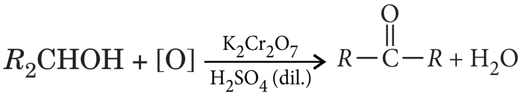
Aldehydes, Ketones and Carboxylic Acids

Recap Notes

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 :** $\begin{matrix}R\\R\end{matrix}\!\!>\!C{=}O$; where R = alkyl or aryl.
- **Nomenclature :** The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.
  - The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.
- **Structure :** The C-atom of carbonyl group is sp^2 hybridised and forms three σ-bonds and one π-bond with O atom. Carbonyl carbon with three atoms attached to it lie in a same plane with bond angle 120° (trigonal coplanar structure) and π-electron cloud lies above and below of this plane.
- **Preparation :**
  - **Oxidation of alcohols :**

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



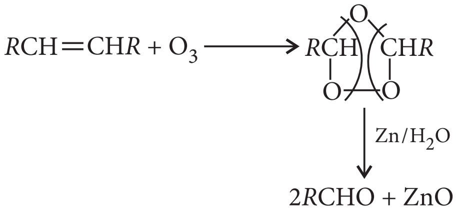
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(\text{dil.})]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O$$

  - **Catalytic dehydrogenation of alcohols :**

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

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

  - **Reductive ozonolysis of alkenes :**



  - **Rosenmund reduction :**

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{\text{Pd-BaSO}_4,\text{ S}} RCHO + HCl$$

  - **Reduction of nitriles :**

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

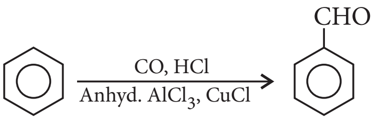
$$RC{\equiv}N \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }R'MgX/\text{dry ether}} RCOR'$$

$$RC{\equiv}N \xrightarrow[\substack{\text{Dry ether}\\\text{(ii) }H_3O^+}]{\text{(i) SnCl}_2+\text{HCl}} \underset{\text{(Stephen reduction)}}{RCHO + NH_4Cl}$$

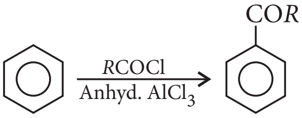
  - **From esters :**

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

  - **Gatterman-Koch reaction :**



  - **Friedel-Crafts acylation :**

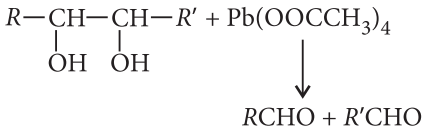


  - **From alkynes :**

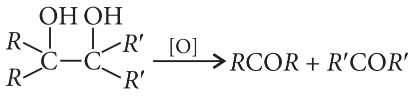
$$-C{\equiv}C- \xrightarrow[\text{HgSO}_4,\ 333\text{ K}]{\text{dil. }H_2SO_4} RCHO \text{ or } RCOR$$

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

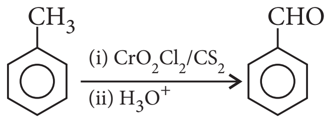
- **Oxidation of 1,2-glycols :**



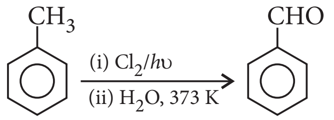
$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO$$



- **Etard reaction :**

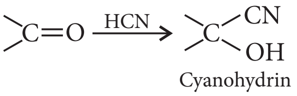


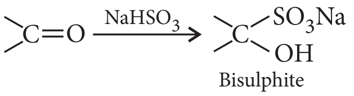
- **Side chain chlorination :**

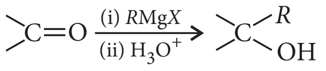


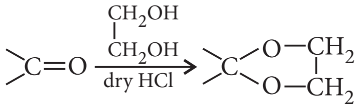
- **Physical properties :**
  - **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
  - **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.
  - Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
  - Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.
  - **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - All carbonyl compounds are fairly soluble in organic solvents.

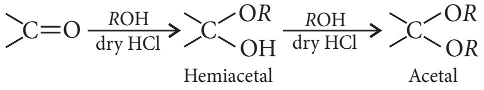
- **Chemical properties :**
  - **Nucleophilic addition reactions :**



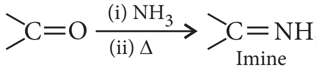


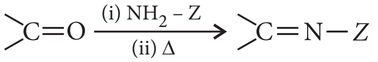


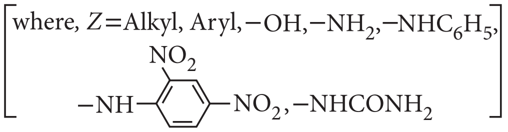




  - **Nucleophilic addition-elimination reactions :**

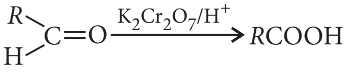


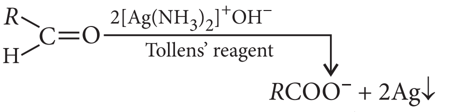




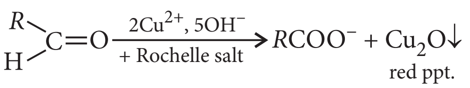
[where, Z = Alkyl, Aryl, $-OH$, $-NH_2$, $-NHC_6H_5$, $-NH-C_6H_3(NO_2)-NO_2$, $-NHCONH_2$]

  - **Oxidation :**

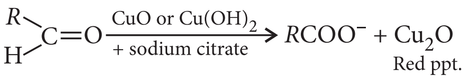




Silver mirror test
(Only aldehydes)

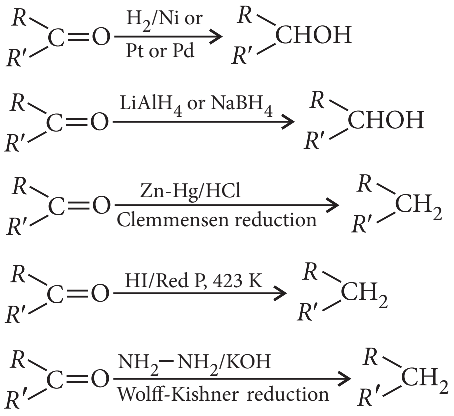


Fehling's solution test
(Only aldehydes)



Benedict's solution test
(Only aldehydes)

- **Reduction :**



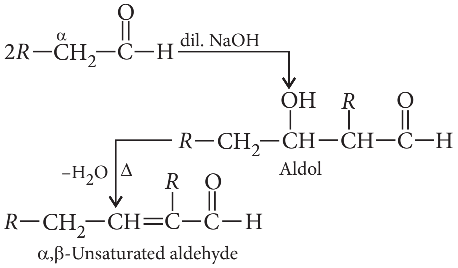
- **Haloform reaction :**

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

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

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

- **Aldol condensation :**

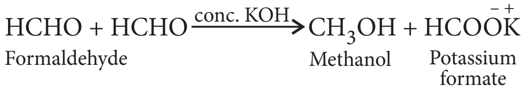


(aldehydes and ketones having at least one α-hydrogen)

– **Intramolecular aldol condensation :** It takes place in diketones and give rise to cyclic products.

– **Cross aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if both of them contain α-hydrogen atoms, it gives a mixture of four products.

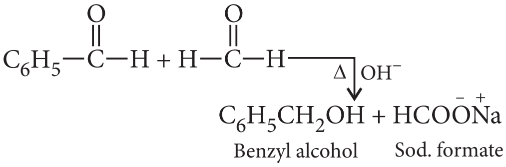
- **Cannizzaro reaction :**



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

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

- **Cross Cannizzaro reaction :**



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

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

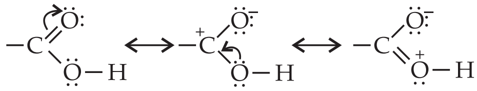
- **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

- **Distinction between aldehydes and ketones :**

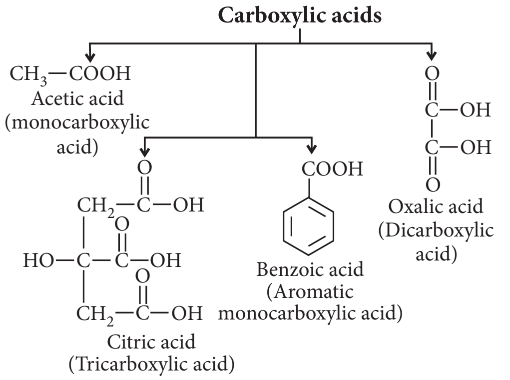
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow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

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

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

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

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

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

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

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

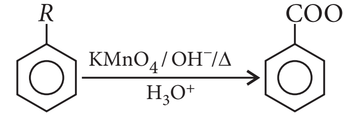
$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow{H_2O} RCOOH$$

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

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

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

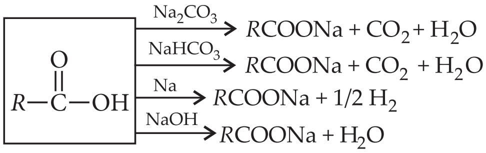
$$\underset{\text{Alkyne}}{RC{\equiv}CR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$



Alkyl benzene

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

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



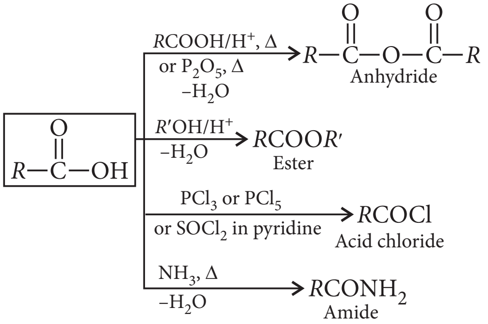
$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH \xrightarrow{Na_2CO_3} RCOONa + CO_2 + H_2O$$

$$\xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$

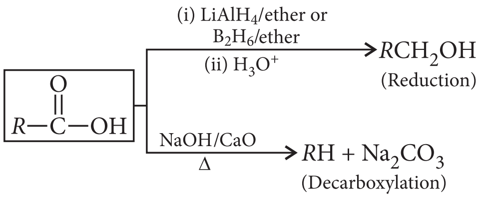
$$\xrightarrow{Na} RCOONa + 1/2\ H_2$$

$$\xrightarrow{NaOH} RCOONa + H_2O$$

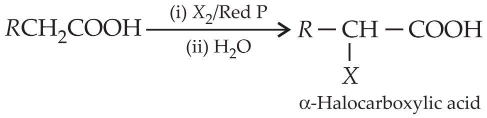
- **Reactions involving cleavage of C—OH bond:**



- **Reactions involving —COOH group :**



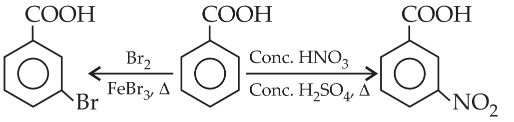
- **Hell—Volhard—Zelinsky reaction :**



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

α-Halocarboxylic acid

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



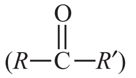
- **Distinction test between phenol and carboxylic acid :**

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

Practice Time

OBJECTIVE TYPE QUESTIONS

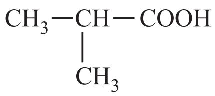
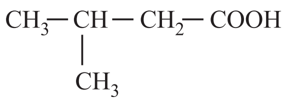
Multiple Choice Questions (MCQs)

1. Ketones  $(R-\overset{\overset{O}{||}}{C}-R')$ can be obtained in one step by (where R and R' are alkyl groups)
(a) hydrolysis of esters
(b) oxidation of primary alcohols
(c) oxidation of secondary alcohols
(d) reaction of alkyl halides with alcohols.

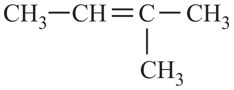
2. Aldehydes other than formaldehyde react with Grignard's reagent to give addition products which on hydrolysis give
(a) tertiary alcohols (b) secondary alcohols
(c) primary alcohols (d) carboxylic acids.

3. Which of the following compounds will undergo Cannizzaro reaction?
(a) CH_3CHO (b) CH_3COCH_3
(c) C_6H_5CHO (d) $C_6H_5CH_2CHO$

4. Propanal on treatment with dilute sodium hydroxide gives
(a) $CH_3CH_2CH_2CH_2CH_2CHO$
(b) $CH_3CH_2CH(OH)CH_2CH_2CHO$
(c) $CH_3CH_2CH(OH)CH(CH_3)CHO$
(d) CH_3CH_2COOH

5. Various products formed on oxidation of 2,5-dimethylhexan-3-one are
(i) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$
(ii) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH$
(iii) CH_3COOH
(iv) $HCOOH$
(a) (i) and (iii) (b) (i), (ii) and (iii)
(c) (i), (ii), (iii) and (iv) (d) (iii) and (iv)

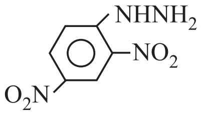
6. Alkene (X) (C_5H_{10}) on ozonolysis gives a mixture of two compounds (Y) and (Z). Compound (Y) gives positive Fehling's test and iodoform test. Compound (Z) does not give Fehling's test but give iodoform test. Compounds (X), (Y) and (Z) are

	X	***Y***	***Z***
(a)	$C_6H_5COCH_3$	CH_3CHO	CH_3COCH_3
(b)	 $CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$	CH_3CHO	CH_3COCH_3
(c)	$CH_3CH_2CH=CH_2$	CH_3CH_2CHO	$HCHO$
(d)	$CH_3-CH=CH-CH_3$	CH_3CHO	CH_3CHO

7. A compound (X) with a molecular formula $C_5H_{10}O$ gives a positive 2,4-DNP test but a negative Tollen's test. On oxidation it gives a carboxylic acid (Y) with a molecular formula $C_3H_6O_2$. Potassium salt of (Y) undergoes Kolbe's reaction and gives a hydrocarbon (Z). (X), (Y) and (Z) respectively are
(a) pentan-3-one, propanoic acid, butane
(b) pentanal, pentanoic acid, octane
(c) 2-methylbutanone, butanoic acid, hexane
(d) 2, 2-dimethylpropanone, propanoic acid, hexane

8. Which of the following statements is incorrect?
(a) $FeCl_3$ is used in the detection of phenols.
(b) Fehling solution is used in the detection of glucose.
(c) Tollens' reagent is used in the detection of unsaturation.
(d) $NaHSO_3$ is used in the detection of carbonyl compounds.

9. Which of the following compounds will give a coloured crystalline compound with



?

(a) CH_3COCl (b) $CH_3COOC_2H_5$
(c) CH_3COCH_3 (d) CH_3CONH_2

10. Which of the following reagents are not correctly matched with the reaction?

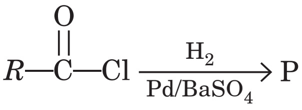
(a) $CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCOOH$: Ammonical $AgNO_3$

(b) $CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_2OH$: H_2/Pt

(c) $R{-}COOH \longrightarrow R{-}CH_2OH : NaBH_4$

(d) $CH_3CH_2COCl \longrightarrow CH_3CH_2CHO$: H_2, $Pd/BaSO_4$

11. In the following reaction, product (P) is



$$R{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow[Pd/BaSO_4]{H_2} P$$

(a) RCHO (b) RCH_3

(c) RCOOH (d) RCH_2OH

12. Which of the following will not give aldol condensation?

(a) Phenyl acetaldehyde

(b) 2-Methylpentanal

(c) Benzaldehyde

(d) 1-Phenylpropanone

13. Which of the following statements is correct regarding formic acid?

(a) It is a reducing agent.

(b) It is a weaker acid than acetic acid.

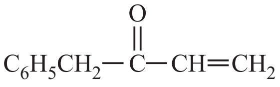
(c) It is an oxidising agent.

(d) When its calcium salt is heated, it forms acetone.

14. The condensation product of benzaldehyde and acetone is

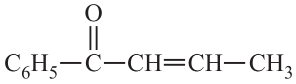
(a) $C_6H_5CH{=}C(CH_3)_2$

(b)



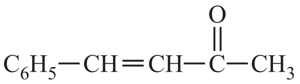
$C_6H_5CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$

(c)



$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH{-}CH_3$

(d)



$C_6H_5{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

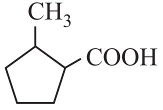
15. Which among the following is most reactive to give nucleophilic addition?

(a) FCH_2CHO (b) $ClCH_2CHO$

(c) $BrCH_2CHO$ (d) ICH_2CHO

16. Which of the following IUPAC names is not correctly matched?

(a)

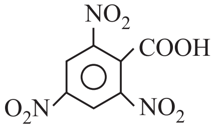


: 3-Cyclopentylpropanoic acid

(b) $(CH_3)_2C{=}CHCOOH$: 3-Methylbut-2-enoic acid

(c) $PhCH_2CH_2COOH$: 3-Phenylpropanoic acid

(d)



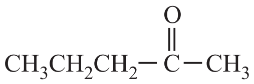
: 2, 4, 6-Trinitrobenzoic acid

17. Which of the following is the most reactive isomer?

(a)

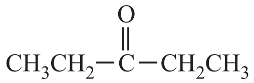
$CH_3CH_2CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$

(b)



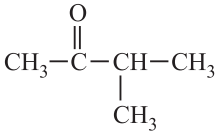
$CH_3CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

(c)



$CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_3$

(d)



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

18. The correct order of increasing acidic strength is

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

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

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

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

19. To differentiate between pentan-2-one and pentan-3-one a test is carried out. Which of the following is the correct answer?

(a) Pentan-2-one will give silver mirror test

(b) Pentan-2-one will give iodoform test.

(c) Pentan-3-one will give iodoform test

(d) None of these.

20. What happens when a carboxylic acid is treated with lithium aluminium hydride?

(a) Aldehyde is formed.

(b) Primary alcohol is formed.

(c) Ketone is formed.

(d) Grignard reagent is formed.

21. Which of the following will not undergo HVZ reaction?

(a) Propanoic acid

(b) Ethanoic acid

(c) 2-Methylpropanic acid

(d) 2,2-Dimethylpropanoic acid

22. When propanal reacts with 2-methylpropanal in presence of NaOH, four different products are formed. The reaction is known as

(a) aldol condensation
(b) cross aldol condensation
(c) Cannizzaro reaction
(d) HVZ condensation.

23. Propanone can be prepared from ethyne by

(a) passing a mixture of ethyne and steam over a catalyst, magnesium at 420°C
(b) passing a mixture of ethyne and ethanol over a catalyst zinc chromite
(c) boiling ethyne with water and H_2SO_4
(d) treating ethyne with iodine and NaOH.

24. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	$RCOCH_3 \xrightarrow[HCl]{Zn\text{-}Hg} RCH_2CH_3$	(i)	Kolbe's reaction
(B)	$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$	(ii)	Clemmensen reduction
(C)	$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anh.} C_6H_5COCH_3$	(iii)	Friedel–Crafts reaction
(D)	$C_6H_5OH + CO_2 + NaOH \longrightarrow HOC_6H_4COONa$	(iv)	Cannizzaro reaction

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

25. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

Ethanal, Propanal, Propanone, Butanone

(a) Butanone < Propanone < Propanal < Ethanal
(b) Propanone < Butanone < Ethanal > Propanal
(c) Propanal < Ethanal < Propanone < Butanone
(d) Ethanal < Propanal < Propanone < Butanone

26. Which of the following reactions will give benzophenone?

(i) Benzoyl chloride + Benzene + $AlCl_3$
(ii) Benzoyl chloride + Phenylmagnesium bromide
(iii) Benzoyl chloride + Diphenyl cadmium

(a) (i) and (ii)
(b) (ii) and (iii)
(c) (i) and (iii)
(d) (i), (ii) and (iii)

27. What are the correct steps to convert acetaldehyde to acetone?

(a) CH_3MgBr, H_2O, Oxidation
(b) Oxidation, $Ca(OH)_2$, Heat
(c) Reduction, KCN, Hydrolysis
(d) Oxidation, C_2H_5ONa, Heat

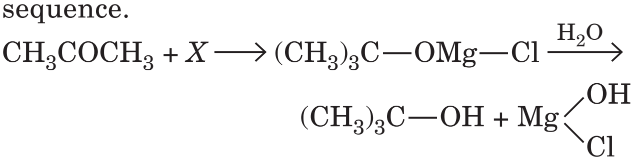
28. Hydrocarbons are formed when aldehydes and ketones are reacted with amalgamated zinc and conc. HCl. The reaction is called

(a) Cannizzaro reaction
(b) Clemmensen reduction
(c) Rosenmund reduction
(d) Wolff-Kishner reduction.

29. The addition of HCN to carbonyl compounds is an example of

(a) nucleophilic addition
(b) electrophilic addition
(c) free radical addition
(d) electromeric addition.

30. Identify reactant (*X*) in the given reaction sequence.



$$CH_3COCH_3 + X \longrightarrow (CH_3)_3C{-}OMg{-}Cl \xrightarrow{H_2O} (CH_3)_3C{-}OH + Mg\begin{smallmatrix}OH\\Cl\end{smallmatrix}$$

(a) CH_3MgCl
(b) $CH_3COCl + Mg$
(c) $MgCl_2$
(d) CH_3CH_2MgCl

31. Which of the following is the correct order of relative strength of acids?

(a) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$
(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$
(d) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$

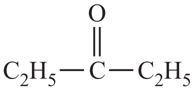
32. An organic compound of molecular formula C_3H_6O did not give a silver mirror with Tollen's reagent but gave an oxime with hydroxylamine. It may be

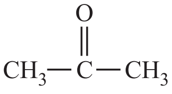
(a) $CH_2{=}CH{-}CH_2{-}OH$
(b) CH_3COCH_3
(c) CH_3CH_2CHO
(d) $CH_2{=}CH{-}OCH_3$

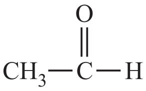
33. What is the test to differentiate between pentan-2-one and pentan-3-one?

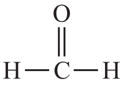
(a) Iodoform test
(b) Benedict's test
(c) Fehling's test
(d) Aldol condensation test

34. Which of the following carbonyl compounds is most polar?

(a) 
$C_2H_5-\overset{O}{\overset{\|}{C}}-C_2H_5$

(b) 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 
$CH_3-\overset{O}{\overset{\|}{C}}-H$

(d) 
$H-\overset{O}{\overset{\|}{C}}-H$

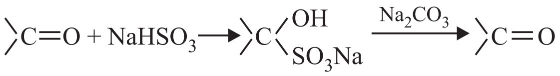
35. In nucleophilic addition reactions, the reactivity of carbonyl compounds follows the order

(a) $HCHO > RCHO > ArCHO > R_2CO > Ar_2CO$
(b) $HCHO > R_2CO > Ar_2CO > RCHO > ArCHO$
(c) $Ar_2CO > R_2CO > ArCHO > RCHO > HCHO$
(d) $ArCHO > Ar_2CO > RCHO > R_2CO > HCHO$

36. Which of the following statements is not correct?

(a) Aldehydes and ketones are functional isomers.
(b) Formaldehyde reacts with ammonia to form hexamethylenetetramine.
(c) $LiAlH_4$ converts ketones into *sec*-alcohols.
(d) Butanal and propanal can be distinguished by iodoform test.

37. Study the given reaction and identify the process which is carried out.


$$>C=O + NaHSO_3 \longrightarrow >C<^{OH}_{SO_3Na} \xrightarrow{Na_2CO_3} >C=O$$

(a) It is used for purification of aldehydes and ketones.
(b) It is used to distinguish aldehydes from ketones.
(c) It is used to prepare cyclic aldehydes and ketones.
(d) It is used to study polar nature of aldehydes and ketones.

38. Which of the following aldehydes will show Cannizzaro reaction?

(a) HCHO
(b) C_6H_5CHO
(c) $(CH_3)_3CCHO$
(d) All of these

39. α-Hydroxypropanoic acid can be prepared from ethanal by following the steps given in the sequence.

(a) Treat with HCN followed by acidic hydrolysis.
(b) Treat with $NaHSO_3$ followed by reaction with Na_2CO_3.
(c) Treat with H_2SO_4 followed by hydrolysis.
(d) Treat with $K_2Cr_2O_7$ in presence of sulphuric acid.

40. Which is the correct method of synthesising acetamide from acetone?

(a) $CH_3COCH_3 \xrightarrow{Pd/BaSO_4} CH_3CHO \xrightarrow{NH_3} CH_3CH_2NH_2 \xrightarrow{H_2O} CH_3CONH_2$

(b) $CH_3COCH_3 \xrightarrow[NaOH]{I_2} CH_3COONa \xrightarrow[NH_3]{H^+} CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2$

(c) $CH_3COCH_3 \xrightarrow{CrO_3} CH_3COOH \xrightarrow{NH_3} CH_3CONH_2$

(d) $CH_3COCH_3 \xrightarrow[NaOH]{I_2} CH_3COOH \xrightarrow{HCl} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$

41. There is a large difference in the boiling points of butanal and butan-1-ol due to

(a) intermolecular hydrogen bonding in butan-1-ol
(b) intramolecular hydrogen bonding in butanal
(c) higher molecular mass of butan-1-ol
(d) resonance shown by butanal.

42. A compound (*X*) having molecular formula $C_4H_8O_2$ is hydrolysed by water in presence of an acid to give a carboxylic acid (*Y*) and an alcohol (*Z*). (*Z*) on oxidation with chromic acid gives (*Y*). (*X*), (*Y*) and (*Z*) are

	X	***Y***	***Z***
(a)	CH_3COOCH_3	CH_3COOH	CH_3OH
(b)	$CH_3COOC_2H_5$	CH_3COOH	C_2H_5OH
(c)	$C_2H_5COOCH_3$	C_2H_5COOH	C_2H_5OH
(d)	$CH_3COOC_2H_5$	C_2H_5COOH	CH_3OH

43. –OH group present in alcohols is neutral while it is acidic in carboxylic acid because

(a) in carboxylic acid –OH group is attached to electron withdrawing carbonyl group
(b) in alcohols –OH group is attached to alkyl group which is electron withdrawing
(c) carboxylic group is an electron releasing group
(d) alcoholic group is an electron withdrawing group.

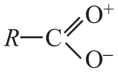
44. Which of the following orders is not correct for the decreasing order of acidic character?

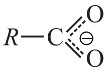
(a) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)\ CH_2COOH > CH_2(Cl)CH_2CH_2COOH > CH_3CH_2CH_2COOH$
(b) $ICH_2COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

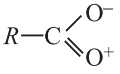
(c) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

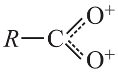
(d) $HCOOH > CH_3COOH > C_2H_5COOH > (CH_3)_2CHCOOH$

45. The correct structure representation of carboxylate ion is

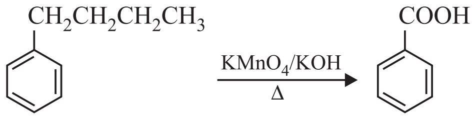
(a) 

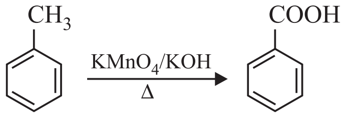
(b) 

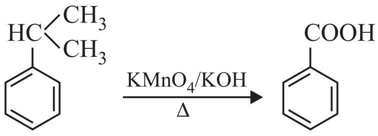
(c) 

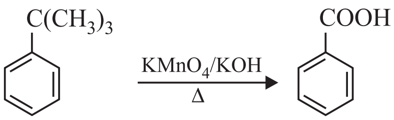
(d) 

46. Which of the following reactions does not occur?

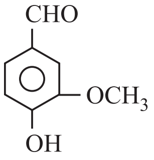
(a) 

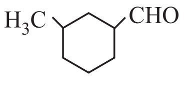
(b) 

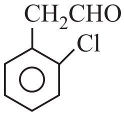
(c) 

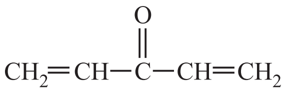
(d) 

47. Which of the following names of the organic compounds is not correctly written?

(a)  – 4-Hydroxy-3-methoxybenzaldehyde

(b)  – 5-Methylcyclohexanecarbaldehyde

(c)  – 2-(2-Chlorophenyl)ethanal

(d) 

$CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2$ – Penta-1, 4-dien-3-one

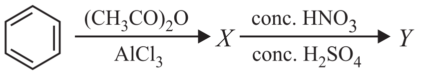
48. In the following sequence of reaction, the final product (Z) is

$$CH{\equiv}CH \xrightarrow[H_2SO_4]{Hg^{2+}} X \xrightarrow[H_2O]{CH_3MgX} Y \xrightarrow{[O]} Z$$

(a) ethanal (b) propan-2-ol

(c) propanone (d) propan-1-ol

49. Identify the products (X) and (Y) in the given reaction :



(a) X = Acetophenone, Y = m-Nitroacetophenone

(b) X = Toluene, Y = m-Nitroacetotoluene

(c) X = Acetophenone, Y = o and p-Dinitroacetophenone

(d) X = Benzaldehyde, Y = m-Nitrobenzaldehyde

50. Benzaldehyde can be prepared from benzene by passing vapours of .... and .... in its solution in presence of catalyst mixture of aluminium chloride and cuprous chloride. The reaction is known as ....

(a) HCl, $SnCl_4$, Rosenmund reduction

(b) CO, HCl, Gattermann–Koch reaction

(c) CO_2, H_2SO_4, Clemmensen reduction

(d) O_3, alcohol, Wolff–Kishner reduction

51. The best oxidising agent for oxidation of $CH_3{-}CH{=}CH{-}CHO$ to $CH_3{-}CH{=}CH{-}COOH$ is

(a) Baeyer's reagent

(b) Tollen's reagent

(c) Schiff's reagent

(d) Acidified dichromate.

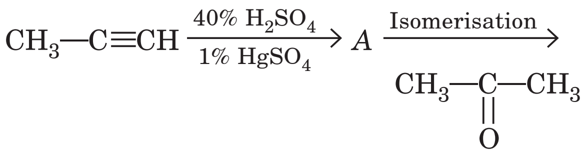
52. The product of hydrolysis of ozonide of 1-butene are

(a) ethanal only

(b) ethanal and methanal

(c) propanal and methanal

(d) methanal only.

53. 

$$CH_3{-}C{\equiv}CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_3$$

Structure of A and type of isomerism in the above reaction are

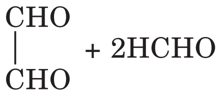
(a) Prop-1-en-2-ol, metamerism

(b) Prop-1-en-1-ol, tautomerism

(c) Prop-2-en-2-ol, geometrical isomerism

(d) Prop-1-en-2-ol, tautomerism.

54. A diene, buta-1,3-diene was subjected to ozonolysis to prepare aldehydes. Which of the following aldehydes will be obtained during the reaction?

(a) 

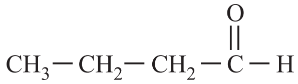
$\begin{array}{c}CHO\\ |\\ CHO\end{array} + 2HCHO$

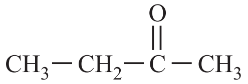
(b) $CH_3CHO + 2HCHO$

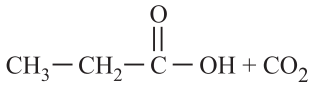
(c) $CH_3CH_2CHO + CH_3CHO$

(d) $2CH_3CH_2CHO$

55. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?

(a) 
$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

(b) 
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + CO_2$

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

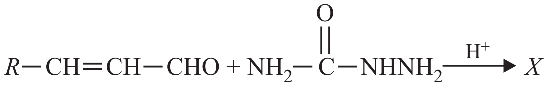
56. An organic compound (X) with molecular formula $C_9H_{10}O$ gives positive 2,4-DNP and Tollen's tests. It undergoes Cannizzaro reaction and on vigorous oxidation it gives 1,4-benzenedicarboxylic acid. Compound (X) is

(a) benzaldehyde

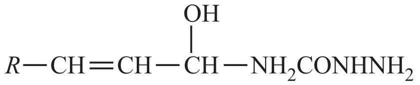
(b) *o*-methylbenzaldehyde

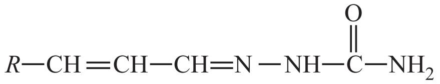
(c) *p*-ethylbenzaldehyde

(d) 2, 2-dimethylhexanal

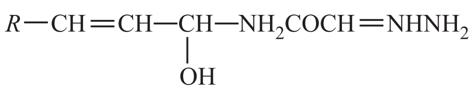
57. 
$R-CH{=}CH-CHO + NH_2-\overset{O}{\overset{\|}{C}}-NHNH_2 \xrightarrow{H^+} X$

(X) in the above reaction is

(a) 
$R-CH{=}CH-\overset{OH}{\overset{|}{CH}}-NH_2CONHNH_2$

(b) 
$R-CH{=}CH-CH{=}N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

(c) $R-CH{=}NH_2CONH_2$

(d) 
$R-CH{=}CH-\underset{OH}{\underset{|}{CH}}-NH_2COCH{=}NHNH_2$

58. Which of the following will not yield acetic acid on strong oxidation?

(a) Butanone (b) Propanone

(c) Ethyl ethanoate (d) Ethanol

59. Which of the following compounds does not react with $NaHSO_3$?

(a) HCHO (b) $C_6H_5COCH_3$

(c) CH_3COCH_3 (d) CH_3CHO

60. Study the following reactions and mark the appropriate choice.

$$(A) + C_2H_5OH \longrightarrow (B) + (C)$$
$$(C) + HOH \xrightarrow{H^+} (B) + (D)$$
$$(D) \xrightarrow{[O]} (B)$$
$$(B) + Ca(OH)_2 \longrightarrow \text{Calcium salt} + H_2O \xrightarrow{\text{dry distillation}} \underset{\text{(Acetone)}}{CH_3COCH_3}$$

	(*A*)	(*B*)	(*C*)	(*D*)
(a)	$(CH_3CO)_2O$	CH_3COOH	$CH_3COOC_2H_5$	C_2H_5OH
(b)	CH_3COCl	HCOOH	CH_3COOCH_3	CH_3OH
(c)	CH_3COOH	CH_3OH	CH_3COOCH_3	CH_3OH
(d)	CH_3NH_2	CH_3COOH	CH_3COOCH_3	C_2H_5OH

61. Compound (X) with molecular formula C_3H_8O is treated with acidified potassium dichromate to form a product (Y) with molecular formula C_3H_6O. (Y) does not form a shining silver mirror on warming with ammoniacal $AgNO_3$. (Y) when treated with an aqueous solution of $NH_2CONHNH_2$. HCl and sodium acetate to give a product (Z). The structure of (Z) is

(a) $CH_3CH_2CH{=}NNHCONH_2$

(b) $(CH_3)_2C{=}NNHCONH_2$

(c) $(CH_3)_2C{=}NCONHNH_2$

(d) $CH_3CH_2CH{=}NCONHNH_2$

62. Aldehydes and ketones are isomers as they have same general formula but different functional groups. Both these functional groups can be distinguished by various tests.

A compound with molecular formula C_9H_{10} has two isomers P and Q which undergo ozonolysis to give two functional isomers (R and S) with formula, C_8H_8O.

$$P \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2} R + HCHO,$$

$$Q \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2} S + HCHO$$

Which of the given options can not be correct for P, Q, R and S?

I. If P is 4-vinyl toluene then R gives Cannizzaro reaction but not haloform reaction.

II. If Q is 4-vinyl toluene then S gives haloform reaction but not Cannizzaro.

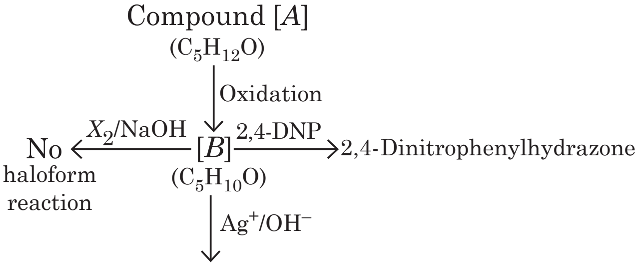
III. If Q is 2-phenylpropene then S gives haloform reaction but not Cannizzaro.

IV. If P is 2-phenylpropene then R gives both Cannizzaro and haloform reaction.

(a) I and II only (b) I and III only

(c) II and III only (d) II and IV only

63. Study the given reactions chart carefully :



No silver mirror is formed

Which is correct for compounds A and B?

(a) B is an aldehyde.

(b) B is a ketone but not methyl ketone.

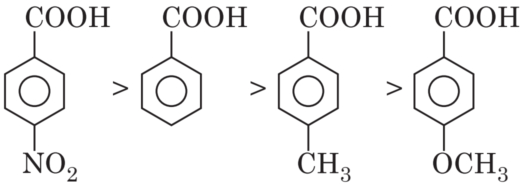
(c) A is a primary alcohol.

(d) B convert to A using Zn–Hg/HCl.

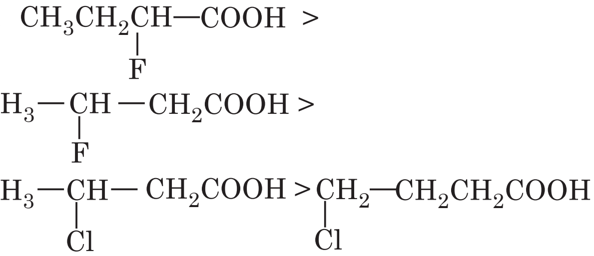
64. Acidic nature of carboxylic groups depends on various factors like presence of electron withdrawing groups ($-I$, $-R$ effect), presence of electron donating groups ($+I$, $+R$ effect), distance of attached groups. Stability of carboxylate ion plays an important role in the acidic nature of carboxylic acid.

Vinita, a class 12 student has written the following orders of acidity for various carboxylic acids :

I :

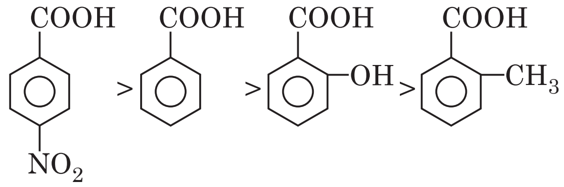


II :



$$CH_3CH_2\underset{F}{CH}-COOH > CH_3-\underset{F}{CH}-CH_2COOH > CH_3-\underset{Cl}{CH}-CH_2COOH > \underset{Cl}{CH_2}-CH_2CH_2COOH$$

III :



Which of the following orders is not correct and what is the reason behind it?

(a) Order I, $+R$ effect of $-OCH_3$ group is not interpreted correctly.

(b) Order II, position of electronegative group is not interpreted correctly.

(c) Order III, *ortho* effect is not considered.

(d) All the orders I, II and III are correct.

65. Carboxylic acids do not undergo Friedel Craft's reaction because

(a) —COOH group is meta directing

(b) —COOH group is resonance stabilised

(c) carboxyl group is deactivating and gets bonded to Friedel Craft's catalyst

(d) all of above.

66. A ketone 'A' (C_4H_8O), which undergoes a haloform reaction, gives a compound 'B' on reduction. 'B' on heating with sulphuric acid gives a compound 'C' which forms mono-ozonide 'D'. 'D' on hydrolysis with zinc dust gives only, 'E'.

Identify the correct statement.

(a) A is butan-2-one; B is butan-2-ol.

(b) B is but-2-ene; C is acetaldehyde.

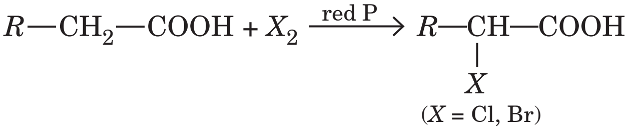
(c) D is acetaldehyde; E is butan-2-ol.

(d) B is butan-1-one; D is but-2-ene.

Case Based MCQs

Case I : Read the passage given below and answer the following questions :

Carboxylic acids having an α-hydrogen atom when treated with chlorine or bromine in the presence of small amount of red phosphorus gives α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



$$R-CH_2-COOH + X_2 \xrightarrow{\text{red P}} R-\underset{X}{CH}-COOH \quad (X = Cl, Br)$$

When sodium salt of carboxylic acid is heated with soda lime it loses carbon dioxide and gives hydrocarbon with less number of C-atoms.

$$\underset{\text{Carboxylic acid}}{R-COOH} \xrightarrow{NaOH} \underset{\text{Sod. carboxylate}}{R-COONa}$$

$$\xrightarrow[\Delta]{NaOH + CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

In the following questions (Q. No. 67-71), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

67. Assertion : $(CH_3)_3CCOOH$ does not give H.V.Z reaction.

Reason : $(CH_3)_3CCOOH$ does not have α-hydrogen atom.

68. Assertion : H.V.Z. reaction involves the treatment of carboxylic acids having α-hydrogens with Cl_2 or Br_2 in presence of small amount of red phosphorus.

Reason : Phosphorus reacts with halogens to form phosphorus trihalides.

69. Assertion : Propionic acid with Br_2/P yields $CH_2Br—CHBr—COOH$.

Reason : Propionic acid has two α-hydrogen atoms.

70. Assertion : $C_6H_5COCH_2COOH$ undergoes decarboxylation easily than $C_6H_5COCOOH$.

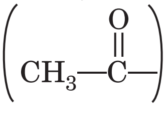
Reason : $C_6H_5COCH_2COOH$ is a β-keto acid.

71. Assertion : On heating 3-methylbutanoic acid with soda lime, isobutane is obtained.

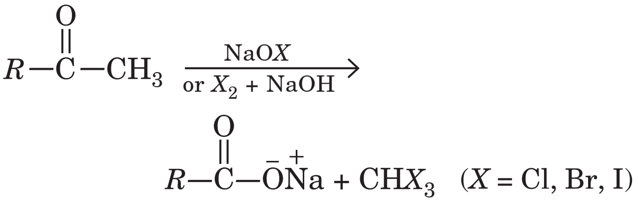
Reason : Soda lime is a mixture of NaOH + CaO in the ratio 3 : 1.

Case II : Read the passage given below and answer the following questions from 72 to 76.

Aldehydes and ketones having acetyl group



$\left(CH_3—\overset{\overset{\large O}{||}}{C}—\right)$ are oxidised by sodium hypohalate (NaOX) or halogen and alkali (X_2 + OH^-) to corresponding sodium salt having one carbon atoms less than the carbonyl compound and give a haloform.



$$R—\overset{\overset{O}{||}}{C}—CH_3 \xrightarrow[\text{or } X_2 + NaOH]{NaOX} R—\overset{\overset{O}{||}}{C}—\overset{-}{O}\overset{+}{Na} + CHX_3 \quad (X = Cl, Br, I)$$

Sodium hypoiodite (NaOI) when treated with compounds containing $CH_3CO—$ group gives yellow precipitate of iodoform. Haloform reaction does not affect a carbon-carbon double bond present in the compound.

72. Which of the following compounds will give positive iodoform test?

(a) Isopropyl alcohol (b) Propionaldehyde

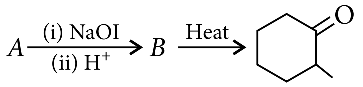
(c) Ethylphenyl ketone (d) Benzyl alcohol

73. Which of the following compounds is not formed in iodoform reaction of acetone?

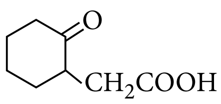
(a) CH_3COCH_2I (b) ICH_2COCH_2I

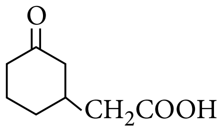
(c) CH_3COCHI_2 (d) CH_3COCI_3

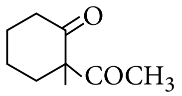
74. For the given set of reactions,

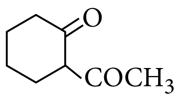


starting compound A corresponds to

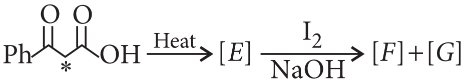
(a)


(b)


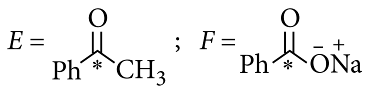
(c)


(d)


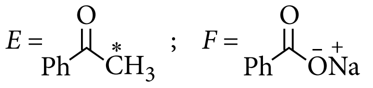
75. In the following reaction sequence, the correct structures of E, F and G are



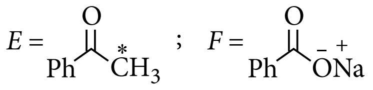
(* implies ^{13}C labelled carbon)

(a)


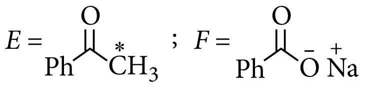
; $G = CHI_3$

(b)


; $G = CHI_3$

(c)


; $G = \overset{*}{C}HI_3$

(d)


; $G = \overset{*}{C}HI_3$

76. An organic compound 'A' has the molecular formula C_3H_6O. It undergoes iodoform test.

When saturated with HCl it gives '*B*' of molecular formula $C_9H_{14}O$. '*A*' and '*B*' respectively are

(a) propanal and mesityl oxide

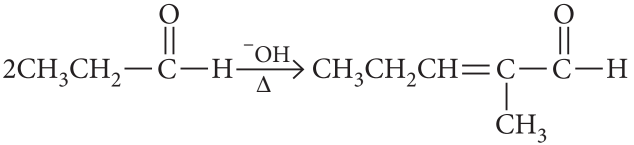
(b) propanone and mesityl oxide

(c) propanone and 2,6-dimethyl-2,5-heptadien-4-one

(d) propanone and propionaldehyde.

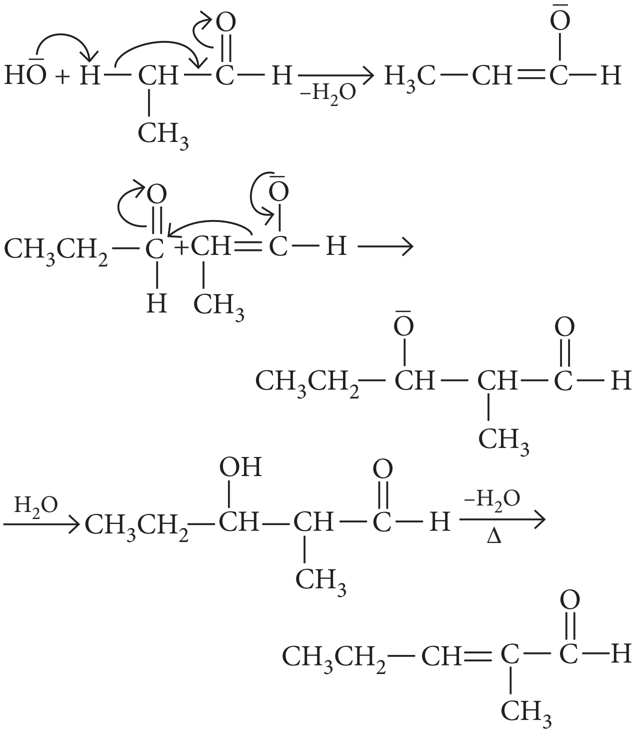
Case III : Read the passage given below and answer the following questions from 77 to 81.

The addition reaction of enol or enolate to the carbonyl functional group of aldehyde or ketone is known as aldol addition. The β-hydroxyaldehyde or β-hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction. Carbonyl compound having α-hydrogen undergoes aldol condensation reaction.



$$2CH_3CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{^-OH} CH_3CH_2CH=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

Mechanism :



77. Condensation reaction is the reverse of which of the following reaction?

(a) Lock and key hypothesis

(b) Oxidation

(c) Hydrolysis

(d) Glycogen formation

78. Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?

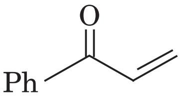
(a) $CH_3CH=CHCHO$

(b) $CH_3CH=CHCOCH_3$

(c) $(CH_3)_2C=CHCHO$

(d) $(CH_3)_2C=CHCOCH_3$

79. Which combination of carbonyl compounds gives phenyl vinyl ketone by an aldol condensation?



(a) Acetophenone and Formaldehyde

(b) Acetophenone and acetaldehyde

(c) Benzaldehyde and acetaldehyde

(d) Benzaldehyde and acetone

80. Which of the following will undergo aldol condensation?

(a) HCHO (b) CH_3CH_2OH

(c) C_6H_5CHO (d) CH_3CH_2CHO

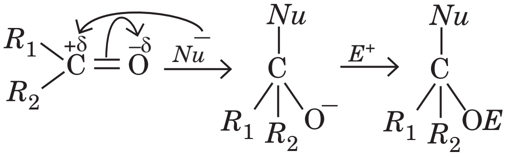
81. Which of the following does not undergo aldol condensation ?

(a) CH_3CHO (b) CH_3CH_2CHO

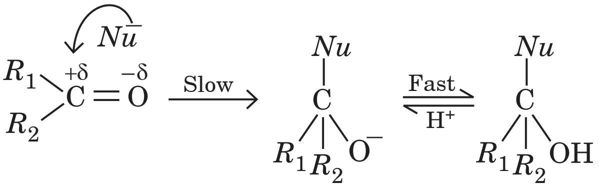
(c) CH_3COCH_3 (d) C_6H_5CHO

Case IV : Read the passage given below and answer the following questions :

Aldehydes and ketones undergo nucleophilic addition reactions.



Carbonyl carbon is electron deficient hence acts as an electrophile. Nucleophile attacks on the electrophilic carbon atom of the carbonyl group from a direction perpendicular to the plane of the molecule.



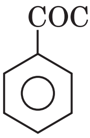
In this process, hybridisation of carbon atom changes from sp^2 to sp^3 and a tetrahedral alkoxide ion is formed as intermediate. This intermediate captures proton from the reaction medium to give the neutral product. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions.

In the following questions (Q. No. 82-86), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

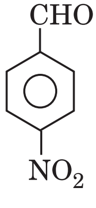
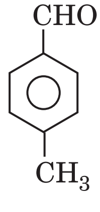
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

82. Assertion : Benzaldehyde is more reactive than ethanal towards nucleophilic attack.
Reason : The overall effect of *–I* and *+R* effect of phenyl group decreases the electron density on the carbon atom of $>C{=}O$ group in benzaldehyde.

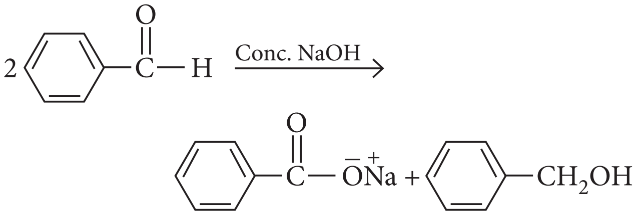
83. Assertion : $(CH_3)_3CCOC(CH_3)_3$ and acetone can be distinguished by the reaction with $NaHSO_3$.
Reason : HSO_3^- is the nucleophile in bisulphite addition.

84. Assertion : Ease of nucleophilic addition of the compounds  (I), CH_3CHO(II) and CH_3COCH_3(III) is I > II > III.
Reason : Aldehydes and ketones undergo nucleophilic addition reactions.

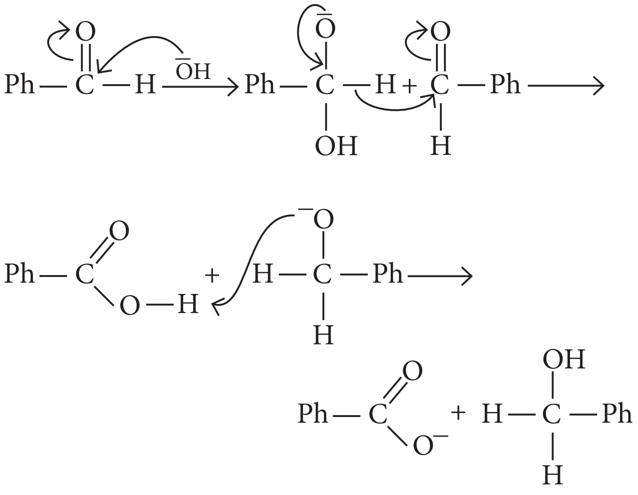
85. Assertion : The formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN. This reaction is catalysed by a base.
Reason : Base generates CN^- ion which is a stronger nucleophile.

86. Assertion :  is more reactive towards nucleophilic addition reaction than  .
Reason : Reactivity of carbonyl group is due to electrophilic nature of carbonyl carbon.

Case V : Read the passage given below and answer the following questions from 87 to 91.
When an aldehyde with no α-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction.



Mechanism :



87. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol.

88. Which of the following compounds will undergo Cannizzaro reaction?
(a) CH_3CHO
(b) CH_3COCH_3
(c) C_6H_5CHO
(d) $C_6H_5CH_2CHO$

89. Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compounds is
(a) 2, 2, 2-trichloroethanol
(b) trichloromethanol

(c) 2, 2, 2-trichloropropanol

(d) chloroform.

90. In Cannizzaro reaction given below :

$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^-$ the slowest step is

(a) the attack OH^- at the carboxyl group

(b) the transfer of hydride to the carbonyl group

(c) the abstraction of proton from the carboxylic group

(d) the deprotonation of $PhCH_2OH$.

91. Which of the following reaction will not result in the formation of carbon-carbon bonds?

(a) Cannizzaro reaction

(b) Wurtz reaction

(c) Reimer-Tiemann reaction

(d) Friedel-Crafts' acylation

Assertion & Reasoning Based MCQs

For question numbers 92-105, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

92. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

93. Assertion : α-Hydrogen atoms in aldehydes and ketones are acidic.

Reason : The anion left after the removal of α-hydrogen is stabilised by inductive effect.

94. Assertion : Hydrogen bonding in carboxylic acids is stronger than alcohols.

Reason : Highly branched carboxylic acids are more acidic than unbranched acids.

95. Assertion : *m*-Chlorobenzoic acid is a stronger acid than *p*-chlorobenzoic acid.

Reason : In *m*-chlorobenzoic acid both $-I$-effect and $+R$-effect of Cl operate but in *p*-chlorobenzoic acid only $+R$-effect of Cl operates.

96. Assertion : Ketones can be converted into acids by haloform reaction.

Reason : Addition of Grignard reagents to dry ice followed by hydrolysis gives ketones.

97. Assertion : Acetic acid in vapour state shows a molecular mass of 120.

Reason : It undergoes intermolecular hydrogen bonding.

98. Assertion : Nitration of benzoic acid gives *m*-nitrobenzoic acid.

Reason : Carboxyl group increases the electron density at the *meta*-position.

99. Assertion : Boiling point of aldehydes lie in between parent alkanes and corresponding alcohols.

Reason : Aldehydes cannot form intermolecular hydrogen bonds like alcohols.

100. Assertion : Carboxylic acids are stabilised by resonance.

Reason : Chloroacetic acid is weaker than acetic acid.

101. Assertion : Benzaldehyde undergoes aldol condensation.

Reason : Aldehydes having α-hydrogen atom undergo aldol condensation.

102. Assertion : Formic acid is a stronger acid than benzoic acid.

Reason : pK_a of formic acid is lower than that of benzoic acid.

103. Assertion : $NaHSO_3$ is used for the purification of carbonyl compounds.

Reason : They are used in the blending of perfumes and flavouring agents.

104. Assertion : Carboxylic acids have higher boiling points than alkanes.

Reason : Carboxylic acids are resonance hybrids.

105. Assertion : *o*-Substituted benzoic acids are generally stronger acids than benzoic acids.

Reason : Increased strength is due to *ortho*-effect.

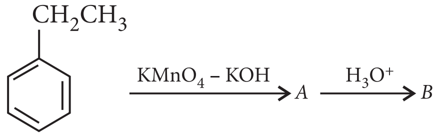
SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

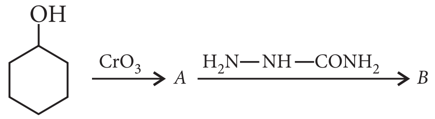
1. Arrange the following in the increasing order of their boiling points.
CH_3CHO, CH_3COOH, CH_3CH_2OH

2. Write chemical equations for the following reactions :
Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$.

3. Write structures of compounds *A* and *B* in each of the following reactions.

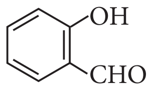


4. Write structures of compounds *A* and *B* in each of the following reactions :



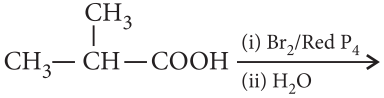
5. Give reasons :
Chloroacetic acid is stronger than acetic acid.

6. Write the IUPAC name of the following compound :



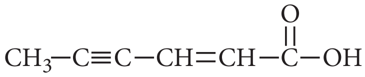
7. Aldehydes and ketones have lower boiling points than corresponding alcohols. Why?

8. Complete the following reactions :



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

9. Write the IUPAC name of the following :



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

10. Write the equation involved in Etard reaction.

Short Answer Type Questions (SA-I)

11. 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 :

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

12. Write chemical equations for the following reactions :

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

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

13. 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.

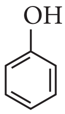
14. Describe how the following conversions can be brought about :

(i) Ethylbenzene to benzoic acid

(ii) Bromobenzene to benzoic acid

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

(i) $F—CH_2—COOH$ or $Cl—CH_2—COOH$

(ii) 

or CH_3COOH

16. The reaction of carbonyl compound with pure HCN is very slow and becomes fast in presence of a base.

17. A compound having the molecular formula C_3H_6O forms a crystalline white ppt. with sodium bisulphite and reduces Fehling's solution. Suggest the structural formula and IUPAC name of this compound. Name an isomer for it from a group other than its own.

18. Account for the following :

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

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

19. (i) What is the advantage of using DIBAL-H as reducing agent?

(ii) Which of the following can be nitrated more easily and why? Benzoic acid or phenol.

20. 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.

Short Answer Type Questions (SA-II)

21. Write the equation of the reactions of ethanal with

(i) Fehling's solution (ii) Phenylhydrazine

(iii) Hydroxylamine.

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

(i) Clemmensen reaction

(ii) Cannizzaro reaction

23. (i) Write the structures of compounds A, B and C in each of the following reactions :

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

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

(ii) Do the following conversion in not more than two steps:

Benzoic acid to benzaldehyde

24. During practical exams, lab assistant provided two test tubes containing 5 mL benzoic acid and 5 mL acetaldehyde to every student. A student, Rahul found that test tubes given to him were unlabelled. He informed the teacher before performing any experiment with the given chemicals.

How can the chemicals be distinguished for correct labelling?

25. (i) Write the equations involved in the following reactions :

(a) Stephen reaction

(b) Etard reaction

(ii) Distinguish between CH_3COOH and HCOOH.

26. 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.

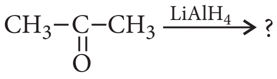
27. (a) Write the chemical reaction involved in Wolff-Kishner reduction.

(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.

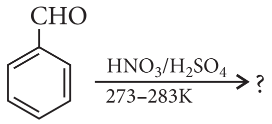
$C_6H_5COCH_3$, $CH_3 - CHO$, CH_3COCH_3

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

28. (a) Write the main product in the following equations :

(i) 

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

(ii) 

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

(b) Write the product in the following reaction :

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

29. 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

30. (a) Draw the structures of the following :

(i) *p*-Methylbenzaldehyde

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

(b) Describe how the following conversions can be brought about :

Cyclohexanol to cyclohexan 1-one

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

(a) Write the structures of (*A*), (*B*), (*C*) and (*D*).

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

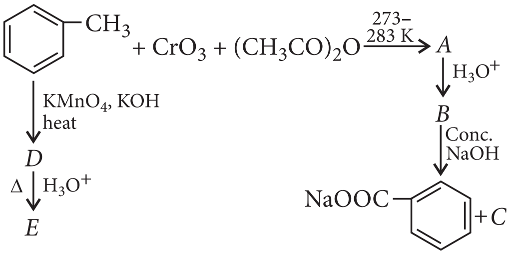
32. In an industry aldehydes are being prepared by controlled oxidation of primary alcohol using acidified $K_2Cr_2O_7$ or aqueous or alkaline $KMnO_4$ as oxidant. Mohan suggested the owner of factory to use Collin's reagent instead of acidic potassium dichromate. The yield of factory increased sharply.

Now answer the following questions :

(i) What is Collin's reagent?

(ii) What are the advantages of using Collin's reagent over conventional oxidising agent?

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

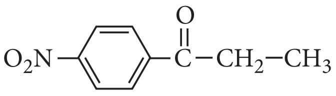


34. (i)How will you bring about the following conversions?

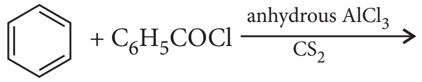
(a) Ethanal to but-2-enal

(b) Propanone to propene

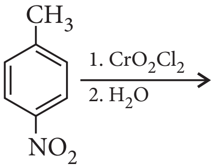
(ii) Write the IUPAC name of the compound :



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

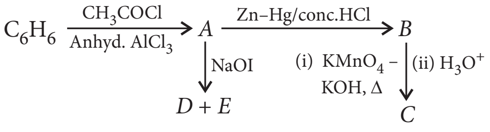
(i) 

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

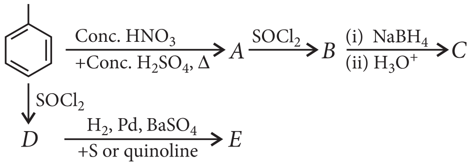
(iii) 

Long Answer Type Questions (LA)

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



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



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

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

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

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

39. (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

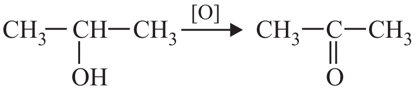
(ii) HNO_3/H_2SO_4 (at 273– 383 K)

40. 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*).

ANSWERS

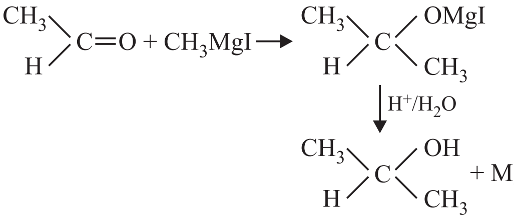
OBJECTIVE TYPE QUESTIONS

1. (c) : Ketones are formed by oxidation of secondary alcohols.



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

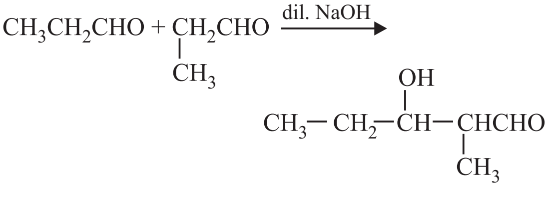
2. (b) : Formaldehyde forms primary alcohol while all other aldehydes form secondary alcohols on reaction with Grignard's reagent followed by hydrolysis.



$$\begin{matrix}CH_3\\H\end{matrix}\!\rangle C{=}O + CH_3MgI \rightarrow \begin{matrix}CH_3\\H\end{matrix}\!\rangle C \langle\!\begin{matrix}OMgI\\CH_3\end{matrix} \xrightarrow{H^+/H_2O} \begin{matrix}CH_3\\H\end{matrix}\!\rangle C \langle\!\begin{matrix}OH\\CH_3\end{matrix} + Mg\langle\!\begin{matrix}OH\\I\end{matrix}$$

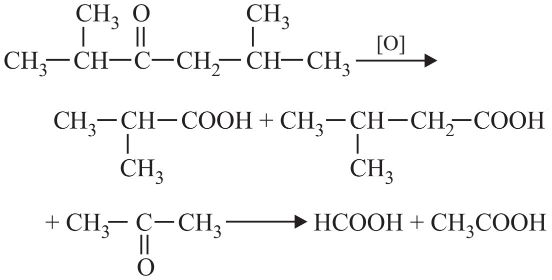
3. (c) : Aldehydes with no α-H atom undergo Cannizzaro reaction on heating with conc. alkali solution. Hence, only C_6H_5CHO will undergo Cannizzaro reaction.

4. (c) :



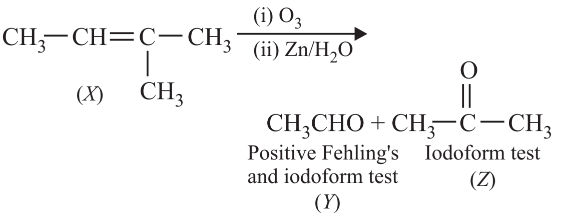
$$CH_3CH_2CHO + \underset{CH_3}{\underset{|}{C}}H_2CHO \xrightarrow{\text{dil. NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{C}}HCHO$$

5. (c) :



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3 \xrightarrow{[O]} CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH + CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-COOH + CH_3-\underset{O}{\underset{||}{C}}-CH_3 \longrightarrow HCOOH + CH_3COOH$$

6. (b) :

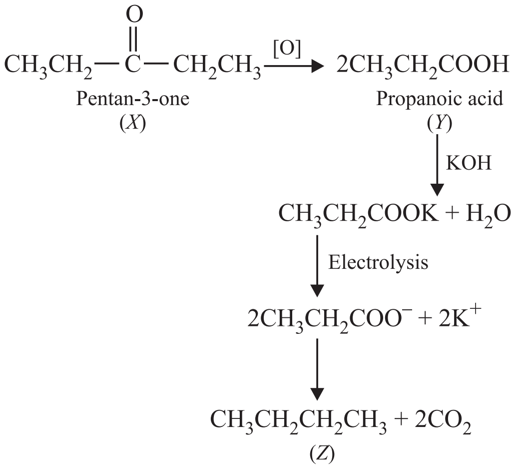


$$\underset{(X)}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CH_3} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} \underset{(Y)}{CH_3CHO} + \underset{(Z)}{CH_3-\overset{O}{\overset{||}{C}}-CH_3}$$

Positive Fehling's and iodoform test (*Y*)

Iodoform test (*Z*)

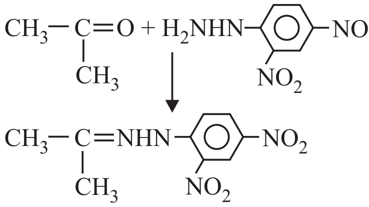
7. (a) : Since the compound gives positive 2, 4-DNP test and negative Tollen's test, it is a ketone.



$$\underset{\text{Pentan-3-one }(X)}{CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_3} \xrightarrow{[O]} \underset{\text{Propanoic acid }(Y)}{2CH_3CH_2COOH} \xrightarrow{KOH} CH_3CH_2COOK + H_2O \xrightarrow{\text{Electrolysis}} 2CH_3CH_2COO^- + 2K^+ \longrightarrow \underset{(Z)}{CH_3CH_2CH_2CH_3} + 2CO_2$$

8. (c) : Tollens' reagent is used to detect aldehyde group.

9. (c) :



$$CH_3-\underset{CH_3}{\underset{|}{C}}{=}O + H_2NHN-C_6H_3(NO_2)_2 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}{=}NHN-C_6H_3(NO_2)_2$$

10. (b) : $CH_3CH{=}CHCHO \xrightarrow{LiAlH_4} CH_3CH{=}CHCH_2OH$

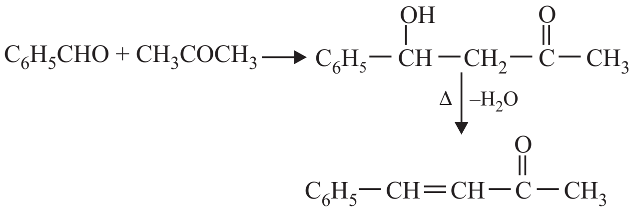
11. (a) : Acid chlorides are reduced to aldehydes on reaction with $BaSO_4$ and Pd.The reaction is called Rosenmund reduction.

$$RCOCl \xrightarrow[Pd/BaSO_4]{H_2} RCHO + HCl$$

12. (c) : Benzaldehyde will not give aldol condensation due to absence of α-H atom.

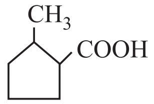
13. (a) : Formic acid acts as a reducing agent it reduces Fehling's and Tollen's reagent, etc.

14. (d) :



$$C_6H_5CHO + CH_3COCH_3 \longrightarrow C_6H_5-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{-H_2O} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

15. (a) : FCH_2CHO is most reactive towards nucleophilic addition since presence of most electronegative F withdraws electrons from carbon of carbonyl group making it more polar.

16. (a) :  is 2-methylcyclopentanecarboxylic acid.

17. (a) : Aldehydes are more reactive than ketones.

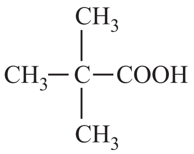
18. (c) : Due to $-I$ effect of Cl, chloroacetic acid is a stronger acid than acetic acid. Due to stabilization of phenoxide ion by resonance, phenol is a stronger acid than ethanol.

19. (b) : Pentan-2-one will give positive iodoform test while pentan-3-one will not give this test.

$$CH_3COCH_2CH_2CH_3 + I_2 + NaOH \longrightarrow \underset{\text{(Iodoform)}}{CHI_3}$$

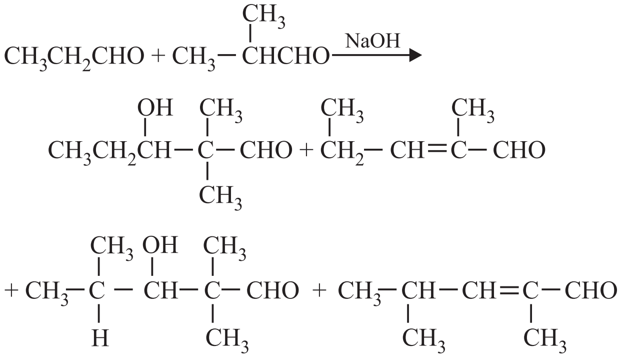
20. (b) : $RCOOH + 4H \xrightarrow{LiAlH_4} RCH_2OH + H_2O$

21. (d) : 2,2-Dimethylpropanoic acid will not undergo HVZ reaction due to absence of an α-H atom.



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

22. (b) :



$$CH_3CH_2CHO + CH_3-\overset{CH_3}{\overset{|}{C}H}CHO \xrightarrow{NaOH}$$

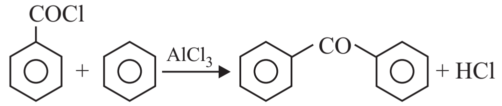
$$CH_3CH_2\overset{OH}{\overset{|}{CH}}-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-CHO + \overset{CH_3}{\overset{|}{CH_2}}-CH=\overset{CH_3}{\overset{|}{C}}-CHO$$

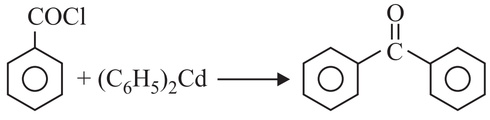
$$+ CH_3-\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}-\overset{OH}{\overset{|}{CH}}-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-CHO + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=\underset{\underset{CH_3}{|}}{C}-CHO$$

23. (a) : $2CH\equiv CH + 3H_2O \xrightarrow[\text{Mg or Zinc vanadate}]{420°C} CH_3COCH_3 + CO_2 + 2H_2$

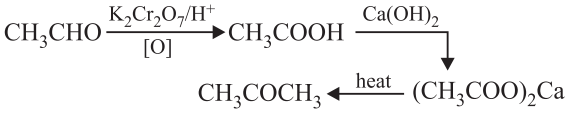
24. (a)

25. (a) : Ketones are less reactive than aldehydes.

26. (c) : (i) 

(iii) 

27. (b) :



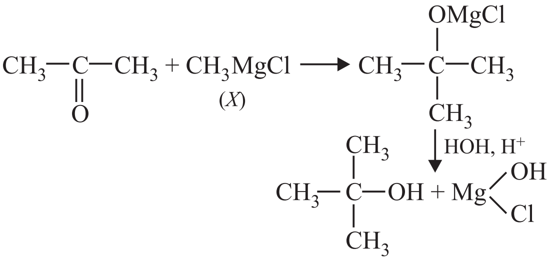
$$CH_3CHO \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{heat} CH_3COCH_3$$

28. (b) : $>C=O \xrightarrow[HCl]{Zn/Hg} >CH_2 + H_2O$ is called Clemmensen reduction.

29. (a) : $>C=O \longleftrightarrow >C^+-O^-$

Nucleophile attacks at the positive C centre of carbonyl group hence the addition is nucleophilic addition.

30. (a) :



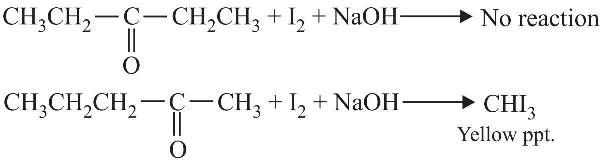
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + \underset{(X)}{CH_3MgCl} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{OMgCl}{\overset{|}{C}}}-CH_3 \xrightarrow{HOH,\ H^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-OH + Mg\begin{matrix}OH\\Cl\end{matrix}$$

31. (c) : The electron withdrawing strength of halogen groups is in the order of F > Cl > Br. Hence, the strength of acids is

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH$.

32. (b) : Aldehydes give silver mirror test with Tollen's reagent while ketones form oximes with hydroxylamine. Hence the compound is a ketone. Alcohol and ethers do not give this test.

33. (a) : Pentan-2-one and pentan-3-one can be differentiated by iodoform test.



$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3 + I_2 + NaOH \longrightarrow \text{No reaction}$$

$$CH_3CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + I_2 + NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3}$$

34. (d) : HCHO will be most polar due to lowest electron density on carbon of carbonyl group.

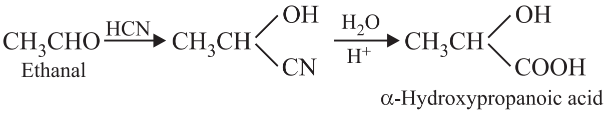
35. (a) : Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Aromatic aldehydes and ketones are less reactive than corresponding aliphatic aldehydes and ketones.

36. (d) : Both butanal and propanal does not give iodoform test, hence cannot be distinguished from each other.

37. (a) : Aldehydes and ketones form insoluble crystalline compounds with $NaHSO_3$ which can be filtered. These on distillation with saturated solution of Na_2CO_3 again give the aldehydes and ketones.

38. (d) : All the given aldehydes will give Cannizzaro reaction.

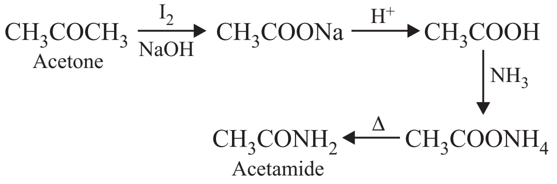
39. (a) :



$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{HCN} CH_3CH\begin{array}{l}\diagup OH\\ \diagdown CN\end{array} \xrightarrow[H^+]{H_2O} CH_3CH\begin{array}{l}\diagup OH\\ \diagdown COOH\end{array}$$

α-Hydroxypropanoic acid

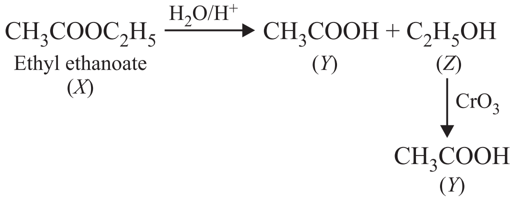
40. (b) :



$$\begin{tikzcd} \underset{\text{Acetone}}{CH_3COCH_3} \arrow[r, "I_2", "NaOH"'] & CH_3COONa \arrow[r, "H^+"] & CH_3COOH \arrow[d, "NH_3"] \\ & \underset{\text{Acetamide}}{CH_3CONH_2} & CH_3COONH_4 \arrow[l, "\Delta"'] \end{tikzcd}$$

41. (a) : Butan-1-ol has higher boiling point due to intermolecular hydrogen bonding.

42. (b) :

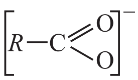


$$\begin{tikzcd} \underset{\substack{\text{Ethyl ethanoate}\\(X)}}{CH_3COOC_2H_5} \arrow[r, "H_2O/H^+"] & \underset{(Y)}{CH_3COOH} + \underset{(Z)}{C_2H_5OH} \arrow[d, "CrO_3"] \\ & \underset{(Y)}{CH_3COOH} \end{tikzcd}$$

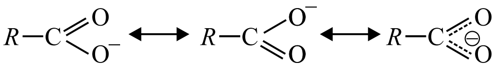
43. (a) : In alcohols –OH group is attached to an electron releasing group while in carboxylic acids –OH group is attached to an electron withdrawing group making it more acidic.

44. (b) : $ICH_2COOH < BrCH_2COOH < ClCH_2COOH < FCH_2COOH$

45. (b) : $R{-}COOH \xrightarrow{-H^+} R{-}COO^-$

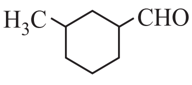


is a resonance hybrid of structures



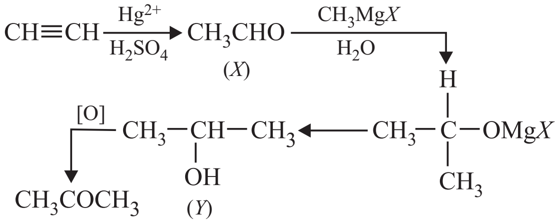
46. (d)

47. (b) :



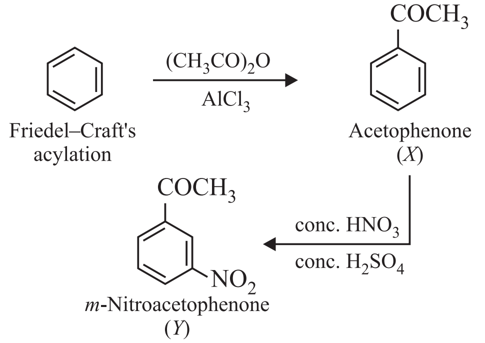
3-Methylcyclohexanecarbaldehyde.

48. (c) :



$$CH{\equiv}CH \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{(X)}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX} CH_3{-}\overset{H}{\underset{CH_3}{C}}{-}OMgX \longrightarrow CH_3{-}\underset{\substack{OH\\(Y)}}{CH}{-}CH_3 \xrightarrow{[O]} CH_3COCH_3$$

49. (a) :

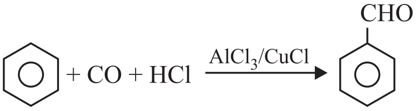


Friedel–Craft's acylation

Acetophenone (*X*)

m-Nitroacetophenone (*Y*)

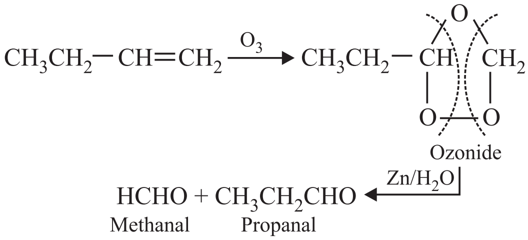
50. (b) : Benzaldehyde can be prepared from benzene by passing vapours of CO and hydrochloric acid in its solution in presence of catalyst mixture of $AlCl_3/CuCl$. The reaction is known as Gattermann–Koch reaction.



51. (b) : Tollen's reagent oxidises only –CHO to –COOH group.

$$CH_3CH{=}CHCHO \xrightarrow{Ag(NH_3)_2^+} CH_3CH{=}CHCOOH$$

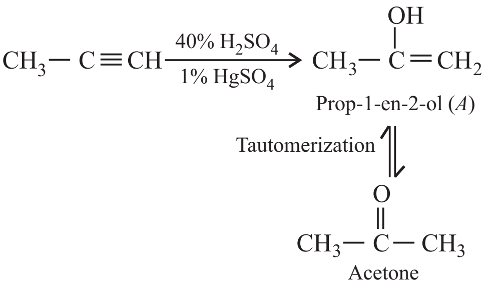
52. (c) :



Ozonide

$$\underset{\text{Methanal}}{HCHO} + \underset{\text{Propanal}}{CH_3CH_2CHO}$$

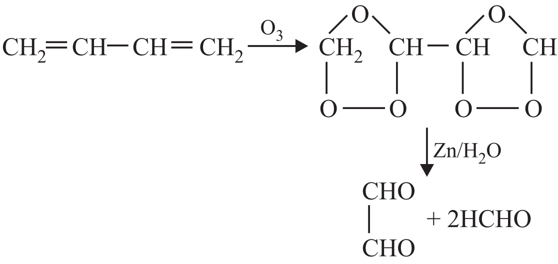
53. (d) :



$$CH_3{-}C{\equiv}CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Prop-1-en-2-ol }(A)}{CH_3{-}\overset{OH}{C}{=}CH_2} \overset{\text{Tautomerization}}{\rightleftharpoons} \underset{\text{Acetone}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

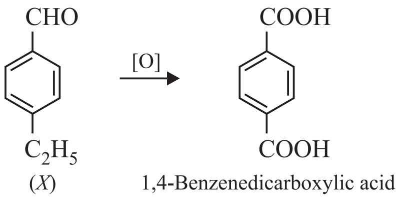
Prop-1-en-2-ol (*A*) and acetone show tautomerism.

54. (a) :



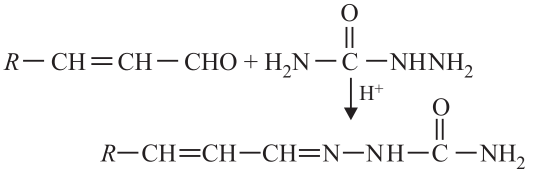
55. (b) : $CH_3CH_2C\equiv CH \xrightarrow{H^+/H_2O,\ Hg^{2+}} CH_3CH_2COCH_3$

56. (c) :



1,4-Benzenedicarboxylic acid

57. (b) :



$$R-CH=CH-CHO + H_2N-\overset{\overset{\Large O}{\|}}{C}-NHNH_2 \xrightarrow{H^+} R-CH=CH-CH=N-NH-\overset{\overset{\Large O}{\|}}{C}-NH_2$$

58. (c) : $CH_3COOC_2H_5$ will not give acetic acid on oxidation.

59. (b) : Aromatic ketones are less reactive than aliphatic ketones which in turn are less reactive than aldehyde. Hence, acetophenone does not react with $NaHSO_3$.

60. (a) :

$$\underset{(A)}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

$$\underset{(C)}{CH_3COOC_2H_5} + HOH \xrightarrow{H^+} \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

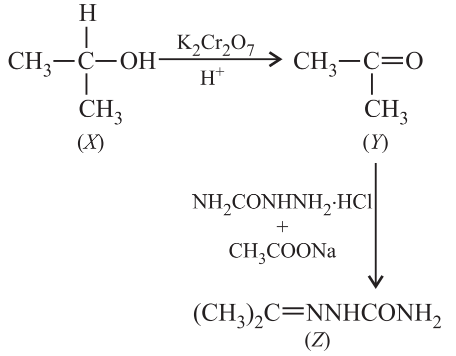
$$\underset{(D)}{C_2H_5OH} \xrightarrow{[O]} \underset{(B)}{CH_3COOH}$$

$$\underset{(B)}{2CH_3COOH} + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + H_2O$$

$$\big\downarrow \text{dry distillation}$$

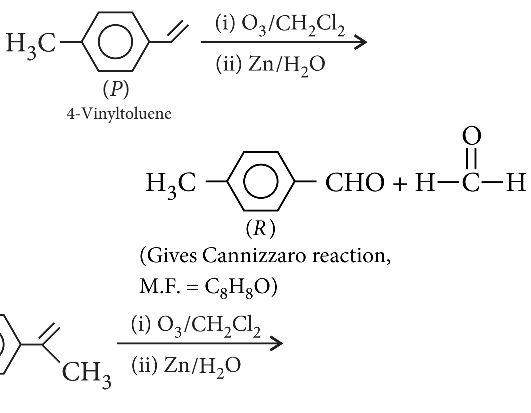
$$\underset{\text{(Acetone)}}{CH_3COCH_3}$$

61. (b) :

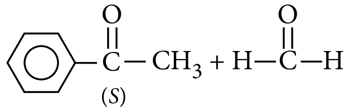


$$\underset{(X)}{CH_3-\overset{\overset{\Large H}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-OH} \xrightarrow[H^+]{K_2Cr_2O_7} \underset{(Y)}{CH_3-\underset{\underset{\Large CH_3}{|}}{C}=O} \xrightarrow{NH_2CONHNH_2\cdot HCl\ +\ CH_3COONa} \underset{(Z)}{(CH_3)_2C=NNHCONH_2}$$

62. (d) :

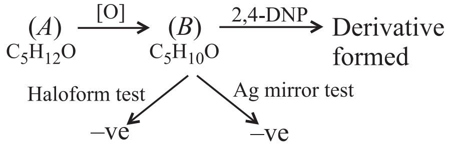


(Gives Cannizzaro reaction, M.F. = C_8H_8O)



(Gives haloform reaction, M.F. = C_8H_8O)

63. (b) :



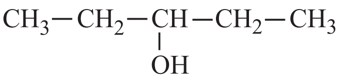
Since (*B*) on reaction with 2,4-DNP forms a derivative, it implies that (*B*) has $>C=O$ group.

(*B*) gives –ve Tollens' test, hence it is not an aldehyde, but it is a ketone.

(*B*) gives –ve haloform test, thus it is not a methyl ketone.

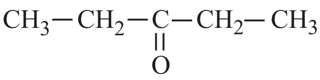
(*B*) is formed from the oxidation of (*A*), thus (*A*) is a 2°alcohol, and among the given options,

(*A*) is



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

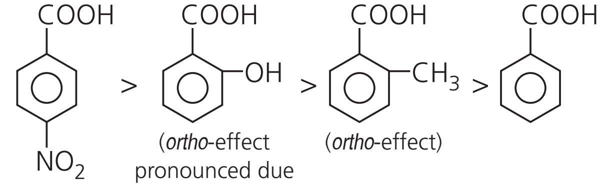
and (*B*) is



$$CH_3-CH_2-\underset{\underset{\Large O}{\|}}{C}-CH_2-CH_3$$

$$\underset{\text{aldehyde/ ketones}}{>C=O} \xrightarrow[HCl]{Zn\text{-}Hg/} \underset{\text{alkanes}}{-CH_2-}$$

64. (c) : *Ortho*-effect says that all the *o*-substituted benzoic acids are stronger acids than benzoic acid, so the correct order is



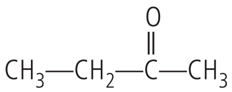
(^-R effect of —NO_2 group)   (*ortho*-effect pronounced due to H-bonding in carboxylate ion)   (*ortho*-effect)

Thus, Order III given is incorrect as in this *ortho*-effect is not considered.

Order I and II are correct.

65. (c) : Carboxylic acids do not undergo Friedel Craft's reaction because carboxyl group is deactivating and gets bonded to the catalyst in Friedel Craft's reaction.

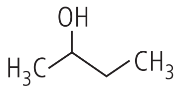
66. (a) : A undergoes Iodoform reaction hence contains a methyl ketone. So the structure of *A* is



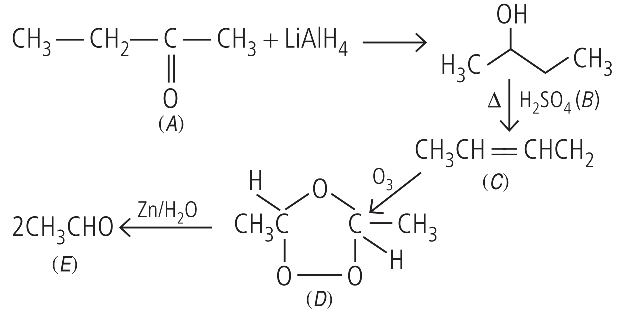
$$CH_3-CH_2-\overset{\overset{\Large O}{\|}}{C}-CH_3$$

(Butan-2-one)

A (butan-2-one) on reduction gives butan-2-ol (*B*).



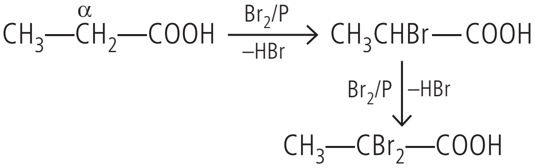
B on heating with H_2SO_4 gives an alkene named but-2-ene (*C*). $CH_3CH = CHCH_3$
C forms an ozonide *D* which on hydrolysis in presence of Zn dust to form acetaldehyde (*E*) CH_3CHO (2 moles)
The reaction sequence is as follows :



67. (a)

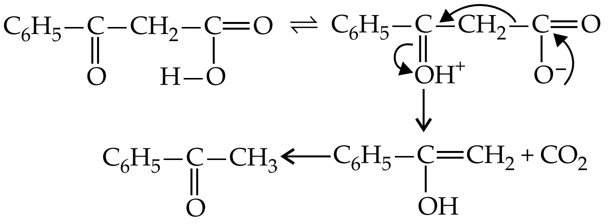
68. (c) : Phosphorus converts a little of the acid into acid chloride which is more reactive than the parent carboxylic acid. Thus, it is the acid chloride, not the acid itself, that undergoes chlorination at the α-carbon.

69. (d) : Bromination occurs at α-positions.

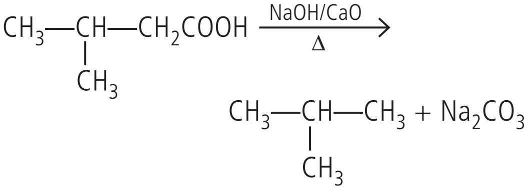


$$CH_3-\overset{\alpha}{C}H_2-COOH \xrightarrow[-HBr]{Br_2/P} CH_3CHBr-COOH \xrightarrow[-HBr]{Br_2/P} CH_3-CBr_2-COOH$$

70. (a) : β-ketoacids are unstable acids. They readily undergo decarboxylation through a cyclic transition state.



71. (b) :



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2COOH \xrightarrow[\Delta]{NaOH/CaO} CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_3 + Na_2CO_3$$

72. (a) : Iodoform test is given by the organic compounds having $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\overset{OH}{\overset{|}{C}H}-$ group.

$CH_3-\underset{CH_3}{\underset{|}{C}H}-OH$: Isopropyl alcohol

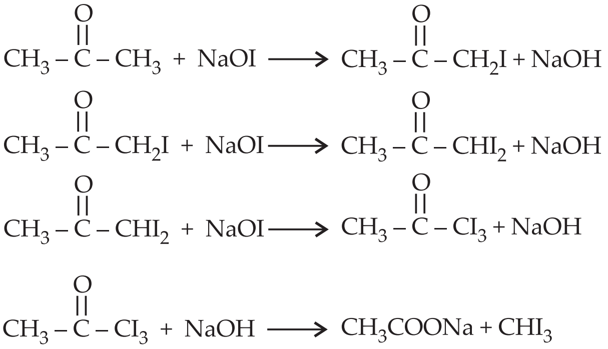
CH_3CH_2CHO : Propionaldehyde

$C_2H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$: Ethylphenyl ketone

$C_6H_5-CH_2-OH$: Benzyl alcohol

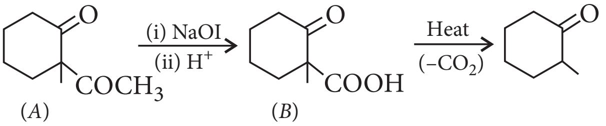
Therefore, isopropyl alcohol will give positive iodoform test.

73. (b) : Iodoform reaction of acetone occurs in following steps :

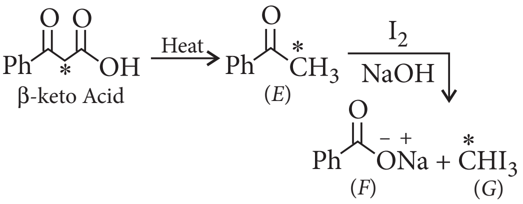


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaOI \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2I + NaOH$$
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2I + NaOI \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CHI_2 + NaOH$$
$$CH_3-\overset{O}{\overset{\|}{C}}-CHI_2 + NaOI \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CI_3 + NaOH$$
$$CH_3-\overset{O}{\overset{\|}{C}}-CI_3 + NaOH \longrightarrow CH_3COONa + CHI_3$$

74. (c) : Given reagents indicate the presence of $-COCH_3$ group in the starting compound *A*. Further, since the $-COOH$ group introduced in *B* due to iodoform reaction is absent in the final product, *B* should be a β-keto acid. Hence, *A* should have structure given in option (c).



75. (d) :



76. (c) : Since compound $A(C_3H_6O)$ undergoes iodoform test, it must be CH_3COCH_3 (propanone). Further, the compound '*B*' obtained from '*A*' has three times more the number of carbon atoms as in '*A*' (propanone), '*B*' must be phorone, *i.e.*, 2, 6-dimethyl-2, 5-heptadien-4-one.

$$\underset{A,\ \text{propanone (3 molecules)}}{(CH_3)_2C{=}O + H_3CCOCH_3 + O{=}C(CH_3)_2}$$
$$\xrightarrow{HCl} \underset{\text{2,6-dimethyl-2,5-heptadien-4-one}}{(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2}$$

77. (c) : Condensation reaction is the reverse of hydrolysis, which splits a chemical entity into two parts through the action of the polar water molecule.

78. **(b) :**

$$\mathrm{CH_3CHO + CH_3COCH_3} \longrightarrow \mathrm{CH_3CH(OH)CH_2COCH_3} \xrightarrow[\Delta]{-\mathrm{H_2O}} \mathrm{CH_3CH{=}CHCOCH_3}$$

79. **(a)**

80. **(d)**

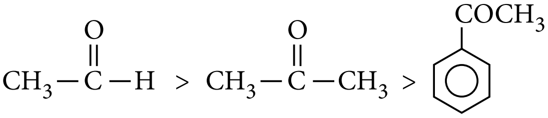
81. **(d) :** Benzaldehyde(C_6H_5CHO) with no α-hydrogen cannot undergo aldol condensation.

82. **(a)**

83. **(b) :** HSO_3^- is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

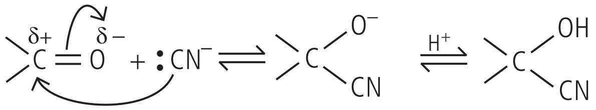
84. **(d) :** Aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues towards nucleophilic addition reactions due to the +*R* effect of benzene ring. Further, aldehydes are more reactive than ketones due to +*I* effect and steric effect of alkyl group.

Therefore, the ease of nucleophilic addition will follow the order :



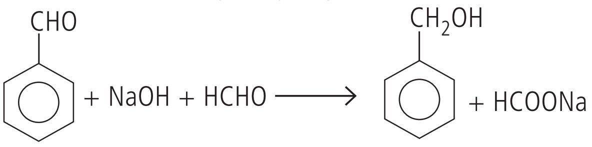
85. **(a) :** Formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN because it is feebly ionised. This reaction is catalysed by a base. Base generates CN^- ion which is a stronger nuclephile and readily adds to carbonyl compound.

$$OH^- + HCN \rightleftharpoons :\bar{C}N + H_2O$$



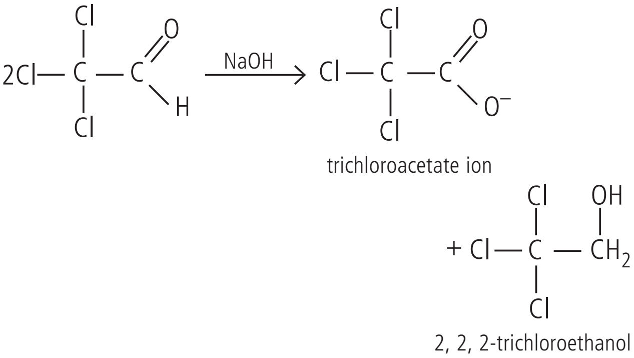
86. **(b) :** Electron withdrawing group ($-NO_2$) increases the reactivity towards nucleophilic addition reactions, whereas electron donating group ($-CH_3$) decreases the reactivity towards nucleophilic addition reactions.

87. **(a) :** It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any α-hydrogen).

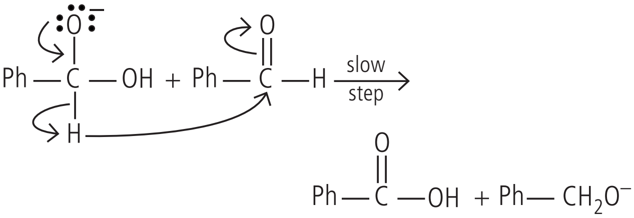


88. **(c)**

89. **(a) :** The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



90. **(b) :** Hydride transfer is the slowest step.



91. **(a) :** C—C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C—C bond.

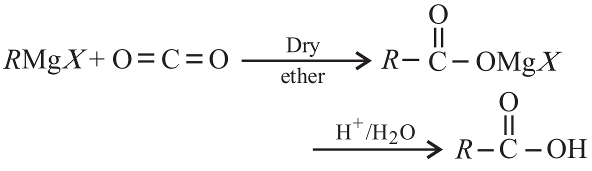
92. **(c) :** Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

93. **(c) :** The anion left after the removal of α-hydrogen is stabilized by resonance effect.

94. **(c) :** Highly branched carboxylic acids are less acidic than unbranched acids. The +*I* effect of alkyl groups in branched acid increases the magnitude of negative charge. Thus, –COOH group is shielded from solvent molecules and cannot be stabilized by solvation as effectively as in unbranched carboxylic acids.

95. **(c) :** In *p*-chlorobenzoic acid, both +*R* and –*I* effect operate together but in *m*-chlorobenzoic acid only –*I* effect operates. Therefore, *m*-chlorobenzoic acid is a stronger acid than *p*-chlorobenzoic acid.

96. **(c) :** Addition of Grignard reagents to dry ice followed by hydrolysis gives carboxylic acid not ketone.



$$RMgX + O=C=O \xrightarrow[\text{ether}]{\text{Dry}} R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+/H_2O} R-\overset{\overset{O}{\|}}{C}-OH$$

97. **(a)**

98. **(c) :** Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*- and *p*-positions.

99. **(b) :** Aldehydes have higher molecular weight than parent alkanes as well as polarity in aldehydes shows higher boiling point than parent alkanes. Aldehydes do not have any hydrogen atom attached directly to the oxygen so they cannot form hydrogen bond with each other.

100.(c) : Chlorine atom has –*I* effect which increases the ionisation of chloroacetic acid and stabilizes the chloroacetate ion by dispersal of negative charge. In acetic acid, methyl group due to +*I* effect destabilizes the acetate ion by intensification of negative charge. Hence, chloroacetic acid dissociates to a greater extent than acetic acid.

101.(d) : Aldehydes having a methyl or methylene group in the α-position or more correctly having atleast one hydrogen atom in the α-position undergo dimerisation in presence of a base at low temperature to form β-hydroxy aldehydes called aldols. As benzaldehyde does not have any α-hydrogen hence it does not undergoes aldol condensation.

102.(b) : Due to overall electron-donating effect of the phenyl group, benzoate ion is less stable than formate ion.

103.(b) : Carbonyl compounds form solid additive products with $NaHSO_3$ which are separated out. The solid bisulphites of carbonyl compounds on hydrolysis with dilute acid regenerate original carbonyl compounds and thus, this property is used for the purification of carbonyl compounds as well as for their separation.

104.(b) : Boiling points of carboxylic acids are higher due to their tendency to associate and form dimers to a greater extent by hydrogen bonding.

105.(a) : *o*-Substituted benzoic acids are generally stronger acids than benzoic acid. This is regardless of the nature (+*I* or –*I*) of the substituent. This is called *ortho*-effect and is probably due to a combination of steric and electronic factors.

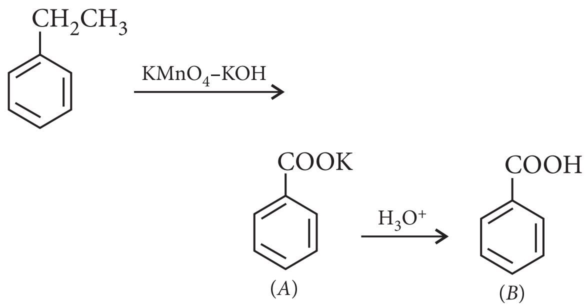
SUBJECTIVE TYPE QUESTIONS

1. Increasing order of boiling point :

$CH_3—CHO < C_2H_5OH < CH_3—COOH$

2. $C_6H_5COCl \xrightarrow[\text{Pd-BaSO}_4]{H_2} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

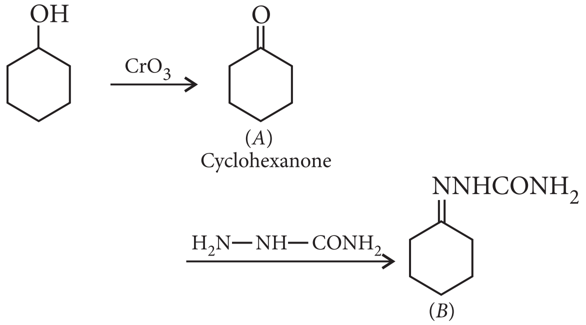
3.



(*A*) Potassium benzoate

(*B*) Benzoic acid

4.

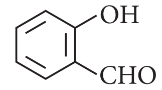


(*A*) Cyclohexanone

(*B*) Cyclohexanone-semicarbazone

5. Chloroacetic acid has lower p*K*$_a$ 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.

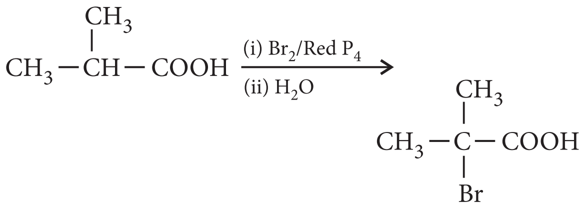
6.



2-Hydroxybenzaldehyde

7. 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.

8.

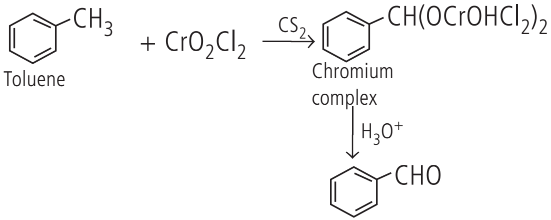


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\text{Red } P_4} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-COOH$$

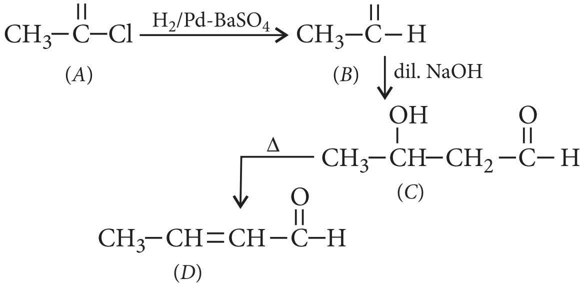
2-Bromo-2-methyl propanoic acid

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

10. Etard reaction :

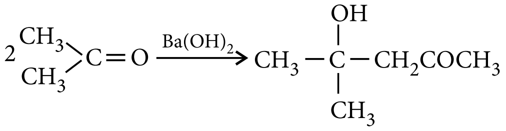


11.



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

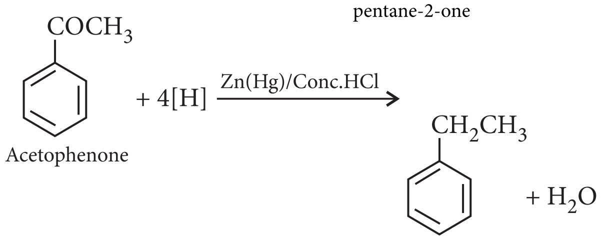
12. (i)



$$2\,\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow{Ba(OH)_2} CH_3-\underset{\large CH_3}{\overset{\large OH}{C}}-CH_2COCH_3$$

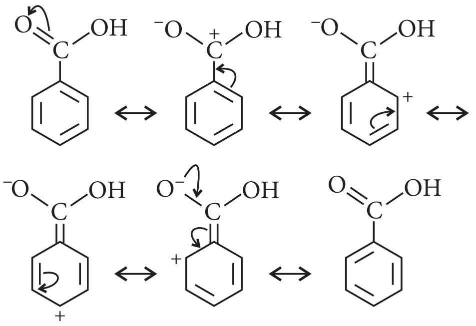
4-Hydroxy-4-methyl-pentane-2-one

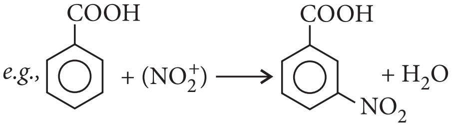
(ii)



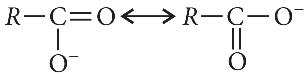
Ethylbenzene

13. (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.



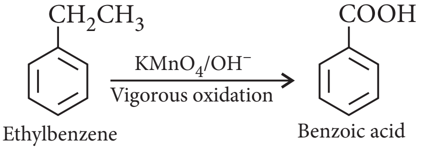


(ii) The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :

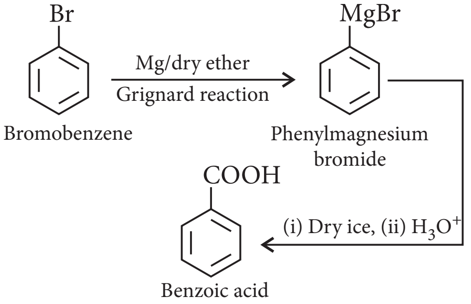


$$R-\underset{\large O^-}{C}=O \longleftrightarrow R-\underset{\large O}{\overset{}{C}}-O^-$$

14. (i)

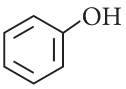


(ii)



15. (i) F—CH$_2$COOH > Cl—CH$_2$COOH

(ii) CH$_3$COOH is stronger than



16. With pure HCN reaction occurs very slowly because it is a weak nucleophile. With base it produces CN$^-$ ion which is a strong nucleophile and readily adds to the carbonyl compound.

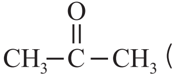
$$HCN + \bar{O}H \longrightarrow H_2O + CN^-$$

17. Since the compound forms crystalline white precipitate with sodium bisulphite, it contains a carbonyl group. The compound reduces Fehling's solution so, the carbonyl group is an aldehyde.

Structure : CH_3-CH_2-CHO

IUPAC name : Propanal

Isomer :



$CH_3-\overset{\large O}{\overset{\|}{C}}-CH_3$ (Propanone)

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

(b) Due to presence of strong electron withdrawing group (—NO$_2$), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, pKa value is lower.

19 (i) DIBAL–H reduces alkynes to alkenes but does not reduce ethylenic double bonds and hence this reagent can be used to reduce unsaturated nitriles to the corresponding unsaturated aldehydes.

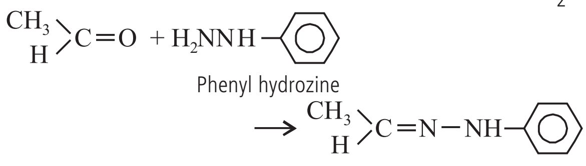
(ii) Phenol gets easily nitrated than benzoic acid. Because carboxyl group is ring deactivating group whereas hydroxyl group is ring activating group.

20. (i) It is a nucleophilic addition reaction, in which CN$^-$ acts as a nucleophile. CH$_3$CHO undergoes nucleophilic addition reactions faster than CH$_3$COCH$_3$ as in CH$_3$COCH$_3$ 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$_3$CHO, there is only one methyl group attached to carbonyl carbon.

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

21. (i) $CH_3CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_3COO^- + \underset{\text{(Red ppt.)}}{Cu_2O} + 3H_2O$

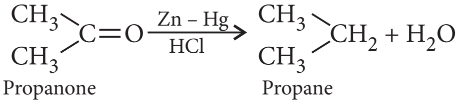
(ii)



(iii)

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O + \underset{\text{Hydroxylamine}}{NH_2OH} \longrightarrow \underset{\text{Ethanal oxime}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C=N-OH}$$

22. (a)(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.

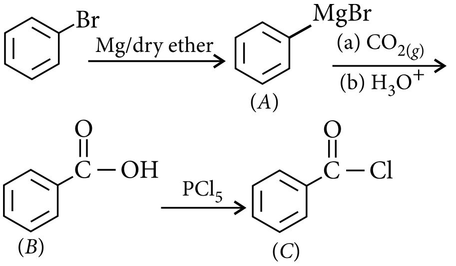


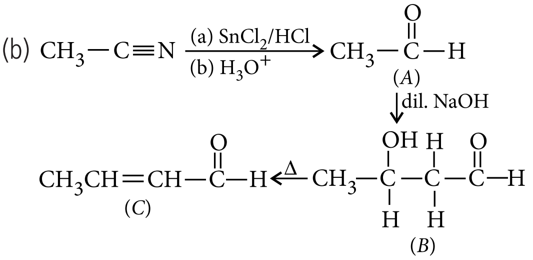
$$\underset{\text{Propanone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O} \xrightarrow[HCl]{Zn-Hg} \underset{\text{Propane}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH_2} + H_2O$$

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

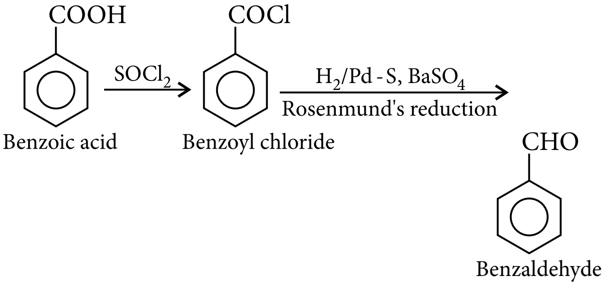
$$\underset{\text{Methanal}}{HCHO + HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methanol}}{CH_3OH}$$

23. (i) (a)





(ii)



24. Chemicals can be distinguished by sodium bicarbonate test and iodoform test.

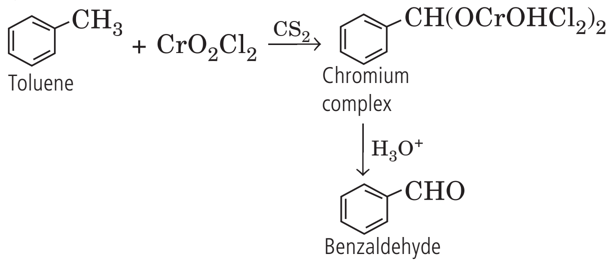
Benzoic acid will give brisk effervescence due to evolution of carbon dioxide gas with sodium bicarbonate solution while acetaldehyde does not.

Acetaldehyde will give yellow precipitate of iodoform with iodine and sodium hydroxide solution while benzoic acid does not.

25. (i) (a) Stephen reduction :

$$R—CN + SnCl_2 + HCl \longrightarrow R—CH{=}NH \xrightarrow{H_3O^+} R—CHO$$

(b) Etard reaction :



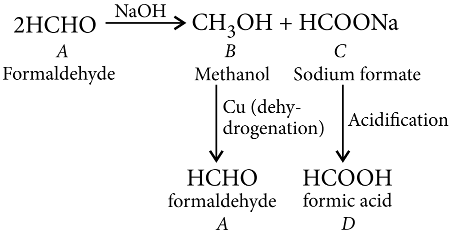
(ii) Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

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

Acetic acid does not give this test.

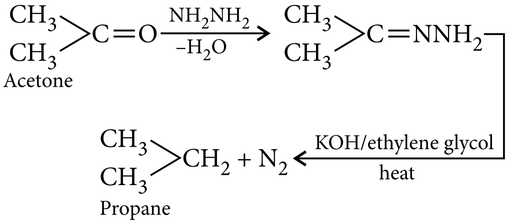
26. Since the molecular formula of *D* is CH_2O_2, thus, *D* is HCOOH (formic acid). *D* is obtained by the acidification of *C*, so, *C* is sodium formate (HCOONa).

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)

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



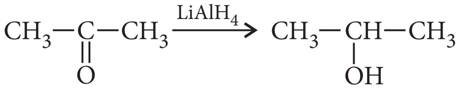
(b) Increasing order of reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$

(c) Formula of compounds *A* and *B* is C_3H_6O. *B* forms yellow precipitate of iodoform. Hence, *B* must contain —$COCH_3$ group. Therefore, compound '*B*' must be $CH_3-\overset{O}{\overset{||}{C}}-CH_3$.

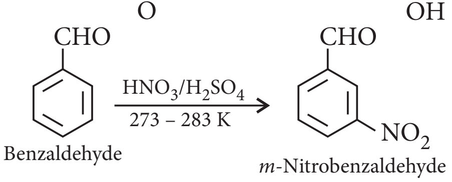
A does not give iodoform test and it is functional isomer of *B* thus, it may be CH_3CH_2CHO.

28. (a) (i)



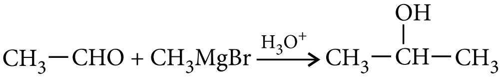
$$CH_3-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

(ii)



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

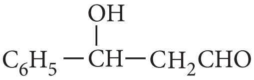
29. (i)



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

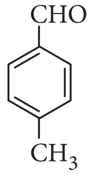
(ii) $CH_3CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} CH_3-CH_3$

(iii) $CH_3-CHO + C_6H_5CHO \xrightarrow{\text{dil. NaOH}}$



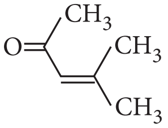
$$C_6H_5-\overset{\overset{OH}{|}}{CH}-CH_2CHO$$

30. (a) (i)

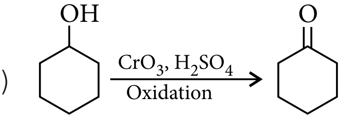


p-Methylbenzaldehyde

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



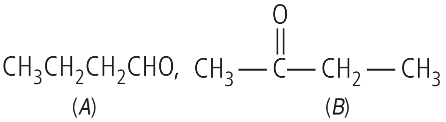
(b)



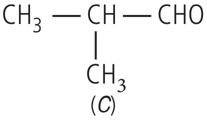
Cyclohexanol Cyclohexan-1-one

31. (a) As (*A*) and (*C*) give positive Tollens' test thus these two should be aldehyde while (*B*) should be a ketone (does not give Tollens' test) with $-\underset{\underset{O}{\|}}{C}-CH_3$ group (as it gives positve iodoform test).

Three isomers are

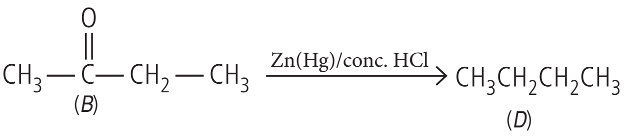


$$\underset{(A)}{CH_3CH_2CH_2CHO}, \quad \underset{(B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3}$$



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

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



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

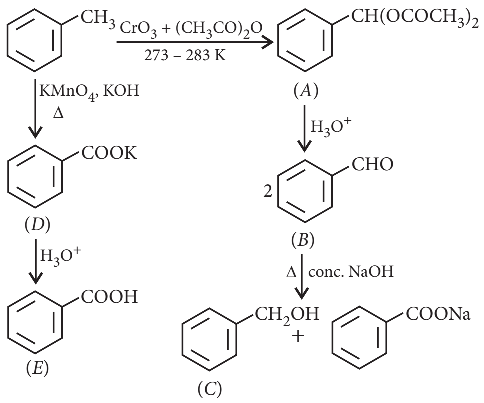
(b) out of (*A*), (*B*) and (*C*) isomers, (*B*) is least reactive towards addition of HCN.

32. (i) Collin's reagent is a mixture of pyridine (C_5H_5N) and CrO_3 in dichloromethane (CH_2Cl_2).

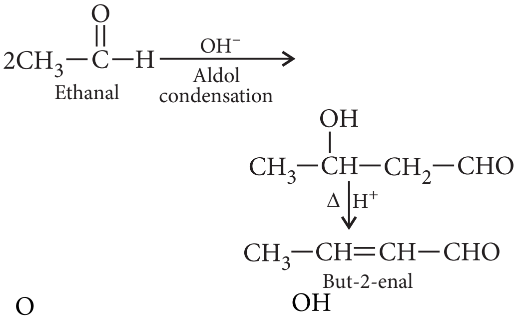
(ii) Collin's reagent is a mild oxidant. It oxidises 1°-alcohols to aldehydes and 2°-alcohols are oxidised to ketones.

In case of using acidic $K_2Cr_2O_7$ as oxidant, the aldehydes and ketones formed by the oxidation of alcohols undergo oxidation to give carboxylic acids.

33.

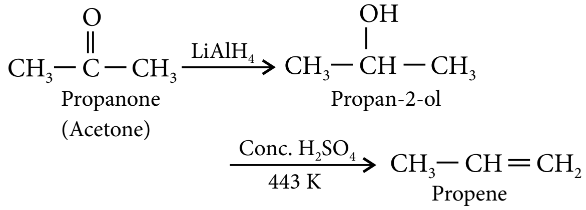


34. (a) (i)



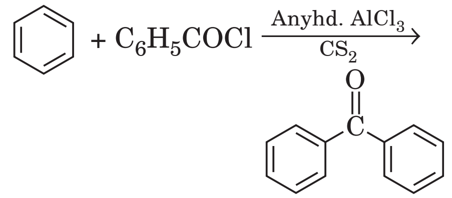
$$\underset{\text{Ethanal}}{2CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow[\text{Aldol condensation}]{OH^-} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[\Delta]{H^+} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

(ii)

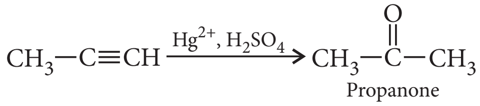


$$\underset{\substack{\text{Propanone}\\\text{(Acetone)}}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3} \xrightarrow[443\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

35. (i)

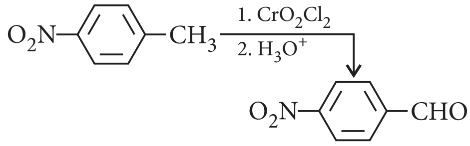


(ii)



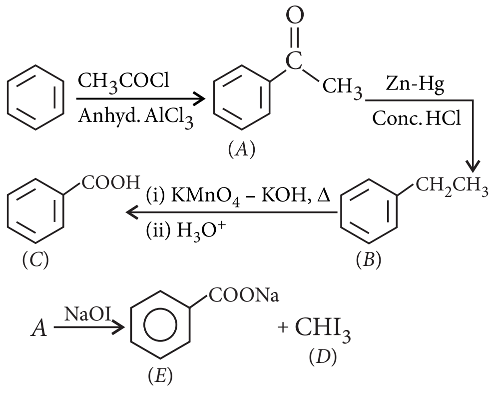
$$CH_3-C\equiv CH \xrightarrow{Hg^{2+},\, H_2SO_4} \underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

(iii)

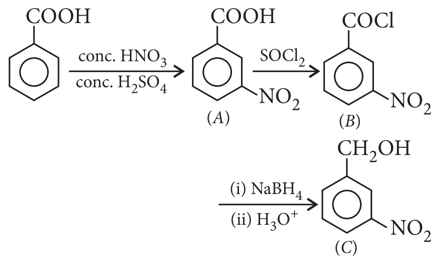


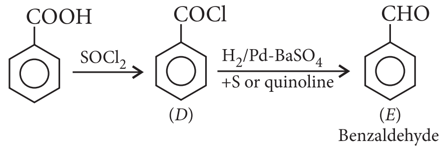
p-Nitrobenzaldehyde

36.

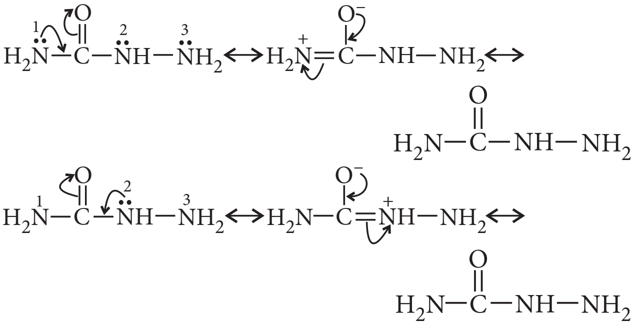


37.



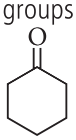


38. (a) (i) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.

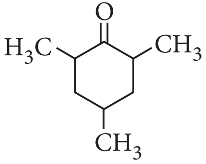


Lone pairs of N-1 and N-2 are involved in conjugation with >C=O group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

(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.

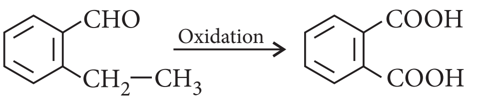


Cyclohexanone



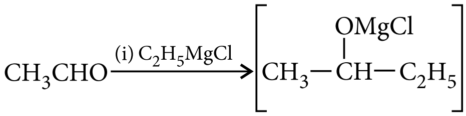
2,4,6-Trimethylcyclohexanone

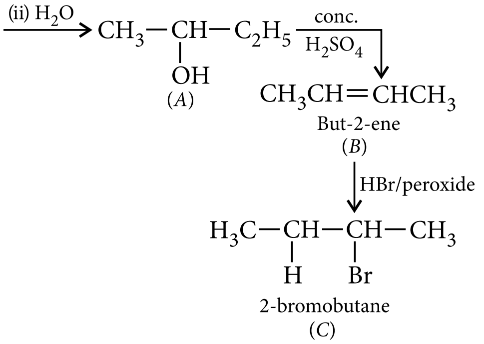
(b) The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α-hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic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



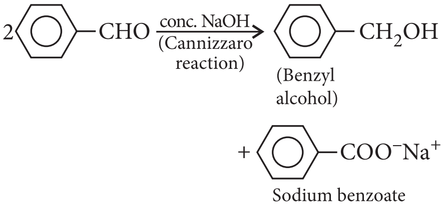
2-Ethylbenzaldehyde 1,2-Benzenedicarboxylic acid

39. (a)

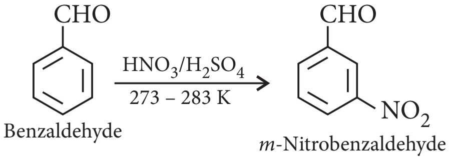




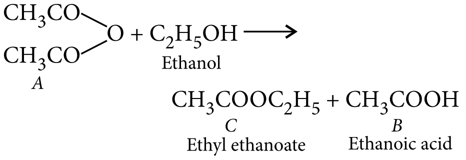
(b) (i)



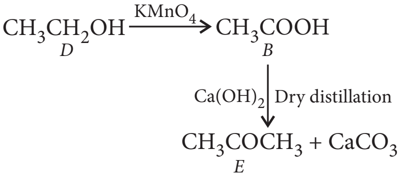
(ii)



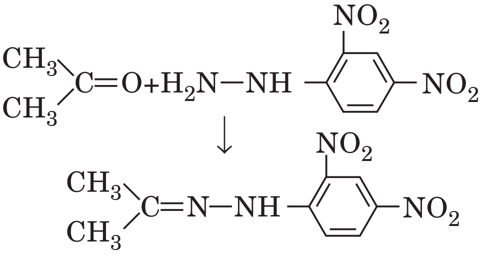
40.



$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} \underset{B}{CH_3COOH} + \underset{D}{CH_3CH_2OH}$$

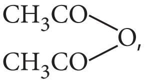


E does not give Tollens' test and does not reduce Fehling's solution as it is ketone.



2,4-dinitrophenyl hydrazone

A =



B = CH_3COOH, *C* = $CH_3COOC_2H_5$,

D = CH_3CH_2OH, *E* = CH_3COCH_3

☺☺☺