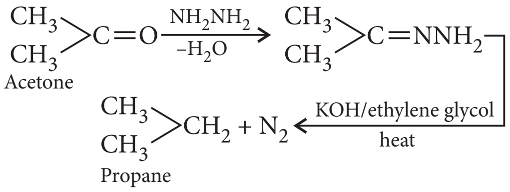
57. Tollens' reagent is an ammoniacal silver nitrate solution.

Tollens' reagent is used to test an aldehyde. Both aliphatic and aromatic aldehydes reduce Tollens' reagent and give silver mirror.

58.



59. Wolff-Kishner reduction reaction : 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.



60. Cannizzaro's reaction : Aldehydes which do not contain α-H atom undergo disproportionation when heated with concentrated (50 %) NaOH.

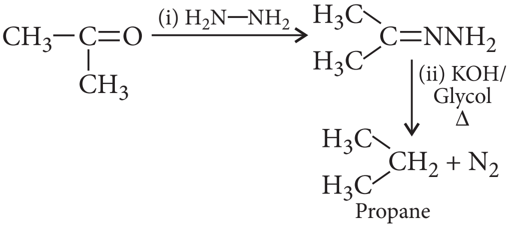
$$\underset{\text{Methanal}}{HCHO + HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methanol}}{CH_3OH}$$

61. Propanal reduces Tollen's reagent into silver mirror while propanone does not gives this test.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 2OH^- \longrightarrow$$
$$CH_3CH_2COONH_4 + \underset{\text{Silver mirror}}{2Ag} + H_2O + 2NH_3$$

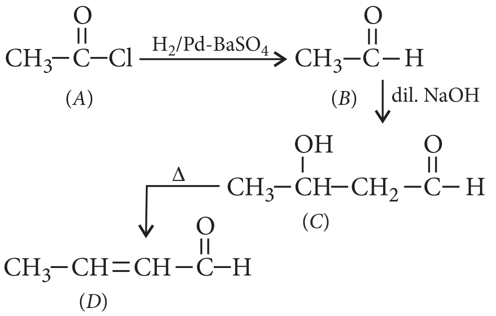
62. *Refer to answer 60.*

63. (i)

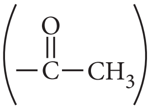


(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} \underset{\text{Iodoform}}{CHI_3\downarrow} + C_6H_5COONa$

64.

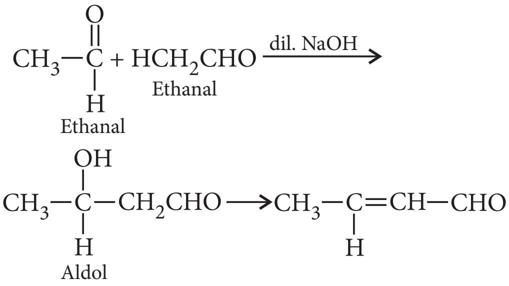


65. (i) Acetylation : Introduction of acetyl group



$\left(-\overset{O}{\overset{\|}{C}}-CH_3\right)$ in alcohols, phenols or amines is called their acetylation.

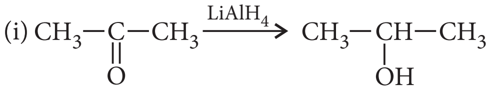
(ii) Aldol condensation : Two molecules of an aldehyde or ketones having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating give α,β-unsaturated aldehyde or ketone.



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

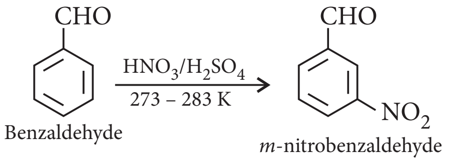
$$\underset{\text{Aldol}}{CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO} \longrightarrow CH_3-\underset{H}{C}=CH-CHO$$

66. (i)

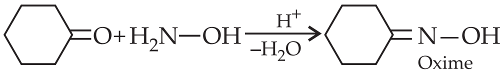


$$CH_3-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3-\underset{OH}{CH}-CH_3$$

(ii)



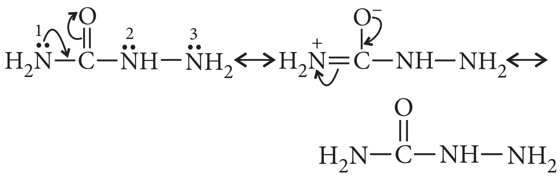
67. (i)

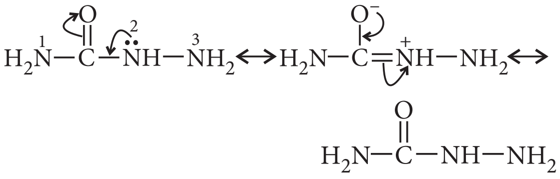


(ii) $2C_6H_5CHO$ + conc. NaOH $\longrightarrow$ $C_6H_5COONa + C_6H_5CH_2OH$

68. (i) *Refer to answer 45.*

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





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.

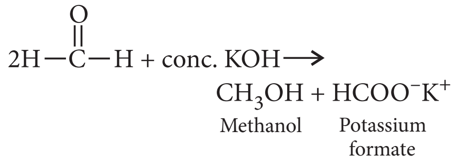
69. (i) **Rosenmund's reaction :**

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

Ethanoyl chloride (Acetyl chloride) → Ethanal (Acetaldehyde)

(ii) *Refer to answer 60.*

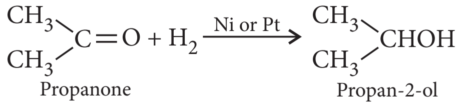
70. (i)



$$2H-\overset{O}{\overset{\|}{C}}-H + \text{conc. KOH} \longrightarrow \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOO^-K^+}$$

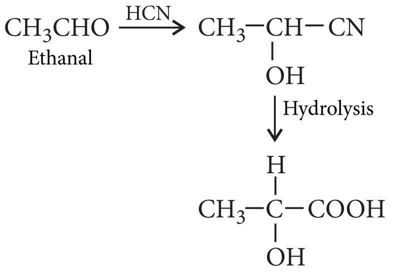
(ii) *Refer to answer 66(ii).*

71. (i)



$$\underset{\text{Propanone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Propan-2-ol}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH}$$

(ii)



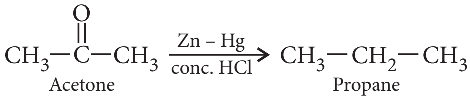
$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{HCN} CH_3-\underset{OH}{CH}-CN \xrightarrow{\text{Hydrolysis}} CH_3-\underset{OH}{\overset{H}{C}}-COOH$$

2-Hydroxypropanoic acid

72.

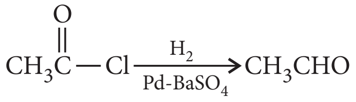
(a) NaOI	$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$ Pentan-3-one $\longrightarrow$ No reaction	$CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_2CH_3$ Pentan-2-one gives iodoform test.
(b) NaOI	CH_3CHO Ethanal gives iodoform test.	$CH_3CH_2CHO \longrightarrow$ Propanal No reaction

73. (i)



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

(ii)

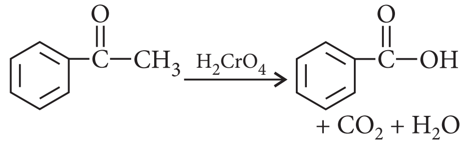


$$CH_3\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} CH_3CHO$$

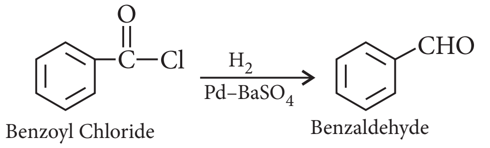
74. (i) *Refer to answer 46.*

(ii) *Refer to answer 38.*

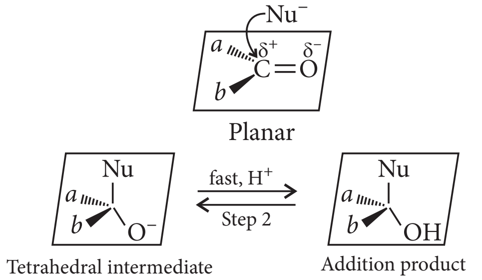
75. (i)



(ii)



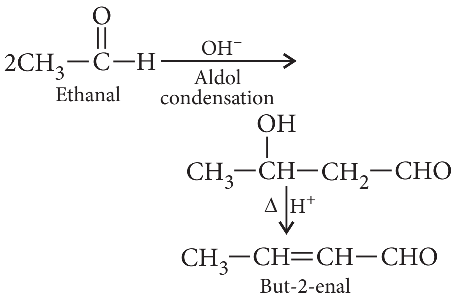
76. Mechanism of nucleophilic addition reactions : Nucleophile attacks from the top face :



A nucleophile attacks the electrophilic carbon atom from a direction perpendicular to the plane of sp^2 hybridised orbital of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

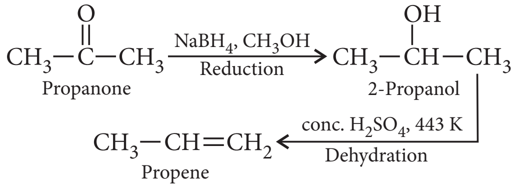
77. (i)



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{Aldol condensation}]{OH^-} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CHO \xrightarrow[\Delta]{H^+} CH_3-CH=CH-CHO$$

Ethanal; But-2-enal

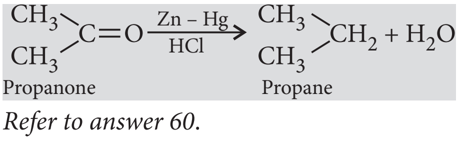
(ii) Propanone to propene



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{Reduction}]{NaBH_4,\ CH_3OH} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[\text{Dehydration}]{\text{conc. } H_2SO_4,\ 443\text{ K}} CH_3-CH=CH_2$$

Propanone; 2-Propanol; Propene

78. (i) **Clemmensen reduction :** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[HCl]{Zn-Hg} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH_2 + H_2O$$

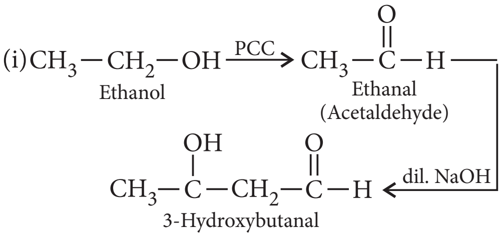
Propanone; Propane

(ii) *Refer to answer 60.*

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

(ii) *Refer to answer 33(i).*

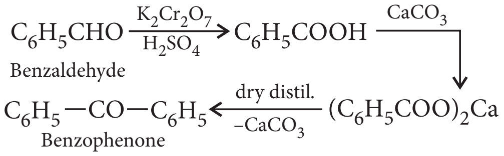
80. (i)



$$CH_3-CH_2-OH \xrightarrow{PCC} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{\text{dil. NaOH}} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Ethanol; Ethanal (Acetaldehyde); 3-Hydroxybutanal

(ii)

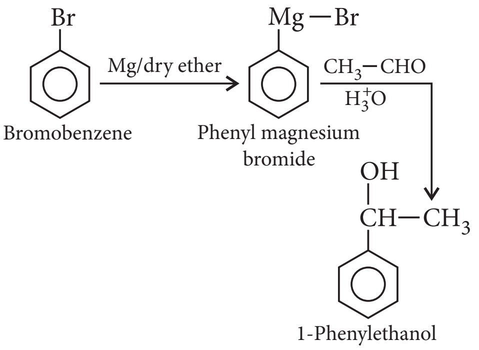


$$C_6H_5CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_6H_5COOH \xrightarrow{CaCO_3} (C_6H_5COO)_2Ca \xrightarrow[-CaCO_3]{\text{dry distil.}} C_6H_5-CO-C_6H_5$$

Benzaldehyde; Benzophenone

81. (i) *Refer to answer 77(ii).*

(ii)



82. (i) *Refer to answer 50.*

(ii) Aldehydes and ketones undergo a number of addition reactions as both possess the carbonyl functional group which reacts with a number of nucleophiles such as HCN, $NaHSO_3$, alcohols, ammonia derivatives and Grignard reagents.

83. (i) Distinction between acetaldehyde and benzaldehyde : Acetaldehyde and benzaldehyde can be distinguish by Fehling solution.

Acetaldehyde gives red coloured precipitate with Fehling solution while benzaldehyde does not.

$$CH_3CHO + \underbrace{2Cu^{2+} + 5\bar{O}H}_{\text{Fehling solution}} \longrightarrow CH_3COO^- + \underset{\text{red ppt.}}{Cu_2O} + 3H_2O$$

(ii) *Refer to answer 46.*

84. (i) *Refer to answer 60.*

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

85. (i) Refer to answer 52.

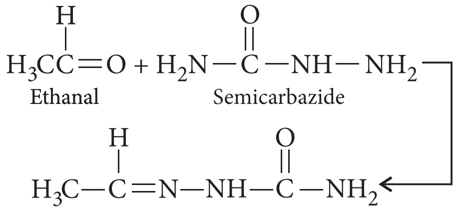
(ii) *Refer to answer 48.*

86. (i) *Refer to answer 69(i).*

(ii) *Refer to answer 60.*

87. (i) *Refer to answer 60.*

(ii)



$$H_3C\overset{H}{C}{=}O + H_2N{-}\overset{O}{\overset{\|}{C}}{-}NH{-}NH_2 \longrightarrow H_3C{-}\overset{H}{C}{=}N{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH_2$$

(Semicarbazone of ethanal)

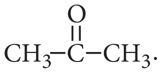
(iii) *Refer to answer 44(ii).*

88. (i) *Refer to answer 59.*

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

$$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$$

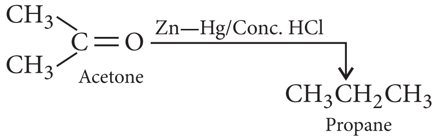
(iii) Formula of compounds *A* and *B* = C_3H_6O *B* forms yellow precipitate of iodoform. Hence, *B* must contain —$COCH_3$ group. Therefore, compound '*B*' must be



$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3$.

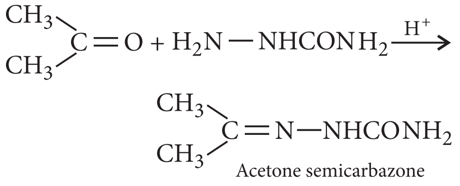
A does not give iodoform test and it is functional isomer of *B* thus, it may be CH_3CH_2CHO.

89. (i)



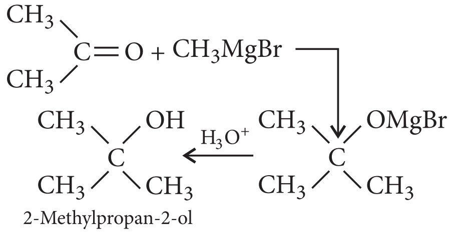
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O \xrightarrow{\text{Zn—Hg/Conc. HCl}} CH_3CH_2CH_3$$

(ii)



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O + H_2N{-}NHCONH_2 \xrightarrow{H^+} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}N{-}NHCONH_2$$

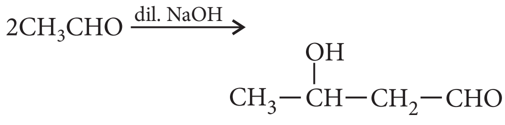
(iii)



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O + CH_3MgBr \longrightarrow (CH_3)_3C{-}OMgBr \xrightarrow{H_3O^+} (CH_3)_3C{-}OH$$

90. (i) $CH_3CHO \xrightarrow{\text{Zn – Hg/conc. HCl}} CH_3{-}CH_3$

(ii)



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

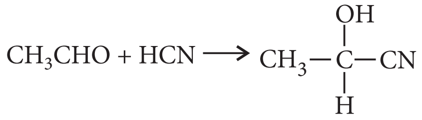
(iii) $CH_3CHO \xrightarrow{H_2/Ni} CH_3{-}CH_2{-}OH$

91. (i) *Refer to answer 59.*

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

(iii) *Refer to answer 60.*

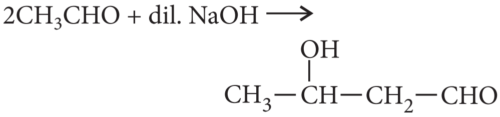
92. (i)



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

(ii) $CH_3CHO + H_2NOH \longrightarrow CH_3{-}CH{=}N{-}OH$

(iii)

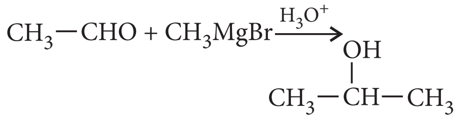


$$2CH_3CHO + \text{dil. NaOH} \longrightarrow CH_3{-}\overset{OH}{\overset{|}{C}H}{-}CH_2{-}CHO$$

93. (a) *Refer to answers 69(i) and 60.*

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

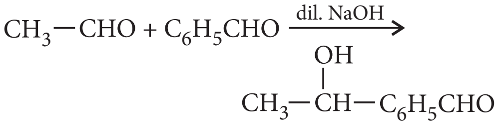
94. (i)



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

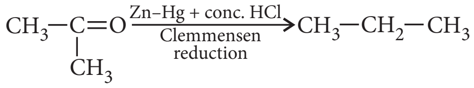
(ii) $CH_3CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} CH_3{-}CH_3$

(iii)



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

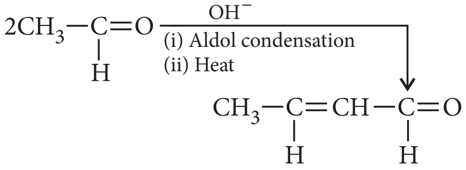
95. (i)



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

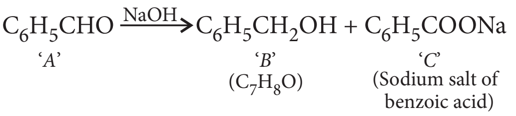
(ii) *Refer to answer 75(ii).*

(iii)

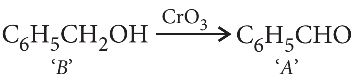


$$2CH_3{-}\underset{H}{\underset{|}{C}}{=}O \xrightarrow[\text{(i) Aldol condensation (ii) Heat}]{OH^-} CH_3{-}\underset{H}{\underset{|}{C}}{=}CH{-}\underset{H}{\underset{|}{C}}{=}O$$

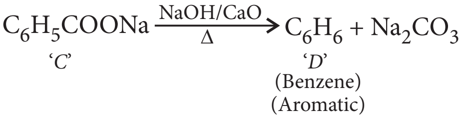
96. Benzaldehyde has a characteristic odour. Reaction of '*A*' with NaOH appears to be Cannizzaro reaction which gives '*B*' (benzyl alcohol) and '*C*' (Sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime given benzene (*D*).



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

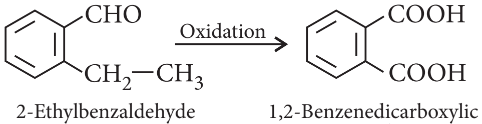


$$\underset{'B'}{C_6H_5CH_2OH} \xrightarrow{CrO_3} \underset{'A'}{C_6H_5CHO}$$



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

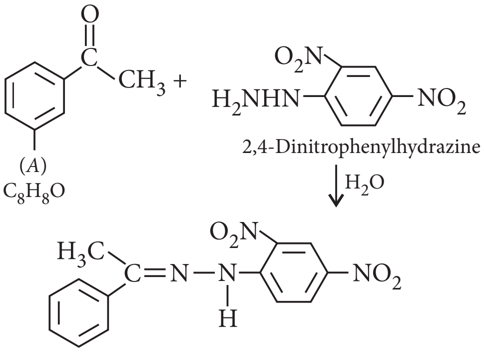
97. The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α-hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic 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.



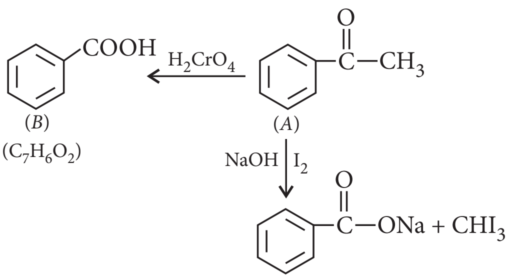
2-Ethylbenzaldehyde 1,2-Benzenedicarboxylic acid

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

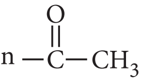
Compound (*B*), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (*B*) indicates that it should be benzoic acid and compound (*A*) should, therefore, be a mono-substituted aromatic methyl ketone.



2,4-DNP derivative

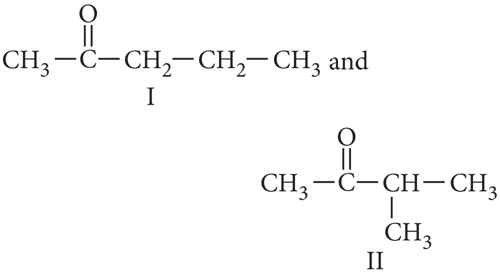


99. The given compound does not reduce Tollens' reagent, so it is not an aldehyde but the formation of addition compound with sodium hydrogen sulphite indicates it to be a carbonyl compound. Since this compound gives positive iodoform test, so it should



contain $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ group.

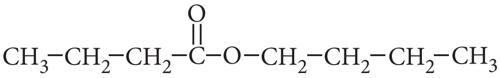
On the basis of this information, two possible structures are written as under :



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

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

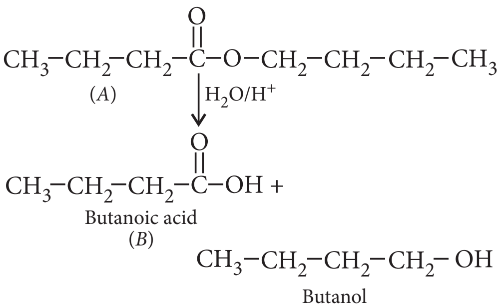
100. Compound '*A*' ($C_8H_{16}O_2$) on hydrolysis gives an acid '*B*' and an alcohol '*C*'. It shows that '*A*' is an ester. Since the oxidation of alcohol '*C*' also gives the acid '*B*' indicates that '*B*' and '*C*' both contain same number of carbon atoms, *i.e,* four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of '*C*' indicates it to be butan-1-ol, so the possible structure for '*A*' could be



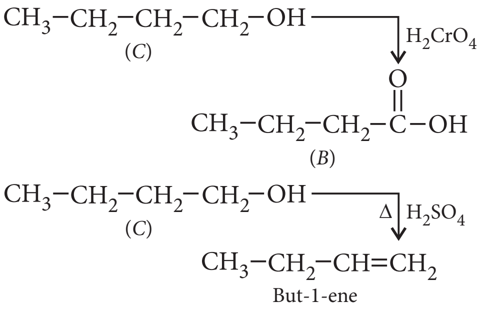
$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_3$$

Butyl butanoate

The various reactions involved are written as follows :



$$\underset{(A)}{CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_3} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Butanoic acid}\\(B)}}{CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\substack{\text{Butanol}\\(C)}}{CH_3-CH_2-CH_2-CH_2-OH}$$



$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{H_2CrO_4} \underset{(B)}{CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH}$$

$$\underset{(C)}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2}$$

101. Calculation of the empirical formula of the compound :

Element	Percentage	Atomic mass	Relative numbers of atoms	Simple molar ratio
C	69.77	12	$\frac{69.77}{12}=5.814$	5
H	11.63	1	$\frac{11.63}{1}=11.63$	10
O	18.6	16	$\frac{18.6}{16}=1.163$	1

So, the empirical formula is $C_5H_{10}O$

Empirical formula mass

$= (5 \times 12) + (10 \times 1) + (1 \times 16) = 86$

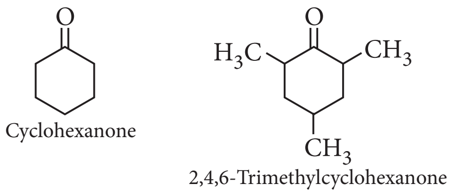
Given that molecular mass of the compound = 86

Hence, the molecular formula of the compound is $C_5H_{10}O$

Refer to answer 99.

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

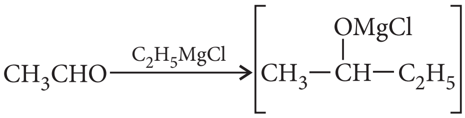
(ii) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN^-) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,4,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.



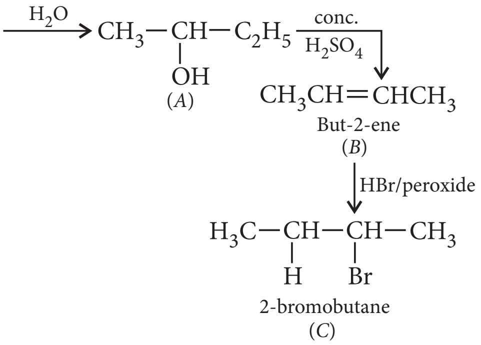
Cyclohexanone 2,4,6-Trimethylcyclohexanone

(b) *Refer to answer 97.*

103. (a)

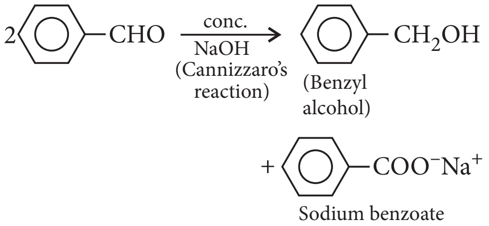


$$CH_3CHO \xrightarrow{C_2H_5MgCl} \left[CH_3-\overset{OMgCl}{\overset{|}{C}H}-C_2H_5 \right]$$



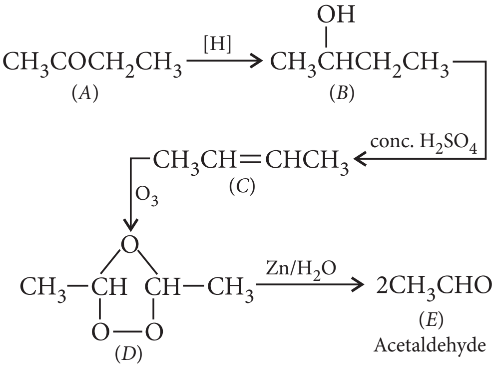
$$\xrightarrow{H_2O} \underset{(A)}{CH_3-\underset{OH}{\underset{|}{C}H}-C_2H_5} \xrightarrow[H_2SO_4]{\text{conc.}} \underset{\substack{\text{But-2-ene}\\(B)}}{CH_3CH=CHCH_3} \xrightarrow{\text{HBr/peroxide}} \underset{\substack{\text{2-bromobutane}\\(C)}}{H_3C-\underset{H}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3}$$

(b) (i)



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

104. The equations involved are :

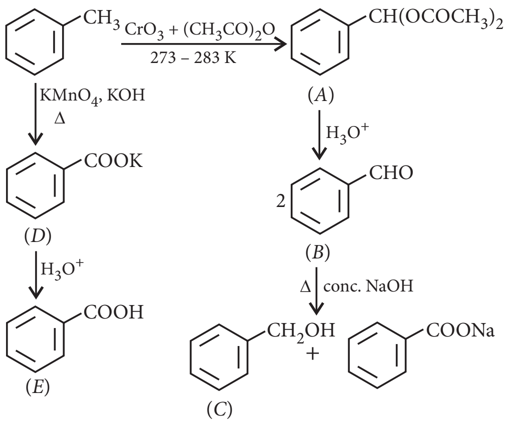


$$\underset{(A)}{CH_3COCH_2CH_3} \xrightarrow{[H]} \underset{(B)}{CH_3\overset{OH}{\overset{|}{C}H}CH_2CH_3} \xrightarrow{\text{conc. } H_2SO_4} \underset{(C)}{CH_3CH=CHCH_3} \xrightarrow{O_3} (D) \xrightarrow{Zn/H_2O} \underset{\substack{(E)\\\text{Acetaldehyde}}}{2CH_3CHO}$$

A gives haloform reaction as :

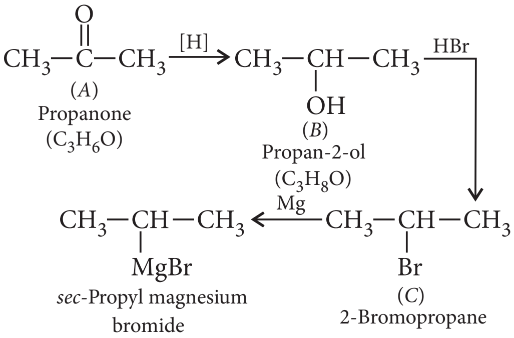
$$CH_3COCH_2CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + C_2H_5COONa + 3NaI + 2H_2O$$

105.

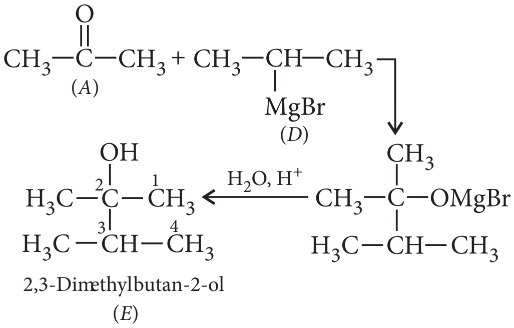


106. (a) (i) *Refer to answer 60.*
(ii) *Refer to answer 78(i).*
(b) *Refer to answer 101.*

107. Ketones are oxidised under vigrous conditions.



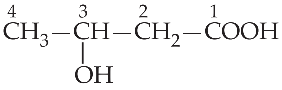
$$\underset{\substack{(A)\\ \text{Propanone}\\ (C_3H_6O)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{[H]} \underset{\substack{(B)\\ \text{Propan-2-ol}\\ (C_3H_8O)}}{CH_3-\underset{OH}{\underset{|}{C}H}-CH_3} \xrightarrow{HBr} \underset{\substack{(C)\\ \text{2-Bromopropane}}}{CH_3-\underset{Br}{\underset{|}{C}H}-CH_3} \xrightarrow{Mg} \underset{\substack{sec\text{-Propyl magnesium}\\ \text{bromide}}}{CH_3-\underset{MgBr}{\underset{|}{C}H}-CH_3}$$



$$\underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + \underset{(D)}{CH_3-\underset{MgBr}{\underset{|}{C}H}-CH_3} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{H_3C-CH-CH_3}{\underset{|}{C}}}}-OMgBr \xrightarrow{H_2O,\,H^+} \underset{\substack{\text{2,3-Dimethylbutan-2-ol}\\ (E)}}{H_3\overset{}{C}-\overset{OH}{\overset{|}{\underset{H_3C-\overset{3}{C}H-\overset{4}{C}H_3}{\underset{|}{\overset{2}{C}}}}}-\overset{1}{C}H_3}$$

Therefore, (*A*) : Propanone
(*B*) : Propan-2-ol
(*C*) : 2-Bromopropane
(*D*) : *sec*-Propyl magnesium bromide
(*E*) : 2,3-Dimethylbutan-2-ol

108.



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

3-Hydroxybutan-1-oic acid

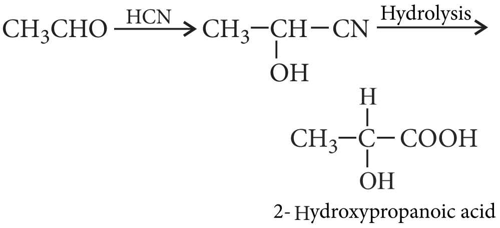
109. Hex-2-en-4yn-oic acid

110. 3-Bromo-5-chloro Benzoic acid

111. Ethyl-4-chlorobenzoate

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

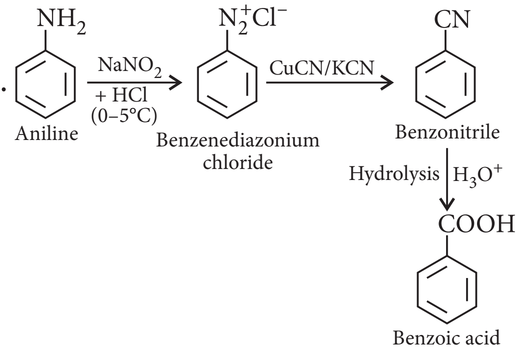
113.



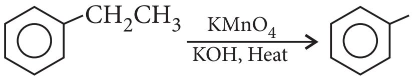
$$CH_3CHO \xrightarrow{HCN} CH_3-\underset{OH}{\underset{|}{C}H}-CN \xrightarrow{\text{Hydrolysis}} CH_3-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-COOH$$

2- Hydroxypropanoic acid

114.

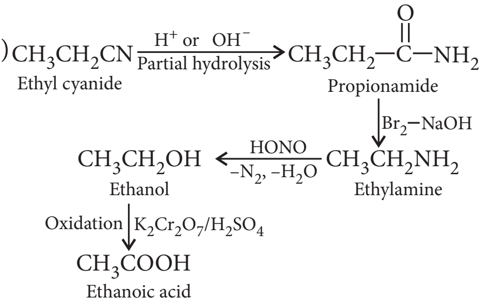


115.



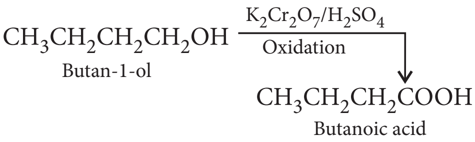
116. *Refer to answer 115.*

117. (i)



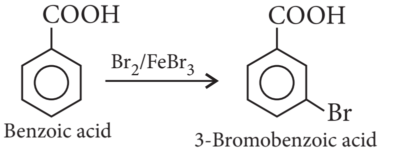
$$\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{H^+ \text{ or } OH^-} \underset{\text{Propionamide}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow{Br_2-NaOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\,-H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}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

(ii)



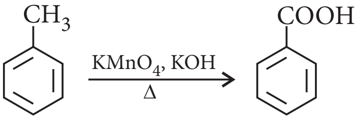
$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(iii)



118. (i) *Refer to answer 117(i).*
(ii) *Refer to answer 117(ii).*

(iii)

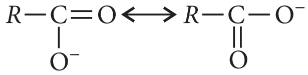


119. Increasing order of boiling point :
$CH_3-CHO < C_2H_5OH < CH_3-COOH$

120.

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

121. 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 :



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

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

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

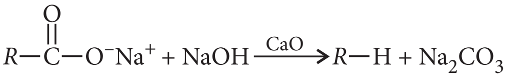
Acetic acid does not give this test.

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

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

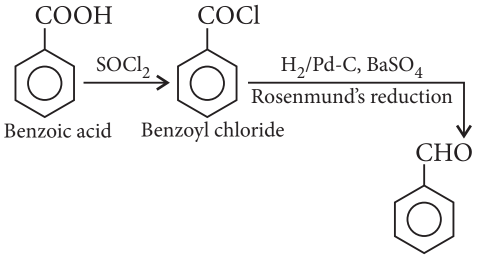
125. *Refer to answer 124.*

126. 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.



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

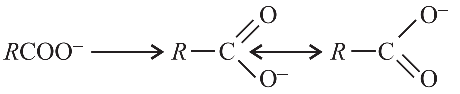
127.



Benzaldehyde

128. In carboxylic acid C = O is in resonance and not available for reaction.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$



129. 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.

130. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$.

131. 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.

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

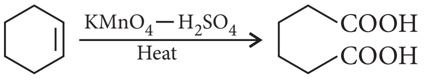
$$ClCH_2-COOH + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} + HCl$$

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

132. *Refer to answer 117(iii).*

133. 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. In case of acetic acid, the state of affair is just opposite. Hence, chloroacetic acid is stronger than acetic acid.

134.



Cyclohexene Hexane-1,6-dioic acid (Adipic acid)

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

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

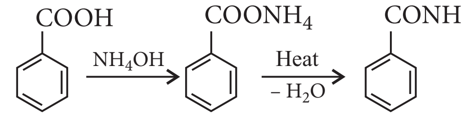
136. Acetic acid to methyl amine :

$$\begin{tikzcd}\underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "NH_3"] & CH_3COONH_4 \arrow[d, "\Delta"', "H_2O"] \\ \underset{\text{Methyl amine}}{CH_3NH_2} & CH_3CONH_2 \arrow[l, "NaOBr"']\end{tikzcd}$$

137. Fischer esterification :

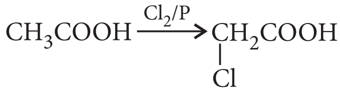
$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \rightleftharpoons RCOOR' + H_2O$$

138. Benzoic acid to benzamide :



Benzoic acid Ammonium benzoate Benzamide

139. (a)

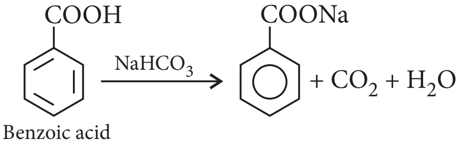


$$CH_3COOH \xrightarrow{Cl_2/P} \underset{Cl}{\underset{|}{C}}H_2COOH$$

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

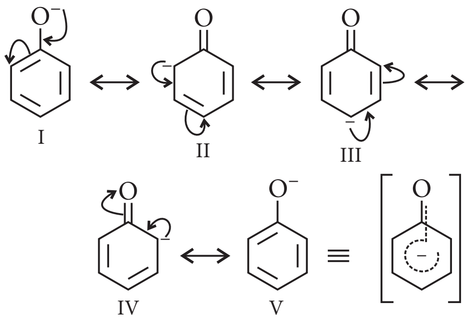
$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ 3OH^- \longrightarrow C_6H_5COO^- + \underset{\text{Siliver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Benzoic acid reacts with sodium bicarbonate to liberate CO_2.

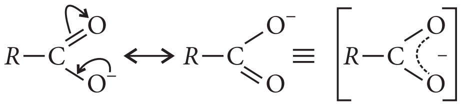


140. *Refer to answer 133.*

141. Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonating structures.

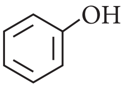


(i) Phenoxide ion is a resonance hybrid of structures I to V, where each structure has a contribution of 20% in the resonance hybrid. On the other hand, each of the two contributing structures of carboxylate ion contribute 50% towards the resonance hybrid. Therefore, the carboxylate ion tends to be more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

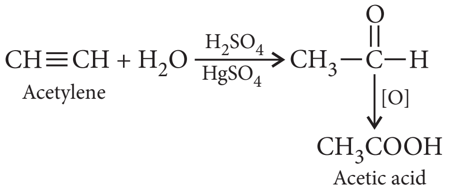
(ii) The negative charge rests on the electronegative O atom in carboxylate ion. The presence of negative charge on an electronegative atom makes the ion more stable. For the same reason $RCOO^-$ is more stable than the phenoxide ion where the carbon has negative charge on it. For the above two reasons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

142. (i) $F—CH_2COOH > Cl—CH_2COOH$.

(ii) CH_3COOH is stronger than

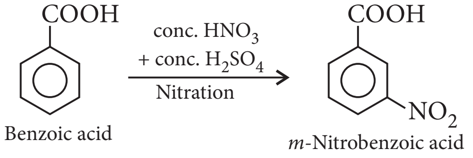


143. (i)

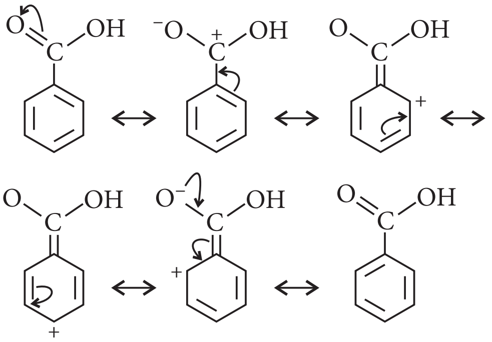


$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—H \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

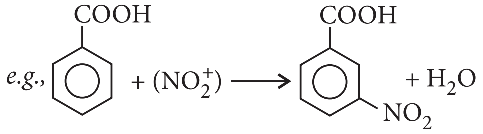
(ii)



144. (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.

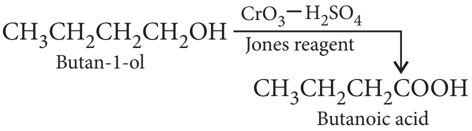


e.g.,



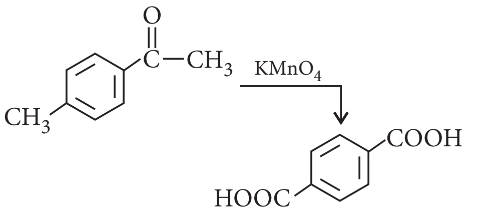
(ii) *Refer to answer 128.*

145. (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)



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

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

(ii) *Refer to answer 135.*

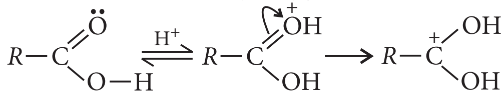
147. Esterification : Carboxylic acids react with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas as catalyst and give ester.

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

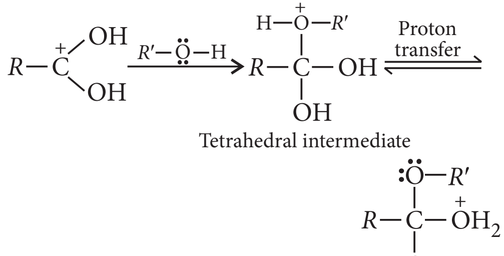
$$e.g., \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

Mechanism of esterification : It is a nucleophilic acyl substitution.

(a) Protonation of carboxyl oxygen :

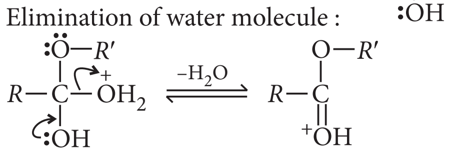


(b) Nucleophilic addition of alcohol :



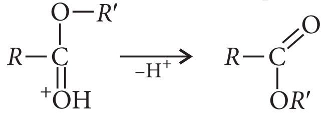
Tetrahedral intermediate

(c) Elimination of water molecule :



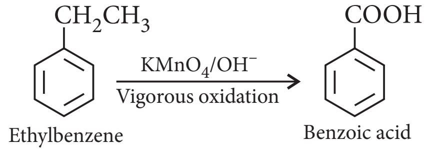
Protonated ester

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



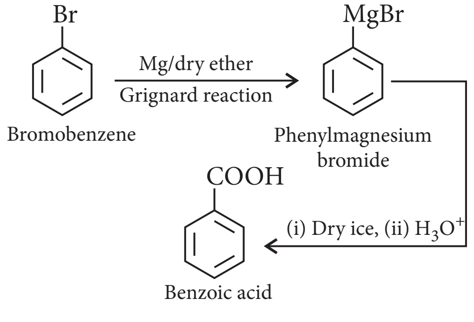
Ester

148. (i)



Ethylbenzene → Benzoic acid

(ii)



Bromobenzene → Phenylmagnesium bromide → Benzoic acid

149. (i) 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

(ii) The overall acidic strength increases in the order :
$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

150. (i) The strength of an acid is indicated by pK_a value, where, $pK_a = -\log K_a$
Since monochloroethanoic acid is weaker than dichloroethanoic acid so it has lower value of dissociation constant K_a.
Therefore, it has higher value of pK_a.

(ii) The —COOH group in benzoic acid is attached to sp^2 - carbon of the phenyl ring and is more acidic than acetic acid in which —COOH group is attached to sp^3 – carbon atom of CH_3 group.
So, benzoic acid is stronger than acetic or acetic acid is weaker acid than benzoic acid.

151. (i) *Refer to answer 126.*
(ii) *Refer to answer 129.*

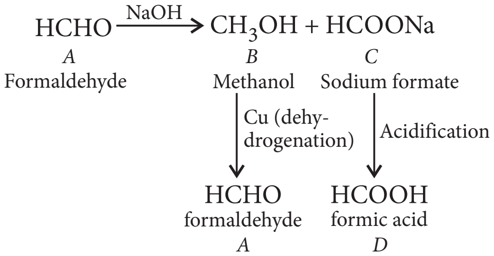
152. (i) Ethylacetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow CH_3COOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \longrightarrow CH_3COOH + \underset{\text{Methyl alcohol}}{CH_3OH}$$

The hydrolysis product of ethyl acetate undergo iodoform test with iodine and alkali.
(ii) *Refer to answer 139(b).*

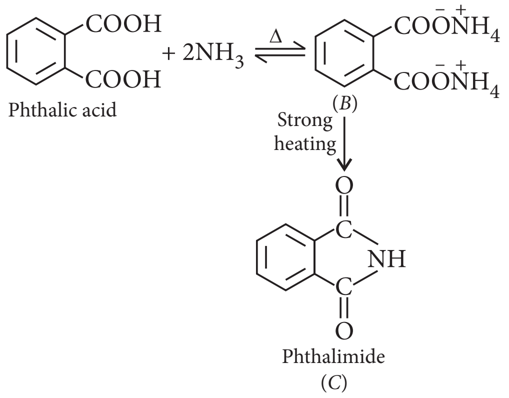
153. Since the molecular formula of *D* is CH_2O_2, thus, *D* is HCOOH (formic acid). *D* is obtained by the acidification of *C*, so, *C* is sodium formate (HCOONa).
Thus, *A* must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



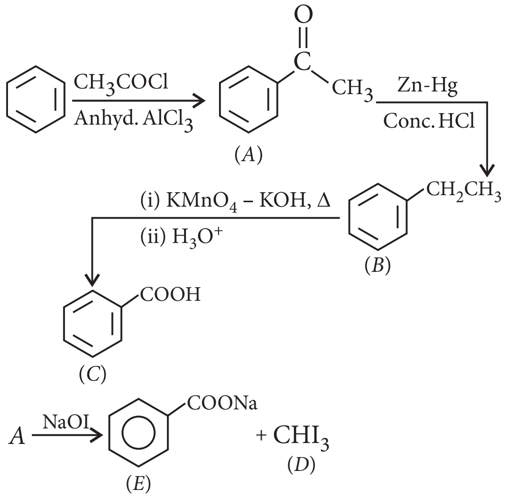
Thus, *A* = Formaldehyde (HCHO)
B = Methanol (CH_3OH)

C = Sodium formate (HCOONa)
D = Formic acid (HCOOH)

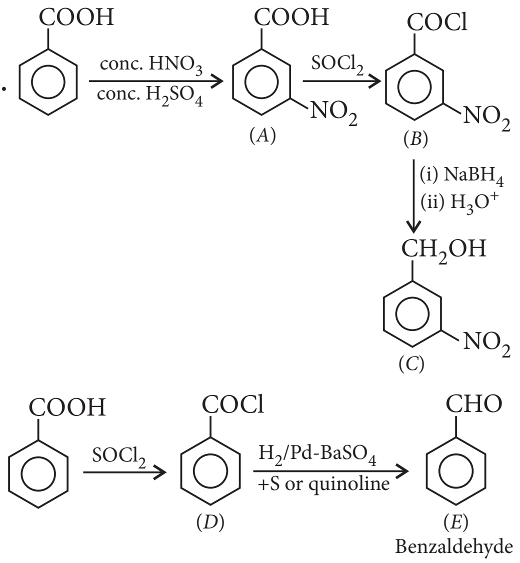
154.



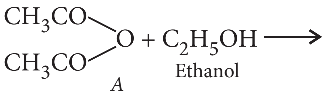
155.



156.



157.



$$\underset{A}{\begin{matrix}CH_3CO\\CH_3CO\end{matrix}}\!\!>O + \underset{\text{Ethanol}}{C_2H_5OH} \longrightarrow$$

$$\underset{\substack{C\\\text{Ethyl ethanoate}}}{CH_3COOC_2H_5} + \underset{\substack{B\\\text{Ethanoic acid}}}{CH_3COOH}$$

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+}$$

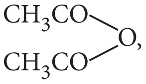
$$\underset{B}{CH_3COOH} + \underset{D}{CH_3CH_2OH}$$

$$\underset{D}{CH_3CH_2OH} \xrightarrow{KMnO_4} \underset{B}{CH_3COOH}$$

$$\Big\downarrow{\scriptstyle Ca(OH)_2 \;|\; \text{Dry distillation}}$$

$$\underset{E}{CH_3COCH_3} + CaCO_3$$

E does not give Tollen's reagent test and does not reduce Fehling's solution as it is ketone.



$$A = \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O, \qquad B = CH_3COOH$$

$C = CH_3COOC_2H_5$, $D = CH_3CH_2OH$

$E = CH_3COCH_3$

158. $$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\substack{\text{Methyl alcohol}\\(A)}}{CH_3OH} \xrightarrow{\substack{\text{conc.}\\H_2SO_4}} \underset{\substack{\text{Methyl acetate}\\(B)}}{CH_3COOCH_3}$$

$$\underset{\substack{\text{Methyl alcohol}\\(A)}}{CH_3OH} \xrightarrow{\text{mild [O]}} \underset{\substack{\text{Formaldehyde}\\(C)}}{HCHO} \xrightarrow[\text{(ii) HCl}]{\text{(i) 50\% KOH}}$$

$$\underset{\substack{\text{Methanol}\\(A)}}{CH_3OH} + \underset{\substack{\text{Methanoic}\\\text{acid}\\(D)}}{HCOOH}$$

$$\underset{\substack{\text{Formic acid}\\(D)}}{HCOOH} \xrightarrow{PCl_5} HCOCl \xrightarrow{NH_3}$$

$$\underset{\substack{\text{Methanamide}\\(E)}}{HCONH_2} \xrightarrow[P_2O_5]{\text{dehydration}} \underset{\substack{\text{Hydrocyanic}\\\text{acid}}}{HCN}$$

Therefore, (A) : Methyl alcohol
(B) : Methyl acetate
(C) : Formaldehyde
(D) : Formic acid
(E) : Formamide