CHAPTER

12

Aldehydes, Ketones and Carboxylic Acids

A Quick Recapitulation of the Chapter

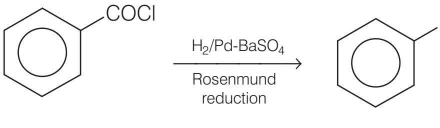
1. **Aldehydes** contain carbonyl group linked to either two H-atoms or one H-atom alongwith one C-atom of an alkyl or aryl group.
2. **Ketones** contain the carbonyl group which is linked to two C-atoms of an alkyl/aryl group.
3. The IUPAC names of open chain aliphatic aldehyde and ketones are derived from the names of the corresponding alkanes by replacing the ending **-'e'** with **-'al'** and **-'one',** respectively.
4. The C-atom of carbonyl group is sp^2-hybridised with bond angle 120° possessing trigonal planar structure.
5. Preparation of aldehyde

(i) $R\text{CH}_2\text{OH} + [\text{O}] \xrightarrow[\text{Oxidation}]{\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4} R\,\text{CHO} + \text{H}_2\text{O}$

(ii) $R\text{CH}_2\text{OH} \xrightarrow[\text{Dehydrogenation}]{\text{Cu/573 K}} R\,\text{CHO} + \text{H}_2 \uparrow$

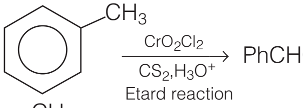
(iii) $R\text{CH}{=}\text{CH}R + \text{O}_3 \xrightarrow[\text{or 196 K Zn/H}_2\text{O ozonolysis}]{2\text{CHCl}_3/3 \text{ or CCl}_4} 2R\text{CHO} + \text{ZnO}$

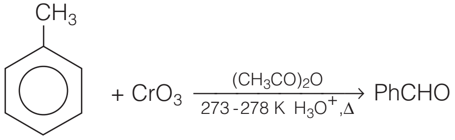
(iv) $\text{HC}{\equiv}\text{CH} + \text{H}_2\text{O} \xrightarrow[\text{Hydration}]{\text{H}_2\text{SO}_4 + \text{HgSO}_4} \text{CH}_3\text{CHO}$

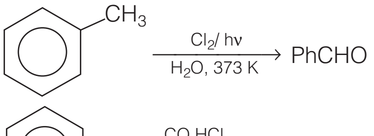
(v) 

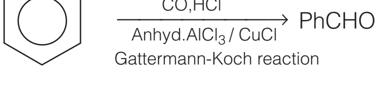
(vi) $R\text{CN} + \text{SnCl}_2 + \text{HCl} \xrightarrow[\text{Stephen reaction}]{\text{H}_3\text{O}^+} R\text{CHO}$

(vii) $\text{Ester} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) DIBAL-H}} \text{Aldehyde}$

(viii) 

(ix) 

(x) 

(xi) 

6. **Preparation of ketones**

(i) $R_2\text{CH OH} + [\text{O}] \xrightarrow[\text{Oxidation}]{\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4} R\text{CO}R + \text{H}_2\text{O}$

(ii) $R_2\text{CHOH} \xrightarrow[\text{Dehydrogenation}]{\text{Cu, 573 K}} R_2\text{CO} + \text{H}_2 \uparrow$

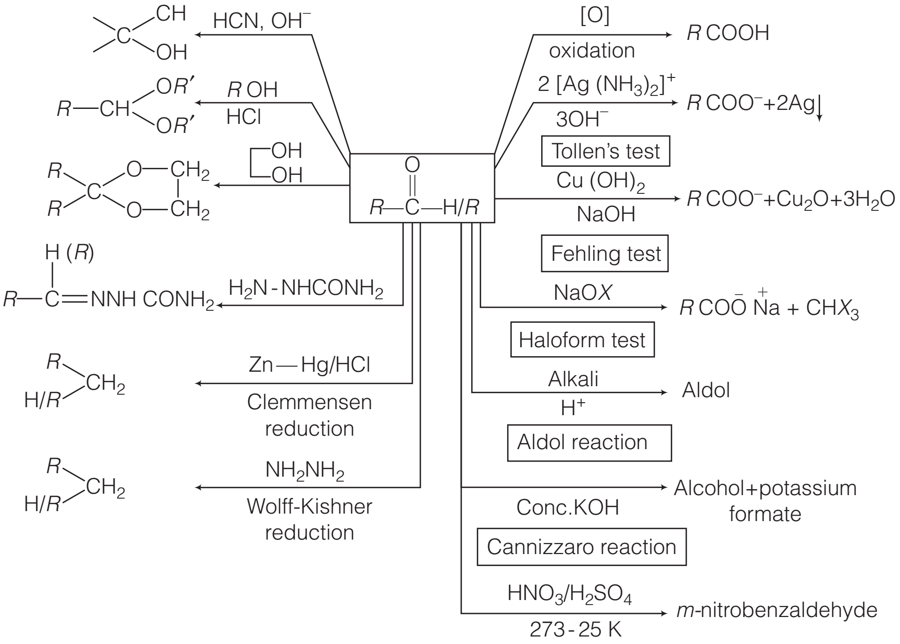
(iii) $R'\text{COCl} + R_2\text{Cd} \longrightarrow 2R'\text{CO}R + \text{CdCl}_2$

(iv) $\text{C}_2\text{H}_5\text{CN} + \text{PhMgBr} \xrightarrow[\text{H}_3\text{O}^+]{\text{Ether}} \text{C}_2\text{H}_5\text{COPh}$

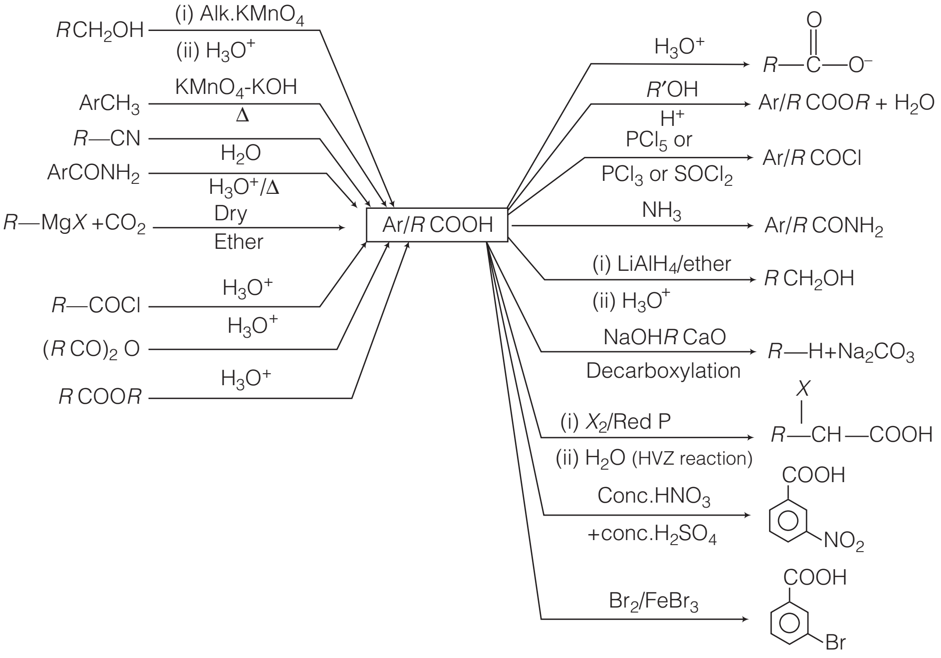
(v) 

Friedel-Craft's acylation reaction.

7. Physical properties of aldehydes and ketones.
   (i) Lower member of aldehydes and ketones upto C_{10} are colourless, volatile liquid, while formaldehyde is a gas at ordinary temperature. Higher members of both are solids with fruity odour.
   (ii) The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers but lower than alcohols of comparable masses.
   (iii) All carbonyl compounds are fairly soluble in organic solvents.
8. Chemical reactions of aldehydes and ketones



9. Methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid and benzoic acid are highly useful compounds in industry.



Objective Questions Based on NCERT Text

Topic 1

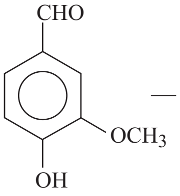
General Characteristics of Aldehydes and Ketones

1. Carbonyl compounds are the constituents of
- (a) fabrics
- (b) flavouring
- (c) plastics and drugs
- (d) All of the above

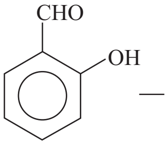
2. Among the following compounds, play an important role in biochemical processes of life.
- (a) Aldehydes
- (b) Ketones
- (c) Carboxylic acids
- (d) All of the above

3. What is/are the role of carbonyl compounds?
- (a) They are used in many food products and pharmaceutical to add flavours
- (b) Some of these families are manufactured for use as solvents and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics etc.
- (c) Both (a) and (b)
- (d) None of the above

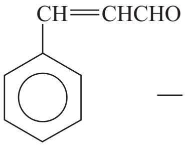
4. Which one of the following carbonyl compound is obtained from the bananas?

(a) 

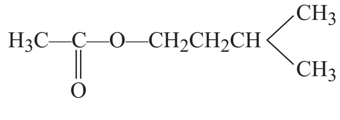
— Vanillin

(b) 

— Salicylaldehyde

(c) 

— Cinnamaldehyde

(d) 
$H_3C—\underset{\underset{O}{\|}}{C}—O—CH_2CH_2CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$ — Isoamyl acetate

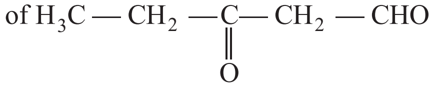
5. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending letters of acid with aldehyde. The ending letters in common names of the acid are usually.

(a) ec (b) ic (c) oc (d) al

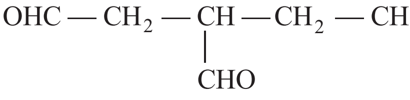
6. What is the common name of dimethyl ketone?
- (a) Ether
- (b) Acetone
- (c) Acetophenone
- (d) Benzophenone

7. When the aldehyde group is attached to a ring, which of the following suffix is added after the full name of the cycloalkane?
- (a) Aldehyde
- (b) Carbaldehyde
- (c) Carboxyaldehyde
- (d) Cycloaldehyde

8. The name of simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is/are
- (a) carbaldehyde
- (b) benzene carbaldehyde
- (c) benzaldehyde
- (d) Both (b) and (c)

9. IUPAC name of 
$H_3C—CH_2—\underset{\underset{O}{\|}}{C}—CH_2—CHO$

I

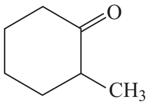
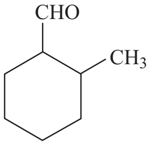
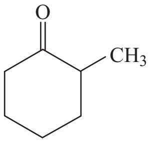
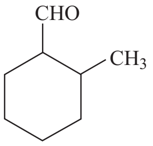
and 
$OHC—CH_2—\underset{\underset{CHO}{|}}{CH}—CH_2—CHO$ is

II

	I	II
(a)	3-onepentanal	β-aldehydepentan-1,2-dial
(b)	3-onepentanal	Pentan-1,2,3-tricarbaldehyde
(c)	3-oxopentanal	Propan-1,2,3-tricarbaldehyde
(d)	3-oxopentanal	Pentan-1,2,3-tricarbaldehyde

10. Identify the missing term I, II, III, IV in the table.

Structure	Common name	IUPAC name
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	I
$(CH_3)_2CHCOCH(CH_3)_2$	II	2,4-dimethylpentan-3-one
III	α-methylcyclohexanone	2-methylcyclohexanone
$(CH_3)_2C═CHCOCH_3$	IV	4-methylpent-3-en-2-one

	I	II	III	IV
(a)	Pentan-2-one	Isopropyl ketone		Mesityl oxide
(b)	Pentan-4-one	Diisopropyl ketone		Vinyl oxide
(c)	Pentan-2-one	Diisopropyl ketone		Mesityl oxide
(d)	Pentan-4-one	Isopropyl ketone		Vinyl oxide

11. The carbonyl C-atom is …I… hybridised and forms …II… 'σ'-bonds. Fourth valence electron of carbon remains in its *p*-orbital and forms a …III… bond with oxygen by overlap with *p*-orbital of an oxygen.

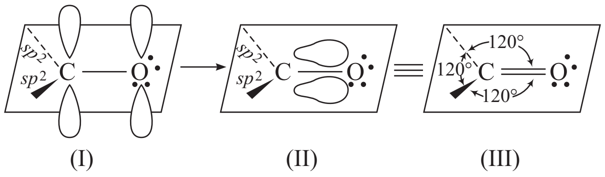
Identify I, II, III from the given options in order to complete the statement.

	I	II	III		I	II	III
(a)	sp^3	2σ	π	(b)	sp^3	3σ	σ
(c)	sp^2	2σ	σ	(d)	sp^2	3σ	π

12. The bond angle and structure of carbonyl compounds respectively are

(a) 120° and trigonal planar
(b) 109°28′ and tetrahedral
(c) 120° and tetrahedral
(d) 109°28′ and trigonal planar

13. The orbital diagram for the formation of carbonyl group is given as



Which type of bond is involved in I and II?

	I	II		I	II
(a)	σ	π	(b)	π	π
(c)	σ	π	(d)	π	σ

14. Select the correct dissimilarities between C═O and C═C bond.

(a) Carbon-oxygen double bond is polar but carbon-carbon double bond is non-polar
(b) Carbon oxygen bond length is 123 pm than that of carbon-carbon bond length is 134 pm
(c) Carbonyl compounds undergo nucleophilic addition reactions but compounds containing ethylenic double bonds undergo electrophilic addition reactions
(d) All of the above

Topic 2

Preparation of Aldehydes and Ketones

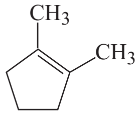
15. Aldehydes and ketones are prepared by the oxidation of

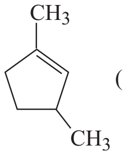
(a) primary and secondary alcohols
(b) secondary and primary alcohols
(c) primary and tertiary alcohols
(d) secondary and tertiary alcohols

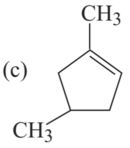
16. Alcohol vapours are passed over which of the following catalysts to give aldehydes and ketones?

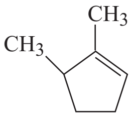
(a) Heavy non-metal
(b) Heavy metal
(c) Light non-metal
(d) Light metal

17. Which compound would give 5-keto-2-methyl upon ozonolysis? **(JEE Main 2015)**

(a) 

(b) 

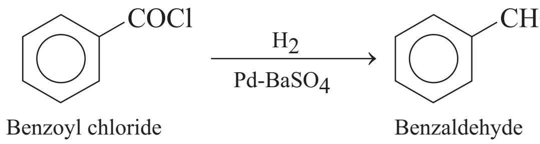
(c) 

(d) 

18. $\text{Ethyne} + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

Product formed in the given reaction is

(a) benzaldehyde
(b) acetaldehyde
(c) ethanoic acid
(d) ethanoyl chloride

19. 

The above reaction is known as
(a) Stephen reaction
(b) Rosenmund reduction
(c) Clemmensen's reaction
(d) Riemer-Tiemann reaction

20. Select the reagent and the intermediate formed in Stephen reaction.

	Reagent	**Intermediate**
(a)	DIBAL-H	Aldehyde
(b)	Stannous chloride	Imine
(c)	Stannous chloride	Aldehyde
(d)	DIBAL-H	Imine

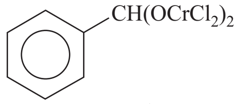
21. Which of the following substrates give the same product on the reduction with DIBAL-H?
(a) $CH_3-(CH_2)_9-CN$ and $CH_3(CH_2)_9-COOH$
(b) $CH_3-(CH_2)_9-CN$ and $CH_3(CH_2)_9-COOC_2H_5$
(c) $CH_3-(CH_2)_9-COOH$ and $CH_3(CH_2)_9-CHO$
(d) $CH_3(CH_2)_9-COOH$ and $CH_3(CH_2)_9COOC_2H_5$

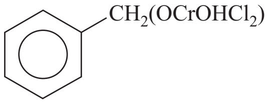
22. In the reaction,

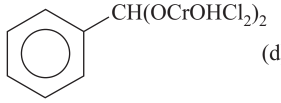
$$H_3C-CH{=}CH-CH_2-CH_2-CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i{-}Bu)_2}$$

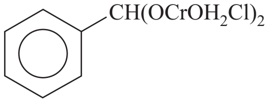
Identify the product formed in the given reaction.
(a) $H_3C-CH_2CH_2CH_2CH_2CN$
(b) $H_3C-CH=CH-CH_2CH_2CHO$
(c) $H_3CCH_2CH_2CH_2CH_2CHO$
(d) None of the above

23. Select the structure of chromium complex formed when the toluene reacts with chromylchloride to give benzaldehyde on hydrolysis.

(a) 

(b) 

(c) 

(d) 

24. The most suitable reagent for the conversion of $R-CH_2-OH \longrightarrow R-CHO$ is **(JEE Main 2014)**
(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (pyridinium chlorochromate)

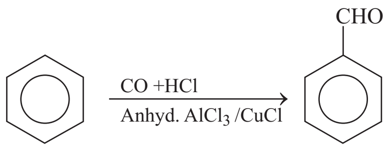
25. Toluene on treating with chromic oxide in acetic anhydride with aqueous acid gives
(a) benzyl diacetate
(b) benzaldehyde
(c) benzyl acetate
(d) benzylidene diacetate

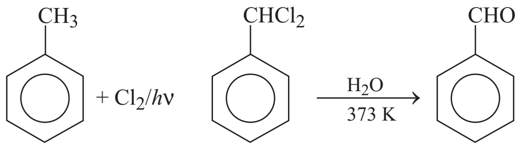
26. The reaction,

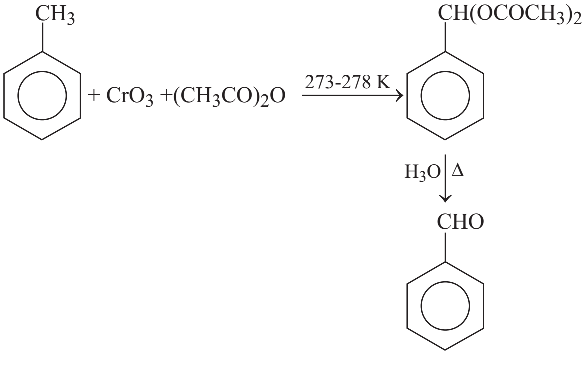
$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

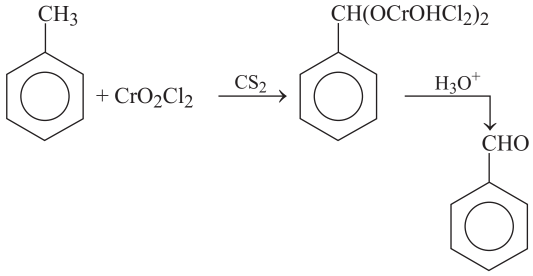
is known as
(a) Etard reaction
(b) Holoform reaction
(c) Gattermann-Koch reaction
(d) Stephen-reaction

27. Choose the Gattermann-Koch reaction.

(a) 

(b) 

(c) 

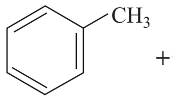
(d) 

28. Which of the following reactions is/are correct regarding the preparation of ketone?
(a) Treatment of acyl chlorides with dialkyl cadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones
(b) When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it gives the corresponding ketone. This reaction is known as Friedel-Craft's acylation reaction
(c) Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone
(d) All of the above

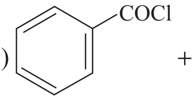
29. Cynohydrin contain

(a) one —OH and two —CN groups
(b) one —CN and two —OH groups
(c) two F—CN groups
(d) one —OH and one —OH group

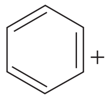
30. Reaction by which benzaldehyde cannot be prepared is **(NEET 2013)**

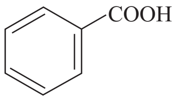
(a) 

$+CrO_2Cl_2$ in CS_2 followed by H_3O^+

(b) 

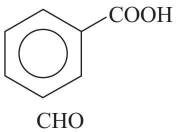
$+H_2$ in the presence of Pd-$BaSO_4$

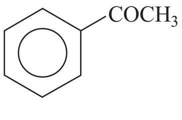
(c) 
+ CO + HCl in the presence of anhyd. $AlCl_3$

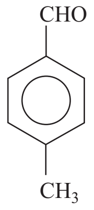
(d) 

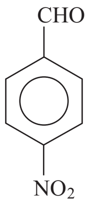
+Zn / Hg and conc. HCl

31. Which one is most reactive towards nucleophilic addition reaction? **(CBSE AIPMT 2014)**

(a) 

(b) 

(c) 

(d) 

Topic 3

Properties and Uses of Aldehydes and Ketones

32. The physical state of methanal and ethanal at room temperature respectively are

(a) volatile liquid and gas
(b) gas and volatile liquid
(c) liquid and solid
(d) solid and volatile liquid

33. The methanal, ethanal and propanone are miscible with water because they form

(a) van der Waals' forces with water
(b) 'H'-bond with water
(c) dipole-dipole bond with water
(d) ion-dipole bond with water

34. Choose the correct alternative from the following regarding physical properties of carbonyl compounds.

(a) When size of aldehyde increases odour becomes less pungent and more fragrant
(b) They are insoluble in organic solvent
(c) Solubility increases rapidly on increasing the length of the alkyl chain
(d) None of the above

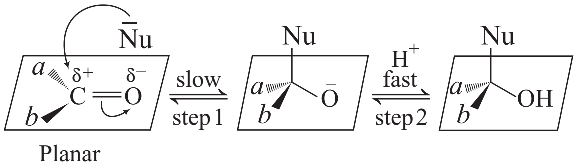
35. Arrange the following compounds in the increasing order of their boiling points.

$$\underset{\text{(I)}}{CH_3CH_2CH_2CHO},\quad \underset{\text{(II)}}{CH_3CH_2CH_2CH_2OH},$$

$$\underset{\text{(III)}}{H_5C_2O—C_2H_5},\quad \underset{\text{(IV)}}{CH_3CH_2CH_2CH_2CH_3}$$

(a) IV< I< II< III
(b) IV< III< II< I
(c) IV< III< I< II
(d) IV< II< III< I

36. Study the mechanism given below carefully,



Select the correct statement(s) for the above diagram from the options given below.

(a) A nucleophile attacks the electrophilic carbon of the non-polar carbonyl group from direction parallel to the plane of sp^2-hybridised orbitals of carbonyl carbon
(b) The hybridisation of carbon changes from sp to sp^2 in this process
(c) The net result is the addition of Nu^{S} and $H^{\oplus}$ across the carbon oxygen double bond
(d) Both (a) and (c)

37. Choose the correct alternative from the following.

(a) Ketones are more reactive than aldehydes towards NSR
(b) Aldehydes are more reactive than ketones towards NSR
(c) Formaldehyde is the least reactive carbonyl compounds towards NSR
(d) Steric hindrance does not play a role to effect the reactivity of carbonyl compounds towards NAR

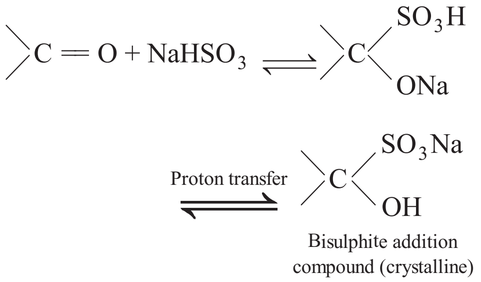
38. Identify the example in which both nucleophilic addition and nucleophilic addition elimination reaction occur respectively in the carbonyl compound.

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

39. Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reaction.

(a) Butanone< propanone< propanal< ethanal
(b) Butanone< propanal< propanone< ethanal
(c) Butanone< ethanal < propanone< propanal
(d) Butanone< ethanal < propanal< propanone

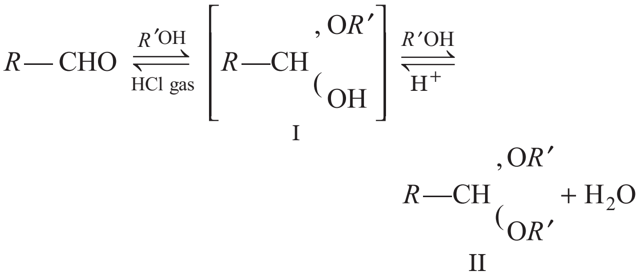
40.



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

(a) electronic reasons (b) steric reasons
(c) bonding reasons (d) Both (a) and (b)

41.



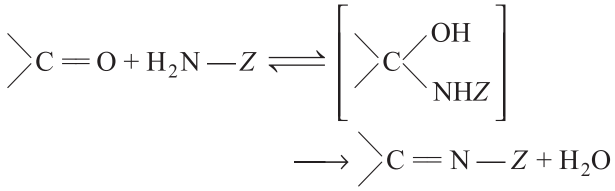
Identify the abbreviation used for I and II for the given reaction.

	I	II
(a)	Acetal or *gem*-dialkoxy	Hemiacetal or alkoxyalcohol
(b)	Acetal or alkoxy alcohol	Hemiacetal or *gem*-dialkoxy
(c)	Hemiacetal or alkoxy alcohol	Acetal or *gem*-dialkoxy
(d)	Hemiacetal or *gem*-dialkoxy	Acetal or alkoxy alcohol

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

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

43.



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

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

44. Some N substituted derivatives of aldehydes and ketones $\left(>C=N—Z\right)$ are

Z	Reagent name	Carbonyl derivative	Product name
—H	Ammonia	I	Imine
—*R*	Amine	$>C=NR$	II
III	Hydroxylamine	$>C=N—OH$	Oxime
$—NH_2$	IV	$>C=N—NH_2$	Hydrazone

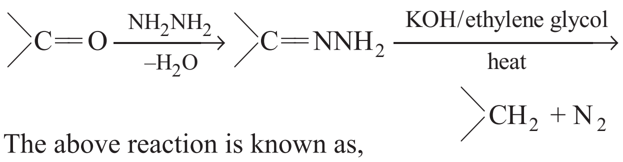
Identify I, II, III and IV in the given table.

	I	II	III	IV
(a)	$—C\equiv N$	Schiff's base	—OH	Hydrazine
(b)	$>C=NH$	Substituted imine	—H	Hydrazine
(c)	$—C\equiv N$	Substituted imine	—OH	Hydrazine
(d)	$>C=NH$	Schiff's base	—OH	Hydrazine

45. Reagent(s) used for the reduction of aldehydes and ketones are

(a) $LiAlH_4$ (b) $NaBH_4$
(c) Catalytic hydrogenation (d) All of these

46.



The above reaction is known as,

(a) Wolff-Kishner reduction (b) Clemmensen's reduction
(c) Both (a) and (b) (d) None of the above

47. Which of the following reagents is/are used in the given reaction? "*R*CHO ⟶ *R*COOH"

(a) Nitric acid
(b) Potassium dichromate
(c) Tollen's reagent
(d) All of the above

48. Which of the following statements is/are correct?

(a) Aldehydes are generally oxidised under vigorous conditions
(b) Ketones are easily oxidised to carboxylic acids even under mild oxidising agents
(c) Oxidation of ketone involves carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of C-atoms than the parent ketones
(d) All of the above

49. An organic compound *X* having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test. It produces *n*-pentane on reduction. *X* could be

(CBSE AIPMT 2015)

(a) pentanal (b) 2-pentanone
(c) 3-pentanone (d) *n*-amyl alcohol

50. Composition of Fehling solution *A* and Fehling solution *B* is

(a) an aqueous copper sulphate and alkaline sodium potassium tartarate (Rochelle salt) respectively
(b) an alkaline sodium potassium tartarate (Rochelle salt) and aqueous copper sulphate respectively
(c) an aqueous copper sulphate (Rochelle salt) and acidic sodium potassium tartarate respectively
(d) an acidic sodium potassium tartarate (Rochelle salt) and aqueous copper sulphate respectively

51. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained due to

(a) CuO (b) Cu_2O (c) $CuSO_4$ (d) $Cu^{2+} + \overset{-}{O}H$

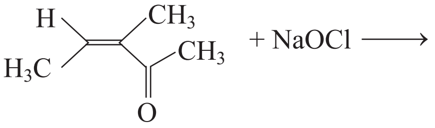
52. Which of the following carbonyl group give the positive Fehling test?

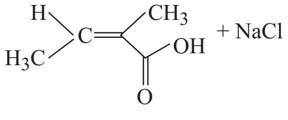
(a) Aliphatic aldehydes (b) Aromatic aldehydes
(c) Ketones (d) Both (a) and (b)

53. Select the correct alternatives for haloform reaction.

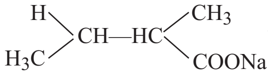
(a) CH_3—O group undergoes this reaction
(b) CH_3CO and $CH_3CH(OH)$ groups take part in this reaction
(c) Sodium hypohalite is used as a reagent in this reaction
(d) Both (b) and (c)

54. Identify the product formed in the given reaction,

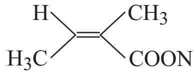


(a)


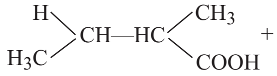
+ NaCl

(b)


+ $CHCl_3$

(c)


+ $CHCl_3$

(d)


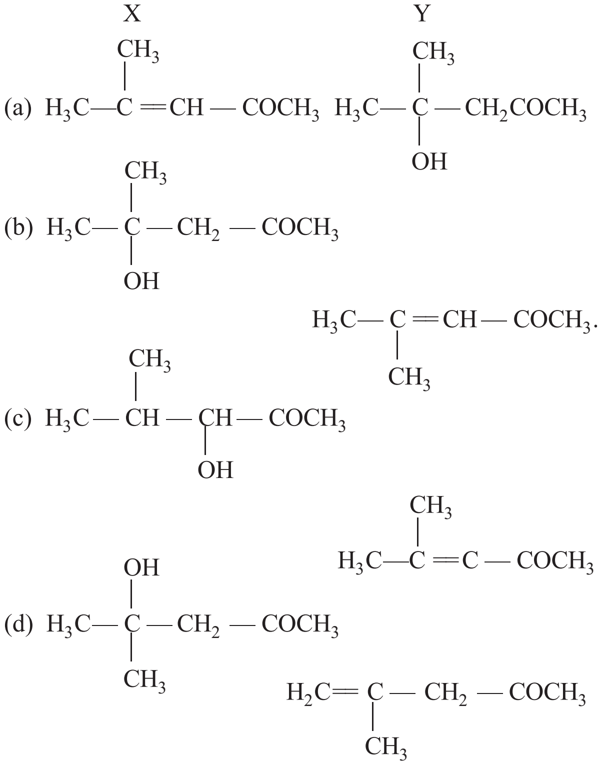
+ NaCl

55. Which of the following statements is/are correct about the aldol reaction?

(a) Aldehyde and ketones having at least one β-hydrogen
(b) The reaction is carried out in the presence of concentrated alkali
(c) The product formed is β-hydroxy aldehydes (aldol) or β-hydroxy ketone (ketol)
(d) All of the above

56. $2CH_3COCH_3 \overset{Ba(OH)_2}{\rightleftharpoons} X \xrightarrow[-H_2O]{\Delta} Y$

Identify *X* and *Y* in the given reaction.



X Y

(a) $H_3C—\overset{CH_3}{\overset{|}{C}}=CH—COCH_3$ $H_3C—\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_2COCH_3$

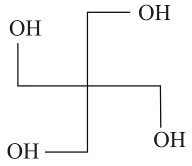
(b) $H_3C—\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—CH_2—COCH_3$ $H_3C—\underset{CH_3}{\underset{|}{C}}=CH—COCH_3.$

(c) $H_3C—\overset{CH_3}{\overset{|}{CH}}—\underset{OH}{\underset{|}{CH}}—COCH_3$ $H_3C—\overset{CH_3}{\overset{|}{C}}=C—COCH_3$

(d) $H_3C—\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}—CH_2—COCH_3$ $H_2C=\underset{CH_3}{\underset{|}{C}}—CH_2—COCH_3$

57. The number of aldol reactions that occurs in the given transformation is

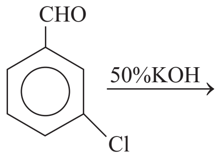
$$CH_3CHO + 4HCHO \xrightarrow{aq.NaOH}$$



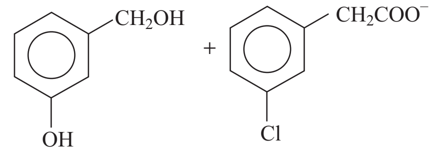
(JEE Main 2012)

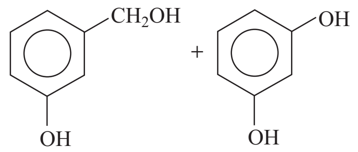
(a) 1 (b) 2 (c) 3 (d) 4

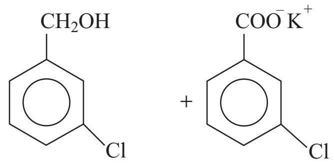
58. Predict the products in the given reaction,

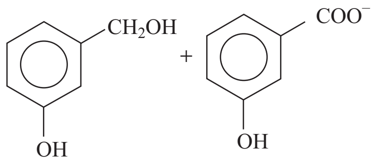


(CBSE AIPMT 2012)

(a) 

(b) 

(c) 

(d) 

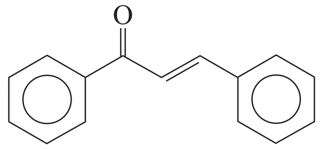
59. Choose the correct option regarding the comparison of reactivity of benzaldehyde and propanal.

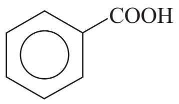
(a) Less reactive in electrophilic addition reactions than propanal
(b) More reactive in nucleophilic addition reactions than propanal
(c) Less reactive in nucleophilic addition reactions than propanal
(d) Equally reactive in nucleophilic addition reactions than propanal

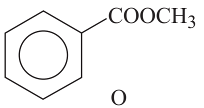
60. Which type of reaction(s) is/are involved in the Cannizzaro reaction?

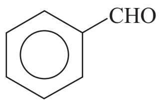
(a) Reduction (b) Oxidation
(c) Both (a) and (b) (d) None of these

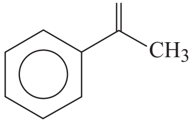
61. Select the *A* used with benzaldehyde in order to synthesis the product given in the reaction.

Benzaldehyde + A $\xrightarrow[\Delta]{\text{NaOH}}$ 

(a) 

(b) 

(c) 

(d) 

62. Which of the following functional group conversion take place by the reagent $I_2 + NaOH$.

(a) $H—CHO \longrightarrow —COOH$
(b) $—COOH \longrightarrow \rangle C=O$
(c) $\overset{HC_3}{\rangle} C = O \longrightarrow —COOH$
(d) All of these

63. Formaldehyde is well known as .... used to preserve biological specimens.

Fill in the blank to complete the above sentence.

(a) Acetylene (40%) solution (b) Acetylene (70%) solution
(c) Formalin (40%) solution (d) Formalin (70%) solution

64. Choose the correct option from the following.

(a) Acetone is one of the constituent of liquid nailpolish
(b) Formalin is used as a disinfectant
(c) Benzaldehyde is used in perfumery
(d) All of the above

Topic 4

General Characteristics and Methods of Preparation of Carboxylic Acids

65. Some higher members of aliphatic carboxylic acids known as fatty acids occur in natural fats as esters of glycerol. How many C-atoms they contain?

(a) $C_{12} - C_{18}$ (b) $C_{10} - C_{15}$ (c) $C_5 - C_{10}$ (d) $C_{20} - C_{30}$

66. IUPAC name of α-acetyl succinic acid is

(a) 2-(1-oxoethyl) butan-1,4-dioic acid
(b) 3-(2-oxoethyl) butan-1,4-dioic acid
(c) Hexan-1,6-dioic acid
(d) Butan-1,4-dicarboxylic acid

67. What is the common name of 2-hydroxypropanoic acid?

(a) Adipic acid (b) Crotonic acid
(c) Lactic acid (d) Acrylic acid

68. The carboxylic carbon is less electrophilic than carbonyl carbon because of

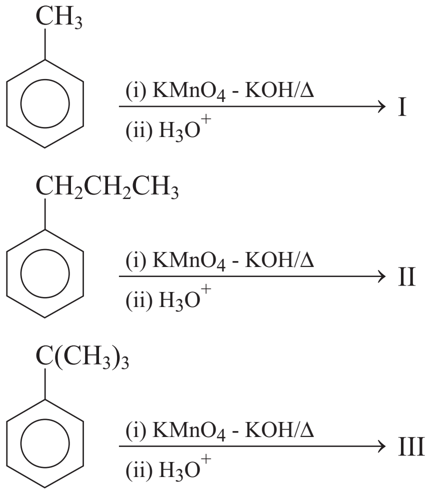
(a) the possible resonating structure
(b) Lewis structure
(c) the possible hyperconjugative structure
(d) Both (a) and (b)

69. Select the reagent for the given conversion.

$$CH_3(CH_2)_8CH_2OH \longrightarrow CH_3(CH_2)_8COOH$$

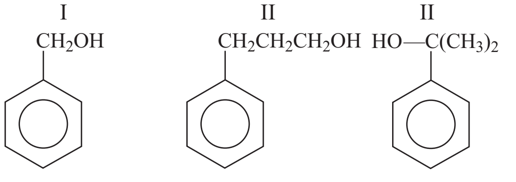
(a) $KMnO_4$ in acidic, neutral, alkaline media
(b) $K_2Cr_2O_7$ in acidic media
(c) CrO_3 in acidic media
(d) All of the above

70.

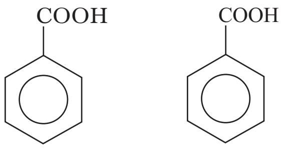


Identify the products formed in the given reaction.

(a)

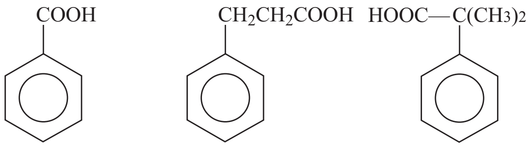


(b)

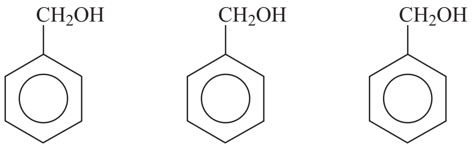


No reaction will occur

(c)



(d)



71. Select the correct statement(s) for the following.

(a) Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst
(b) Mild reaction conditions are used to stop the reaction at the amide stage during the hydrolysis of nitriles
(c) Grignard reagents react with dry ice to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid
(d) All of the above

72. Select the acid(s) which cannot be prepared by Grignard reagent?

(a) Acetic acid (b) Succinic acid
(c) Formic acid (d) All of these

73. In the given reaction,

$$(C_6H_5CO)_2O \xrightarrow{H_2O} I$$
$$C_6H_5COOCOCH_3 \xrightarrow{H_2O} II$$

Identify the products I and II formed in the given reaction.

	I	II
(a)	2 molecules of benzoic acid	2 molecules of ethanoic acid
(b)	2 molecules of benzoic acid	1 molecule of benzoic acid and 1 molecule of ethanoic acid
(c)	1 molecule of ethanoic acid	1 molecule of benzoic acid
(d)	1 molecule of benzoic acid	1 molecule of butanoic acid

74. Which of the following types of hydrolysis of esters give directly carboxylic acids and carboxylates respectively statement?

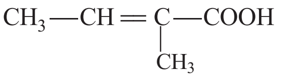
(a) Acidic hydrolysis and basic hydrolysis
(b) Basic hydrolysis and acidic hydrolysis
(c) Acidic hydrolysis and acidic hydrolysis
(d) Basic hydrolysis and basic hydrolysis

75. The major product *H* in the given reaction sequence is

$$CH_3—CH_2—CO—CH_3 \xrightarrow{CN^-} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

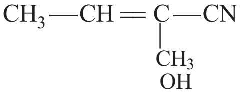
(JEE Main 2012)

(a)



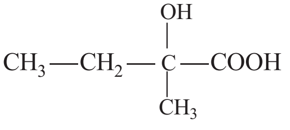
$CH_3—CH=\underset{\displaystyle CH_3}{\underset{|}{C}}—COOH$

(b)



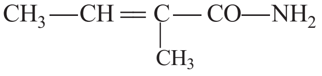
$CH_3—CH=\underset{\displaystyle CH_3}{\underset{|}{C}}—CN$

(c)



$CH_3—CH_2—\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—COOH$

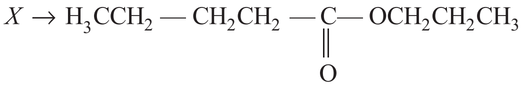
(d)



$CH_3—CH=\underset{\displaystyle CH_3}{\underset{|}{C}}—CO—NH_2$

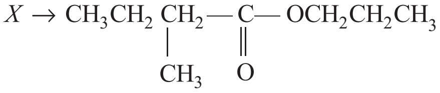
76. An organic compound X $(C_8H_{16}O_2)$ was hydrolysed with dil. H_2SO_4 to give carboxylic acid Y and alcohol Z. Oxidation of Z with chromic acid produced Y. Z on dehydration gives but-1-ene.

Identify X, Y and Z and choose the correct option.

(a) 

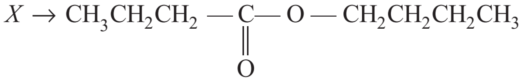
$X \rightarrow H_3CCH_2-CH_2CH_2-\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_3$

$Y \rightarrow CH_3CH_2CH_2COOH,\ Z \rightarrow CH_3CH_2CH_2OH$

(b) 

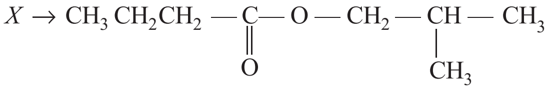
$X \rightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{CH_2}-\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_3$

$Y \rightarrow H_3C-CH_2\underset{\underset{CH_3}{|}}{CH}-COOH, Z \rightarrow CH_3CH_2CH_2OH$

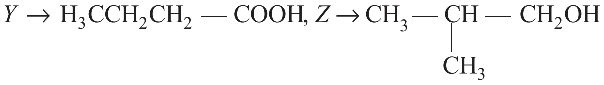
(c) 

$X \rightarrow CH_3CH_2CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2CH_2CH_3$

$Y \rightarrow H_3CCH_2CH_2-COOH,\ Z \rightarrow CH_3CH_2CH_2CH_2OH$

(d) 

$X \rightarrow CH_3\,CH_2CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$



$Y \rightarrow H_3CCH_2CH_2-COOH, Z \rightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

Topic 5
Properties and Uses of Carboxylic Acids

77. In the vapour phase or in the aprotic solvents carboxylic acids exist as

(a) dimer
(b) trimer
(c) tetramer
(d) All of the above

78. Choose the incorrect option regarding the physical properties of carboxylic acid.

(a) Higher carboxylic acids are insoluble in water
(b) Benzoic acid is soluble in cold water
(c) Carboxylic acids have higher boiling point than aldehydes of comparable masses
(d) Aliphatic carboxylic acids upto four C-atoms are coloured

79. In the given reaction,

$$2RCOOH + 2Na \longrightarrow 2RCOO^-Na^+ + X$$
$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$
$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + Y$$

Identify X and Y in the given reaction.

	X	Y
(a)	H_2	CO
(b)	H_2O	CO_2
(c)	H_2	CO_2
(d)	H_2O	CO

80. Arrange the following acids in their increasing order of acid strength.

Acetic acid $(pK_a = 4.76)$ I
Benzoic acid $(pK_a = 4.19)$ II
Trifluoroacetic acid $(pK_a = 0.23)$ III
Hydrochloric acid $(pK_a = -7.0)$ IV

(a) I< II< III< IV
(b) I< III< II< IV
(c) IV< III< II< I
(d) I< II< IV< III

81. Carboxylic acids, in comparision of mineral acids and alcohols respectively are

(a) stronger and weaker
(b) weaker and stronger
(c) of equal strength and weaker
(d) weaker and of equal stronger

82. The following acids are arranged in order of increasing acidity.

$CF_3COOH > CCl_3COOH > I > NO_2CH_2COOH > NC-CH_2COOH >$ ←

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH$ II $> ClCH_2CH_2COOH >$

Continue ←

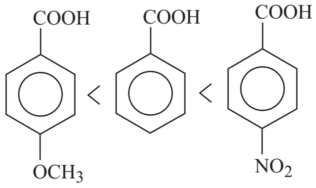
$C_6H_5COOH > C_6H_5CH_2COOH > III > CH_3CH_2COOH$

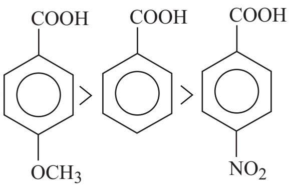
Continue ←

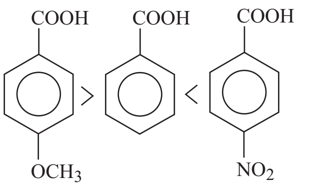
Identify I, II, III in the order of decreasing acidity. and choose the correct option.

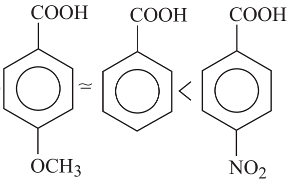
	I	II	III
(a)	$CHCl_2COOH$	H_3CCOOH	HCOOH
(b)	$CHCl_2COOH$	HCOOH	$H_3C-COOH$
(c)	$H_3C-COOH$	HCOOH	$CHCl_2COOH$
(d)	CH_3COOH	$CHCl_2COOH$	HCOOH

83. Arrange the following derivative of carboxylic acid in their increasing order of their acidity.

(a)


(b)


(c)


(d)


84. Arrange the following acids in the decreasing order of the acidic strength.

$\underset{\text{I}}{HC\equiv C-COOH}$ $\quad$ $\underset{\text{II}}{C_6H_5COOH}$

$\underset{\text{III}}{CH_2=CH-COOH}$ $\quad$ $\underset{\text{IV}}{CH_3COOH}$

Choose the correct option.

(a) I > II > III > IV (b) I < II < III < IV
(c) I > III > II > IV (d) I > IV > III > II

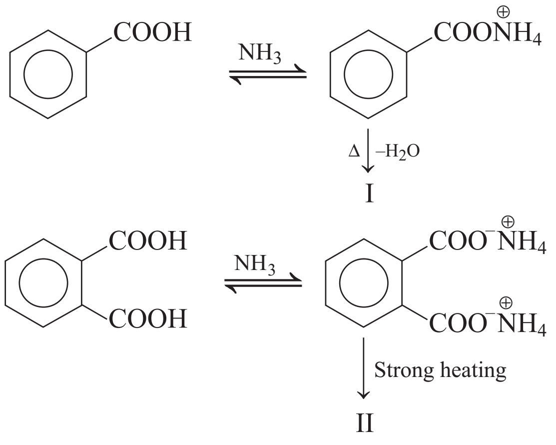
85. Which of the following represents the correct order of the acidic strength in the given compounds?

(a) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(b) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

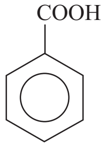
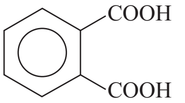
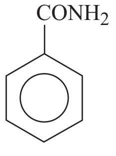
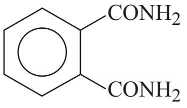
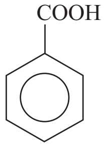
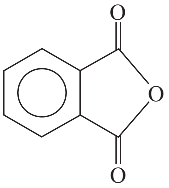
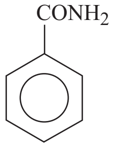
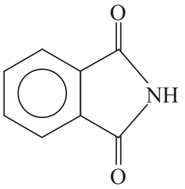
86. Which of the folloiwng reagents is/are used for the conversion of ethanoic acid to ethanoic anhydride?

(a) $SOCl_2, \Delta$ (b) PCl_3, Δ (c) P_2O_5, Δ (d) All of these

87. In the given reaction,



Identify I and II for the above reaction and choose the correct option.

	I	II
(a)		
(b)		
(c)		
(d)		

88. Diborane easily reduce the functional group such as

(a) acid
(b) ester
(c) nitro
(d) halo

89. Sodalime is the mixture of

(a) NaOH and CaO in the ratio of 3 : 2
(b) NaOH and CaO in the ratio of 1 : 3
(c) NaOH and CaO in the ratio of 3 : 1
(d) NaOH and CaO in the ratio of 2 : 3

90. What is the by-product formed in this reaction

$$R\text{—COONa} \xrightarrow[\Delta]{\text{NaOH, CaO}} R\text{—H} + ?$$

(a) $NaHCO_3$ (b) CO_2
(c) Na_2HCO_3 (d) Na_2CO_3

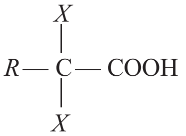
91. Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of C-atoms present in the alkyl group of the acid. The reaction is known as

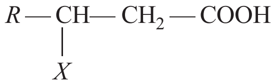
(a) Kolbe electrolysis
(b) decarboxylation
(c) HVZ-reaction
(d) Friedel-Crafts reaction

92. The product formed during Hell-Volhard-Zelinsky reaction is

(a) 
$R-\underset{X}{\underset{|}{CH}}-COOH$

(b) $R-CH_2-COX$

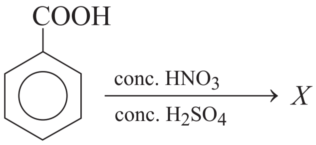
(c) 
$R-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-COOH$

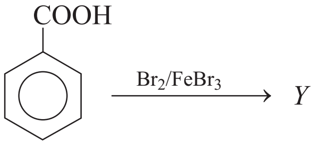
(d) 
$R-\underset{X}{\underset{|}{CH}}-CH_2-COOH$

93. Why the aromatic carboxylic acids do not undergo Friedel-Crafts reaction?

(a) Carboxyl group acts as a activating and *meta*-directing group
(b) Carboxyl group act as a deactivating and *ortho*-directing group
(c) Carboxyl group act as a activating and *ortho*-directing group
(d) Carboxyl group acts as deactivating and the catalyst

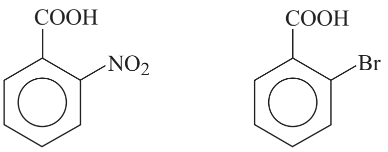
94.

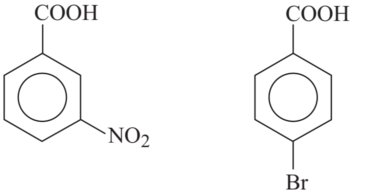


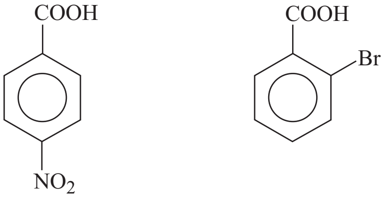


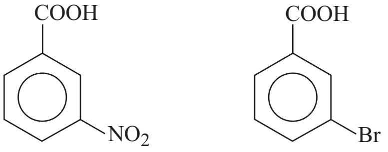
Identify *X* and *Y* for the above reaction.

X *Y*

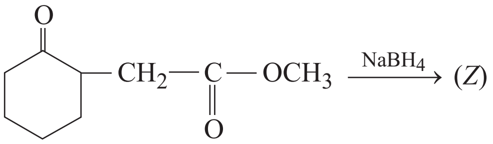
(a) 

(b) 

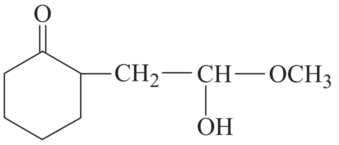
(c) 

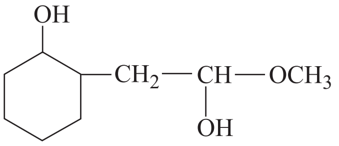
(d) 

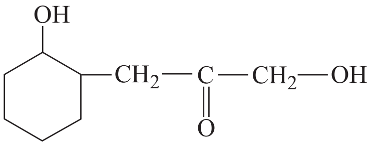
95. In the following reaction,

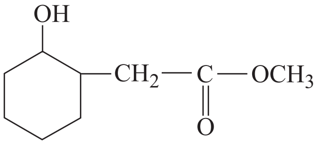


(*Z*) is

(a) 

(b) 

(c) 

(d) 

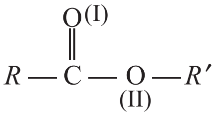
96. Name the product form during the decarboxylation of malonic acid.

(a) Acetic acid (b) Ethanone (c) Propanone (d) Formic acid

97. The reactivity of acid derivatives towards nucleophilic acyl substitution reactions decrease in the order

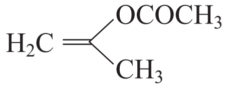
(a) Acid chloride > anhydride > ester > amide
(b) Acid chloride > ester > anhydride > amide
(c) Amide > anhydride > ester > acid chloride
(d) Amide > ester > acid chloride > anhydride

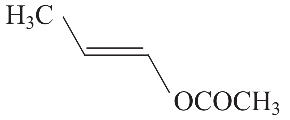
98. Indicate the most basic oxygen in an ester


$R-\overset{\overset{\text{O(I)}}{\|}}{C}-\underset{\text{(II)}}{O}-R'$

(a) O denoted by (I) (b) O denoted by (II)
(c) Both are equal (d) None of these

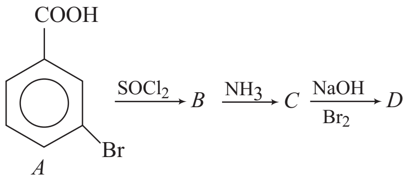
99. The product of acid hydrolysis of *P* and *Q* can be distinguished by

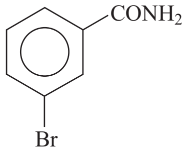
$P \longrightarrow$ 

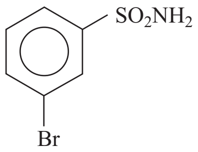
$Q \longrightarrow$ 

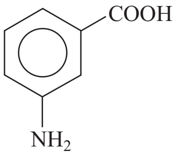
(a) Lucas reagent (b) 2, 4-DNP
(c) Fehling's solution (d) $NaHSO_3$

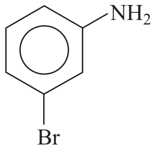
100. In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*. **(CBSE AIPMT 2011)**



(a)


(b)


(c)


(d)


101. Which of the following acid is used in rubber, textile, dyeing, leather and electroplating industries?

(a) Hexanedioic acid
(b) Ethanoic acid
(c) Methanoic acid
(d) Sodium benzoate

102. Choose the correct statement, ketones and aldehydes are used as

(a) Starting motional for manufacturing of acetic acid
(b) Benzaldehydes is used in perfumery industry
(c) Acetone is used as common solvent
(d) All one correct

103. Many aldehydes and ketones are well known for their

(a) reactive nature towards *ortho* and *para*-position while electrophilic substitution
(b) oval shape
(c) odour and flavour
(d) reactivity towards oxidation and reduction even by weak reagents

Special Format Questions

I. More Than One Correct Option

104. Which of the following incorrect statements?

(a) CCl_3CHO exhibits aldol condensation
(b) When mixture of ethanal and propanal is treated with *aq*. NaOH, the product contains four aldols
(c) Mixture of HCHO and CH_3CHO will not give aldol condensation
(d) 2-methyl propanal does not undergo Cannizzaro reaction

105. Which of the following are the incorrect conversion of acetone into acetamide?

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

(b) $CH_3COCH_3 \xrightarrow{I_2/NaOH} CH_3COONa \xrightarrow[NH_3]{H^+} CH_3CO\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} CH_3CONH_2$

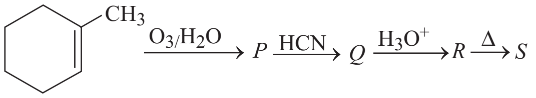
(c) $CH_3COCH_3 \xrightarrow{CrO_3} CH_3COOH \xrightarrow{NH_3} CH_3CONH_2$

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

106. Several simple chemical tests are given to distinguish between the pair of carbonyl compounds. Which of the following pairs are correct?

(a) Propanal and propanone → Silver mirror test
(b) Acetophenone and benzophenone → Iodoform test
(c) Ethanal and propanal → Fehling's test
(d) Benzoic acid and ethylbenzoate → Sodium bicarbonate test

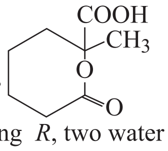
107. Consider the following sequence of reactions,



Which of the following options are correct?

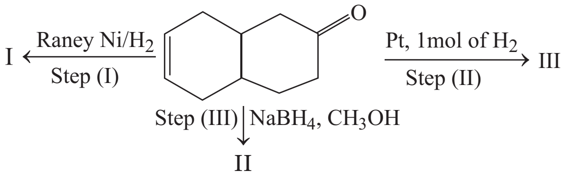
(a) Product *P* has both carbonyl and carboxyl group

(b) Product *Q* is a nucleophilic addition product

(c) Product *S* is


(d) After heating *R*, two water molecules got removed

108. Consider the following reaction,

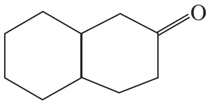


Choose the correct alternatives from the following.

(a) Step (I) is reduction of double bond as well as carbonyl group

(b) Setp (II) is reduction of only double bond

(c) Step (III) is reduction of only carbonyl group

(d) Product (III) would be 

II. Statement Based Questions

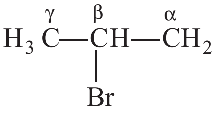
Directions (Q.Nos. 109-118) *In the following questions, a Statement* I *is followed by a corresponding Statement* II. *Of the following Statements, choose the correct one.*

(a) Both Statement I and II are correct and Statement II is the correct explanation of Statement I.

(b) Both Statement I and II are correct and II is not the correct explanation of Statement I.

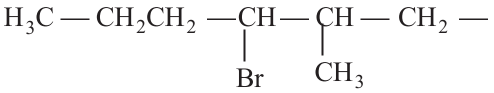
(c) Statement I is correct, Statement II is incorrect.

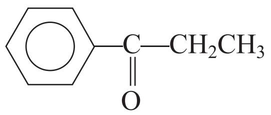
(d) Statement II is correct, Statement I is incorrect.

109. Statement I 
$\overset{\gamma}{H_3C}-\underset{\underset{Br}{|}}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-CHO$ is known as β-bromobutyraldehyde.

Statement II The substituent in the carbon chain is indicated by Greek letters $\alpha, \beta, \gamma, \delta$ etc.

110. Statement I


$H_3C-CH_2CH_2-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CHO$ and



is named as

3-bromo-2- methylheptanol and 3-phenylpropan-3-one.

Statement II In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group, while in case of ketones the numbering begins from the end nearer to the carbonyl group.

111. Statement I The carbonyl carbon is a nucleophilic and carbonyl oxygen is an electrophilic centre.

Statement II The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon.

112. Statement I Aldehydes and ketones have larger dipole moments (2.3 – 2.8 D).

Statement II The carbonyl group is polar in nature.

113. Statement I The dipole moment of alcohols is 2.3-2.8 D and that of aldehydes and ketones is 1.6-1.8 D.

Statement II The π-electrons of the $C=O$ are loosely held and hence can be shifted towards O-atom more readily than the more tightly held σ-electrons of the $C-O$ bond in alcohols.

114. Statement I π -electron cloud of $>C=O$ bond is symmetrical.

Statement II The O-atom in the carbonyl group is far more electronegative than C-atom.

115. Statement I Acetaldehyde cannot be prepared by the Rosenmund reduction.

Statement II Formyl chloride is unstable at room temperature.

116. Statement I The boiling points of aldehydes and ketones are lower than hydrocarbons and ethers of comparable masses.

Statement II It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

117. Statement I The reaction of aldehydes and ketones with pure HCN is very slow to yield cyanohydrin.

Statement II The above reaction is catalysed by a base and generated cyanide ion being a weaker nucleophile adds to carbonyl compounds to yield, corresponding cyanohydrin.

118. Statement I Sodium hydrogen sulphite adds to aldehyde and ketones is the useful method for separation and the purification of aldehydes.

Statement II The hydrogen sulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali.

III. Statement Based Questions Type II

119. The following steps are given for the mechanism of esterification of carboxylic acids.

I. The protonated esters looses a proton to give the ester.
II. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol.
III. Proton transfer in the tetrahedral intermediate occurs.

Arrange the following steps in their correct sequence.

(a) I, II and III
(b) I, III and II
(c) II, III and I
(d) III, II and I

120. I. $R\text{COOH} + \text{PCl}_5 \longrightarrow R\text{COCl} + \text{POCl}_3 + \text{HCl}$

II. $3R\text{COOH} + \text{PCl}_5 \longrightarrow 3R\text{COCl} + \text{H}_3\text{PO}_3$

III. $R\text{COOH} + \text{SOCl}_2 \longrightarrow R\text{COCl} + \text{SO}_2 + \text{HCl}$

Which of the above reactions is/are preferred for the synthesis of RCOCl?

(a) Only I (b) Only II (c) Only III (d) All of these

IV. Assertion-Reason Type Questions

Directions (Q. Nos. 121-131) *In the following questions a statement of Assertion* (A) *followed by a statement of Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Both A and R are correct; and R is the correct explanation of A.

(b) Both A and R are correct; but R is not the correct explanation of A.

(c) A is correct ; but R is incorrect.

(d) R is correct ; but A is incorrect.

121. Assertion (A) A bright silver mirror is produced during the warming of an aldehyde with freshly prepared ammoniacal silver nitrate solution.

Reason (R) A bright silver mirror is produced due to the formation of silver metal.

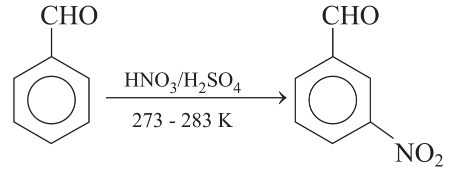
122. Assertion (A) α-hydrogen atoms of carbonyl compounds are acidic.

Reason (R) The strong electron releasing effect of the carbonyl group make the stabilisation of the conjugate base by the resonance.

123. Assertion (A) Benzaldehyde on heating with concentrated alkali give α, β-unsaturated carbonyl compound.

Reason (R) Benzaldehyde do not have an H-atom.

124. Assertion (A)



Reason (R) Carbonyl group acts as a deactivating and *meta*-directing group.

125. Assertion (A) IUPAC name of $\text{CH}_3\text{CH}_2\text{CH}_2\ \text{COOH}$ is butyric acid.

Reason (R) In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending -e in the name of the corresponding alkane with -oic acid.

126. Assertion (A) IUPAC name of $\text{HOOC} \left(\text{CH}_2 \right)_2 \text{COOH}$ is butanedioic acid.

Reason (R) Compounds containing more than one carboxyl group, the ending '-e' of the alkane is retained. Prefix 'di' is added to the term- 'oic'.

127. Assertion (A) Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses.

Reason (R) More extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

128. Assertion (A) The molecular mass of acetic acid in benzene is 120 instead of 60.

Reason (R) The carboxylic acids exist as cyclic dimers.

129. Assertion (A) The melting points and boiling points of aliphatic acids are usually higher than those of aromatic acids of comparable molecular masses.

Reason (R) The planar benzene ring in the aromatic acids can fit more closely in the crystal lattice than *zig-zag* structure of aliphatic acids.

130. Assertion (A) Carboxylic acids are more acidic than phenols.

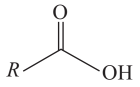
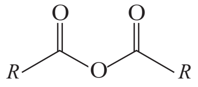
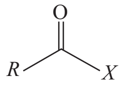
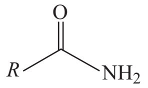
Reason (R) The carboxylate ion is less stabilised than phenoxide ion.

131. Assertion (A) Ester hydrolysis is fast in the beginning and becomes slow after sometime.

Reason (R) The rate of ester hydrolysis increases with the increase in the amount of carboxylic acid produced

V. Matching Type Questions

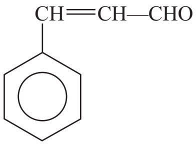
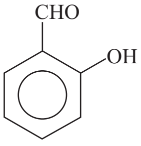
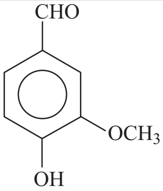
132. Match the following structure given in Column I with their names given in Column II and choose the correct option from the codes given below.

	Column I	Column II
A.		1. Acid anhydride
B.		2. Carboxylic acid
C.		3. Amide
D.		4. Acyl halide

Codes

	A	B	C	D
(a)	2	1	3	4
(b)	2	1	4	3
(c)	1	2	3	4
(d)	1	3	2	4

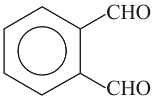
133. Match the following structure given in Column I with their names given in Column II and select the appropriate option from the codes given below.

Column I	Column II
A. 	1. Salicylaldehyde (from meadow's sweet)
B. 	2. Vanillin (from vanilla beans)
C. 	3. Cinnamaldehyde (from cinnamon)

Codes

	A	B	C
(a)	1	3	2
(b)	3	2	1
(c)	1	2	3
(d)	3	1	2

134. Match the following structure given in Column I with their common name given in Column II and choose the correct option from the codes given below.

Column I (Structure)	Column II (Common name)
A. HCHO	1. Valeraldehyde
B. $CH_3CH_2CH_2CH_2CHO$	2. Phthaldehyde
C. $H_2C = CH — CHO$	3. Acrolein
D. 	4. Formaldehyde

Codes

	A	B	C	D
(a)	2	1	3	4
(b)	2	3	1	4
(c)	4	3	1	2
(d)	4	1	3	2

135. Match the following names of reagents given in Column II to bring about the conversions given in Column I and choose the correct option from the codes given below.

Column I (Conversion)	**Column II** (Reagents)
A. Hexan-1-ol to hexanal	1. $C_5H_5\overset{+}{N}HCrO_3Cl^-$(PCC)
B. Cyclohexanol to cyclohexanone	2. CrO_3 in the presence of acetic anhydride
C. *p*-fluorotoluene to *p*-fluorobenzaldehyde	3. $K_2Cr_2O_7$ in acidic medium

Codes

	A	B	C
(a)	1	2	3
(b)	2	3	1
(c)	1	3	2
(d)	2	1	3

136. Match the reactions given in Column I with the suitable reagents given in Column II and choose the correct option from the codes given below.

Column I (Reactions)	Column II (Reagents)
A. Ethane nitrile to ethanal	1. O_3 / H_2O - Zn dust
B. Allyl alcohol to propanal	2. (DIBAL-H)
C. But-2-ene to ethanal	3. PCC

Codes

	A	B	C
(a)	1	2	3
(b)	3	2	1
(c)	2	3	1
(d)	2	1	3

137. Match the following carbonyl compounds given in Column I with their uses given in Column II and choose the correct option from the given codes below.

Column I (Carbonyl compounds)	Column II (Uses)
A. Formaldehyde	1. Perfumery and dye industries
B. Acetaldehyde	2. Bakelite
C. Benzaldehyde	3. Odours and flavours
D. Vanillin, butyraldehyde	4. Manufacture of vinyl acetate and ethyl acetate

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	2	3	4	1
(c)	1	3	4	1
(d)	2	4	1	3

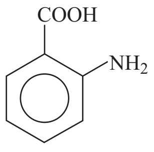
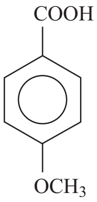
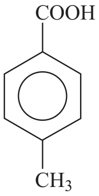
138. Match the acids given in Column I with their correct IUPAC names given in Column II and choose the correct option from the codes given below.

Column I (Acids)	Column II (IUPAC names)
A. Oxalic acid	1. Hexan-1,6-dioic acid
B. Succinic acid	2. Pentan-1,5-dioic acid
C. Adipic acid	3. Butan-1,4-dioic acid
D. Glutaric acid	4. Ethan-1,2-dioic acid

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	4	3	1	2
(c)	4	2	1	3
(d)	4	1	2	3

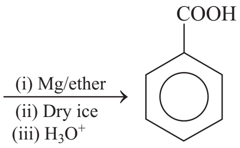
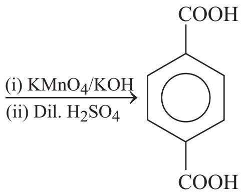
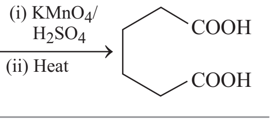
139. Match the following structures given in Column I with their names given in Column II and choose the correct option from the codes given below.

	Column I (Structure)		**Column II** (Name)
A.		1.	Anisic acid
B.		2.	Anthranilic acid
C.		3.	Toluic acid

Codes

	A	B	C
(a)	2	1	3
(b)	1	2	3
(c)	3	2	1
(d)	1	3	2

140. Match the following Column I with the Column II and choose the correct option from the codes given below.

Column I (Starting material)		**Column II** (Reagents with product)
A. Cyclohexene	1.	 (i) Mg/ether (ii) Dry ice (iii) H_3O^+
B. Bromobenzene	2.	 (i) $KMnO_4$/KOH (ii) Dil. H_2SO_4
C. 4-methylacetophenone	3.	 (i) $KMnO_4$/ H_2SO_4 (ii) Heat

Codes

	A	B	C
(a)	1	2	3
(b)	3	1	2
(c)	3	2	1
(d)	2	3	1

141. Match the following compounds given in Column I with their uses given in Column II and choose the correct option from the codes given below.

Column I		**Column II**	
A.	Ethanoic acid	1.	Soaps and detergents
B.	Hexanedioic acid	2.	Nylon-6, 6
C.	Sodium benzoate	3.	Food preservative
D.	Fatty acids	4.	Vinegar

Codes

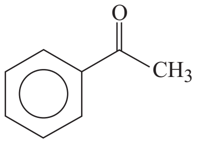
	A	B	C	D
(a)	4	2	3	1
(b)	1	2	3	4
(c)	1	3	2	4
(d)	4	3	2	1

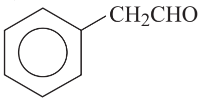
VI. Passage Based Questions

■ **Directions** (Q. Nos.142-143) *Answer the following questions from the passage given below.*

An organic compound (X) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollen's or Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid Y having molecular formula = $C_7H_6O_2$.

142. Identify the compounds X.

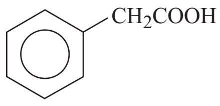
(a) 

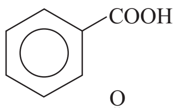
(b) $X \rightarrow$ 

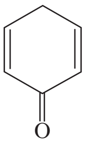
(c) $CH_3C{\equiv}C{-}CH{=}CH{-}CH{=}CH{-}CHO$

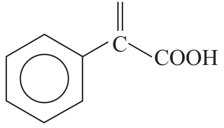
(d) $H_3C{-}CH{=}CH{-}C{\equiv}C{-}CH{=}CH{-}CHO$

143. Identify the compound Y.

(a) 

(b) 

(c) 

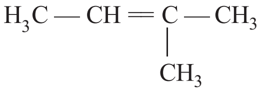
(d) 

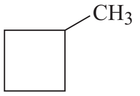
■ **Directions** (Q. Nos. 144 to 145) *Answer the following questions from the passage given below.*

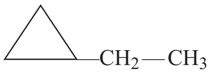
An alkene *A* (molecular formula $= C_5H_{10}$) on ozonolysis gives a mixture of two compounds *B* and *C*. Compound *B* gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound *C* does not give Fehling's test but forms iodoform.

144. Identify the compound *A*.

(a) $H_3C-CH=CH-CH_2-CH_3$

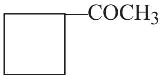
(b) 
$H_3C-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$

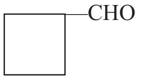
(c) 

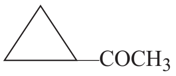
(d) 

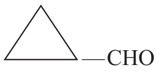
145. Identify the compounds *B* and *C*.

	B	*C*
(a)	H_3C-CHO	$H_3CCO-CH_3$
(b)	H_3CCOCH_3	CH_3-CHO

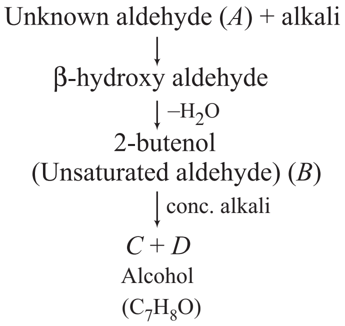
(c) 



(d) 



■ **Directions** (Q. Nos. 146 -148) The given information


Unknown aldehyde (*A*) + alkali
$\downarrow$
β-hydroxy aldehyde
$\downarrow -H_2O$
2-butenol
(Unsaturated aldehyde) (*B*)
$\downarrow$ conc. alkali
C + *D*
Alcohol
(C_7H_8O)

146. What is *A* and *B* in the above information?

	A	*B*
(a)	Benzaldehyde	Acetaldehyde
(b)	Acetaldehyde	Benzaldehyde
(c)	Formaldehyde	Acetaldehyde
(d)	Acetaldehyde	Formaldehyde

147. Name the reaction which occur in the last step of the above information.

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

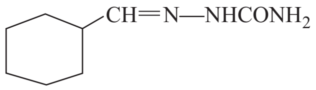
148. What is/are the product formed when *B* reacts with Zn-amalgam and HCl?

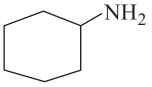
(a) Toluene (b) Benzoic acid
(c) Both (a) and (b) (d) None of the above

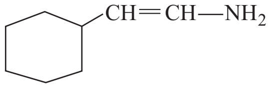
NCERT & NCERT Exemplar Questions

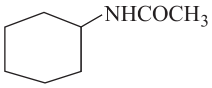
NCERT

149. Predict the products formed when cyclohexane carbaldehyde reacts with following reagents. Semicarbazide and weak acid.

(a) 

(b) 

(c) 

(d) 

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

(a) 2- methylbenzaldehyde (b) 2- ethylbenzaldehyde
(c) 2- ethylbenzoate (d) 2- ethylbenzoic acid

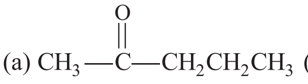
151. Arrange the following compounds in increasing order of their property as indicated:

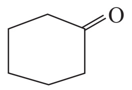
Acetaldehyde, acetone, di-tertiary-butyl ketone, methyl tertiary-butyl ketone (reactivity towards HCN)

(a) Di-tertiary butyl ketone < methyl tertiary butyl ketone < acetone < acetaldehyde
(b) Acetone < acetaldehyde < methyl tertiary butyl ketone < di-tertiary butyl ketone
(c) Acetaldehyde < methyl tertiary butyl ketone < acetone < di-tertiary butyl ketone
(d) Methyl tertiary butyl ketone < di-tertiary butyl ketone < acetone < acetaldehyde

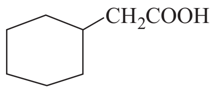
152. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and give positive iodoform test.

On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$

(b) 

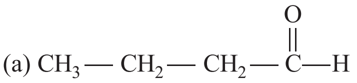
(c) CH_3CH_2COOH

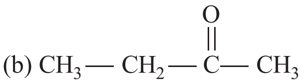
(d) 

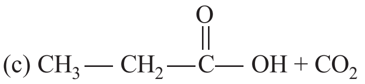
153. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

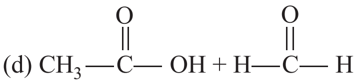
- (a) Because carboxylate ion has negative charge delocalised over only one O-atom
- (b) Because carboxylate ion has negative charge delocalised over two-oxygen atom
- (c) Phenoxide ion has equivalent structure
- (d) Phenoxide ion has negative charge localised on an O-atom

154. 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) 
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

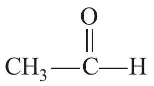
(b) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

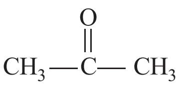
(c) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH + CO_2$

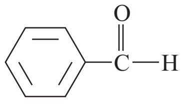
(d) 
$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{O}{\|}}{C}-H$

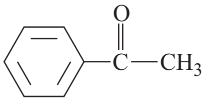
NCERT Exemplar

155. Which of the following compounds is most reactive towards nucleophilic addition reactions?

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

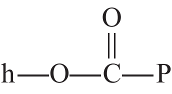
(b) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(c) 

(d) 

156. 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



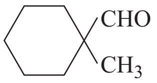
157. Compound $Ph-O-\overset{\overset{O}{\|}}{C}-Ph$ can be prepared by the reaction of

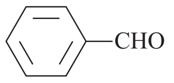
- (a) phenol and benzoic acid in the presence of NaOH
- (b) phenol and benzoyl chloride in the presence of pyridine
- (c) phenol and benzoyl chloride in the presence of $ZnCl_2$
- (d) phenol and benzaldehyde in the presence of palladium

158. The reagent which does not react with both, acetone and benzaldehyde.

- (a) Sodium hydrogen sulphite
- (b) Phenyl hydrazine
- (c) Fehling's solution
- (d) Grignard reagent

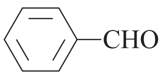
159. Cannizzaro's reaction is not given by ....

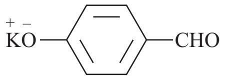
(a) 

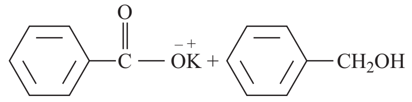
(b) 

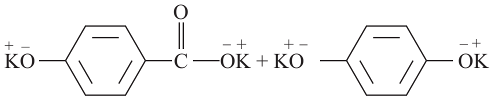
(c) HCHO

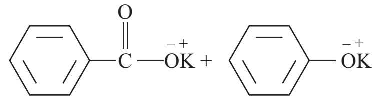
(d) CH_3CHO

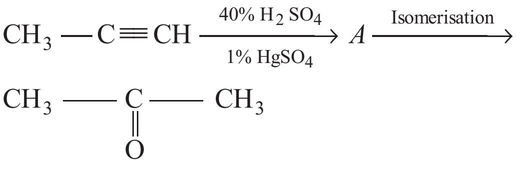
160. Which products is formed, when the compound *aq.*  is treated with conc. KOH solution?

(a) 

(b) 

(c) 

(d) 

161. 

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

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

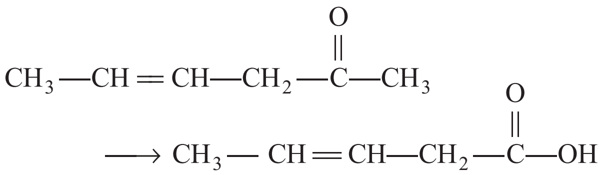
- (a) Prop-1-en-2-ol and metamerism
- (b) Prop-1-en-1-ol and tautomerism
- (c) Prop-2-en-2-ol and geometrical isomerism
- (d) Prop-1-en-2-ol and tautomerism

162. $CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} A \xrightarrow{H_2SO_4,\ \Delta} B \xrightarrow{\text{Hydroboration oxidation}} C$

Compounds *A* and *C* in the following reaction are

(a) identical
(b) positional isomers
(c) functional isomers
(d) optical isomers

163. Which is the most suitable reagent for the following conversion?



$$CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(a) Tollen’s reagent
(b) Benzoyl peroxide
(c) I_2 and NaOH solution
(d) Sn and NaOH solution

164. Which of the following compounds will give butanone on oxidation with alk. $KMnO_4$ solution?

(a) Butan-1-ol
(b) Butan-2-ol
(c) Both (a) and (b)
(d) None of these

165. In Clemmensen reduction, carbonyl compound is treated with

(a) zinc amalgam + HCI
(b) sodium amalgam + HCl
(c) zinc amalgam + nitric acid
(d) sodium amalgam + HNO_3

Answers

1.	(d)	**2.**	(d)	**3.**	(c)	**4.**	(d)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(d)	**9.**	(c)	**10.**	(c)	**11.**	(d)	**12.**	(a)	**13.**	(a)	**14.**	(d)	**15.**	(a)
16.	(b)	**17.**	(a)	**18.**	(b)	**19.**	(b)	**20.**	(b)	**21.**	(b)	**22.**	(b)	**23.**	(c)	**24.**	(d)	**25.**	(b)	**26.**	(d)	**27.**	(a)	**28.**	(d)	**29.**	(d)	**30.**	(d)
31.	(d)	**32.**	(b)	**33.**	(b)	**34.**	(a)	**35.**	(c)	**36.**	(c)	**37.**	(b)	**38.**	(d)	**39.**	(a)	**40.**	(b)	**41.**	(c)	**42.**	(c)	**43.**	(d)	**44.**	(d)	**45.**	(d)
46.	(a)	**47.**	(d)	**48.**	(c)	**49.**	(c)	**50.**	(a)	**51.**	(b)	**52.**	(a)	**53.**	(d)	**54.**	(c)	**55.**	(c)	**56.**	(b)	**57.**	(c)	**58.**	(c)	**59.**	(c)	**60.**	(c)
61.	(d)	**62.**	(c)	**63.**	(c)	**64.**	(d)	**65.**	(a)	**66.**	(a)	**67.**	(c)	**68.**	(a)	**69.**	(d)	**70.**	(b)	**71.**	(d)	**72.**	(c)	**73.**	(b)	**74.**	(a)	**75.**	(a)
76.	(c)	**77.**	(a)	**78.**	(d)	**79.**	(c)	**80.**	(a)	**81.**	(b)	**82.**	(b)	**83.**	(a)	**84.**	(a)	**85.**	(d)	**86.**	(c)	**87.**	(d)	**88.**	(a)	**89.**	(c)	**90.**	(d)
91.	(a)	**92.**	(a)	**93.**	(b)	**94.**	(d)	**95.**	(d)	**96.**	(a)	**97.**	(a)	**98.**	(a)	**99.**	(c)	**100.**	(d)	**101.**	(c)	**102.**	(d)	**103.**	(c)	**104.**	(acd)	**105.**	(acd)
106.	(abd)	**107.**	(abc)	**108.**	(abcd)	**109.**	(a)	**110.**	(d)	**111.**	(d)	**112.**	(a)	**113.**	(d)	**114.**	(d)	**115.**	(d)	**116.**	(d)	**117.**	(c)	**118.**	(a)	**119.**	(c)	**120.**	(c)
121.	(a)	**122.**	(c)	**123.**	(d)	**124.**	(d)	**125.**	(d)	**126.**	(a)	**127.**	(a)	**128.**	(a)	**129.**	(d)	**130.**	(c)	**131.**	(d)	**132.**	(b)	**133.**	(d)	**134.**	(d)	**135.**	(c)
136.	(c)	**137.**	(d)	**138.**	(b)	**139.**	(a)	**140.**	(b)	**141.**	(a)	**142.**	(a)	**143.**	(b)	**144.**	(b)	**145.**	(a)	**146.**	(b)	**147.**	(b)	**148.**	(a)	**149.**	(a)	**150.**	(b)
151.	(a)	**152.**	(a)	**153.**	(b)	**154.**	(b)	**155.**	(a)	**156.**	(c)	**157.**	(b)	**158.**	(c)	**159.**	(d)	**160.**	(b)	**161.**	(d)	**162.**	(b)	**163.**	(c)	**164.**	(b)	**165.**	(a)

Hints & Explanations

1. (*d*) Carbonyl compounds are of almost importance to organic chemistry.They are constituents of fabrics, flavourings, plastics and drugs.

2. (*d*) Aldehydes, ketones and carboxylic acids are widespread in plants and animal kingdom. They play an important role in biochemical processes of life.

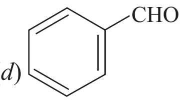
3. (*c*) Carbonyl compounds are used in many food products and pharmaceuticals to add flavours. Some of these families are manufactured for use as solvents (acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics etc.

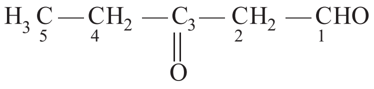
4. (*d*) Isoamyl acetate is obtained from bananas.

5. (*b*) 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.

6. (*b*) Some ketones have historical common names, the simplest ketone, i.e. dimethyl ketone is called acetone.

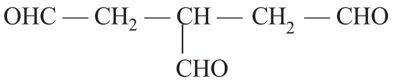
7. (*b*) When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cyclo alkane.

8. (*d*)  Benzaldehyde or benzenecarbaldehyde.

9. (*c*) 

$$\underset{5}{H_3C}-\underset{4}{CH_2}-\underset{\overset{\|}{O}}{C_3}-\underset{2}{CH_2}-\underset{1}{CHO}$$

3-oxopentanal

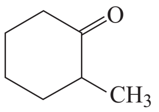


$$OHC-CH_2-\underset{\underset{CHO}{|}}{CH}-CH_2-CHO$$

Propan-1,2,3-tricarbaldehyde

10. (*c*) I → Pentan-2-one

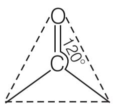
II → Diisopropyl ketone

III → 

IV → Mesityl oxide

11. (*d*) The carbonyl C-atom is *sp*^{2}-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its *p*-orbital and forms a π-bond with oxygen by overlap with *p*-orbital of an oxygen.

12. (*a*) The bond angles are approximately 120° as expected of a trigonal planar structure in the carbonyl compound.



Trigonal planar

13. (*a*) I → Sigma (σ) II → Pi (π)

14. (*d*)(i) Carbon-oxygen double bond is polar but carbon-carbon double bond is non-polar.

$$\overset{\delta^+}{C} \overset{\cdots\cdots}{=} \overset{\delta^-}{O}$$

(ii) Carbon-oxygen bond length is 123 pm than that of carbon-carbon bond length is 134 pm.

(iii) Carbonyl compounds undergo nucleophilic addition reactions but compounds containing ethylenic double bonds undergo electrophilic addition reactions.

15. (*a*) Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols respectively in presence of PCC.

16. (*b*) Alcohol vapours are passed over heavy metal catalysts (Ag or Cu) to give aldehydes and ketones. Primary and secondary alcohols give aldehydes and ketones respectively.

18. (*b*) Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde.

$$HC\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$$

19. (*b*) The given reaction is known as Rosenmund reduction where acyl chloride hydrogenated over palladium catalyst activated on barium sulphate.

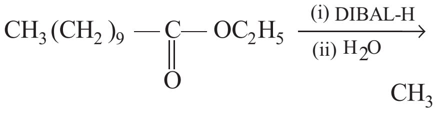
20. (*b*) Nitriles are reduced to corresponding imine with stannous chloride in the presence of HCl, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$$

This reaction is called Stephen reaction.

21. (*b*) Nitrile are selectively reduced by DIBAL-H to imines followed by hydrolysis to aldehyde. Esters are also reduced to aldehydes with DIBAL-H.

$$CH_3 \left(CH_2\right)_9 CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3(CH_2)_9CHO$$



$$CH_3(CH_2)_9-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

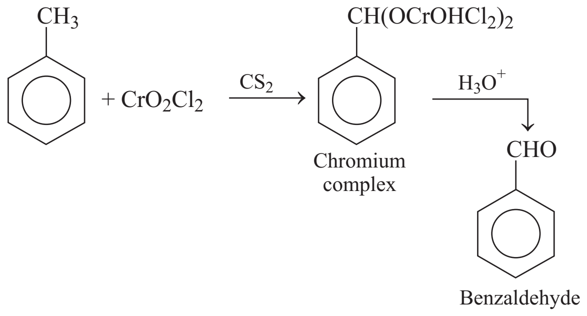
$$CH_3(CH_2)_9-CHO$$

22. (*b*) In the reaction,

$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2}$$

$$CH_3-CH=CH-CH_2-CH_2-CHO$$

23. (*c*) Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



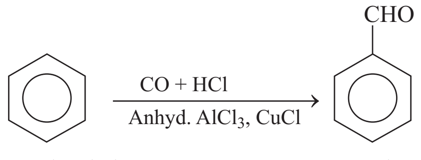
This reaction is called Etard reaction.

24. (*d*) $R\text{—CH}_2\text{OH}\xrightarrow{\text{PCC}}R\text{—CHO}$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

26. (*d*) The said reaction is known as Stephen reaction. In this reaction Nitrites are reduced to corresponding imine, which on hydrolysis given corresponding aldehyde.

27. (*a*) When benzene or its derivative is treated with carbon monoxide and HCl in the presence of anhyd. $AlCl_3$ or CuCl, it gives benzaldehyde or substituted benzaldehyde.

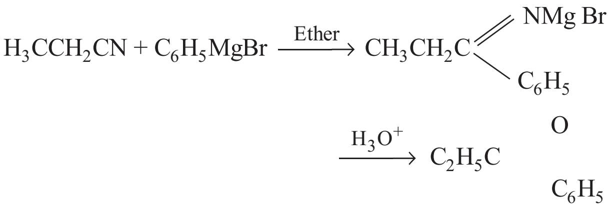


This reaction is known as Gattermann-Koch reaction.

28. (*d*) Treatment of acyl chlorides with dialkyl cadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

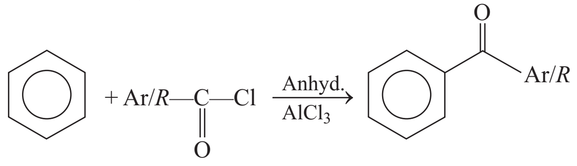
$$2R\text{—Mg—}X + \text{CdCl}_2 \longrightarrow R_2\text{Cd} + 2\text{Mg}(X)\text{Cl}$$
$$2R'\text{—COCl} + R_2\text{Cd} \longrightarrow 2R'\text{—CO}R + \text{CdCl}_2$$

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



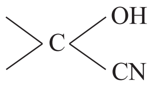
Propiophenone

When benzene or substituted benzene is treated with acid chloride in the presence of anhyd. $AlCl_3$ it gives the corresponding ketone. This reaction is known as Friedel-Craft, acylation reaction.

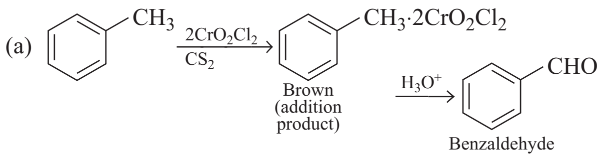


It is the Fries rearrangement.

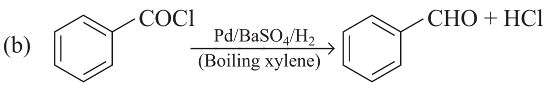
29. (*d*) Cynohydrin contain one —OH and one —CN group as follows.



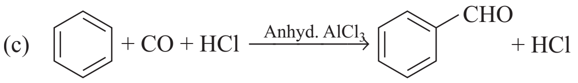
30. (*d*)



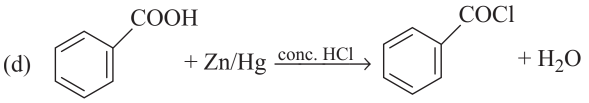
This reaction is known as Etard reaction.



This reaction is known as Rosenmund reduction.



This reaction is known as Gattermann-Koch aldehyde synthesis.



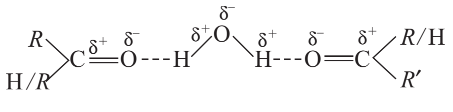
Thus, from the reagents given in option (d) benzaldehyde cannot be prepared.

31. (*d*) Reactivity of carbonyl compounds towards nucleophilic addition reactions depends on the presence of substituted group.

Electron withdrawing $(-I, -M)$ groups increase reactivity towards nucleophilic addition reactions.

32. (*b*) Methanal is a gas at room temperature. Ethanal is a volatile liquid.

33. (*b*) The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water.



34. (*a*) The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

The solubility of aldehyde and ketones decreases rapidly on increasing the length of the alkyl chain. All aldehyde and ketones are fairly soluble in organic solvents like benzene, ether, mathanol, chloroform etc.

35. (*c*) The boiling point of butan-1-ol would be highest, due to extensive intermolecular hydrogen bonding. Butanal is more polar than ethoxyethane. The intermolecular dipole-dipole attraction is stronger in the butanal.

n-pentane molecules have only weak van der Waals'-forces. The increasing order of boiling point of the given compounds are

$$IV < III < I < II$$

36. (*c*) A nucleophile attacks the electrophilic C-atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2-hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

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

37. (*b*) Aldehydes are more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

Due to absence of any alkyl group in formaldehyde, it is the most reactive compound in carbonyl family towards NAR.

38. (*d*) Important examples of nucleophilic addition reactions are :

(i) Addition of hydrogen cyanide (HCN)
(ii) Addition of sodium hydrogen sulphite
(iii) Addition of Grignard reagents

Important examples of nucleophilic addition elimination reactions alongwith nucleophilic addition are.

(i) Addition of alcohols
(ii) Addition of ammonia and its derivatives

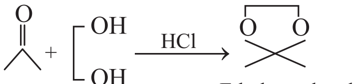
39. (*a*) In ethanal → propanal → propanone → butanone, the electron density on the carbon atom of the carbonyl group increases due to the increase of +*I*-effect of the alkyl group. Thus, the attack by the nucleophile becomes slower and slower. The reactivity increases in the reverse order : butanone < propanone < propanal < ethanal.

40. (*b*) The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons.

41. (*c*) Aldehydes react with one equivalent of monohydric alcohol in the presence of dry HCl to yield alkoxy alcohol intermediate, known as hemiacetals which further react with one more molecule of alcohol to give a *gem*-dialkoxy compound known as acetal. Hence,

I. hemiacetal or alkoxyalcohol.
II. acetal or *gem*-dialkoxy.

42. (*c*) Ketones react with ethylene glycol in the presence of dry HCl to form cyclic products known as ethylene glycol ketals.



Ethylene glycol ketal

In the above reaction dry HCl protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating the nucleophilic attack of ethylene glycol.

43. (*d*) Nucleophiles, such as ammonia and its derivatives $(H_2N—Z)$ add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate $>C<^{OH}_{NHZ}$

44. (*d*) I. $>C = NH$
II. Schiff's base
III. —OH
IV. Hydrazine $[NH_2 — NH_2]$

45. (*d*) Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$ as well as by catalytic hydrogenation.

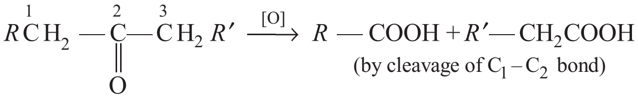
46. (*a*) The chemical reaction in which the carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol is known as Wolff-Kishner reduction.

$$>\!\!=O \xrightarrow[-H_2O]{H_2NNH_2} >\!\!=NNH_2 \xrightarrow[\text{Heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$$

47. (*d*) Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Even mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes.

48. (*c*) Ketones are generally oxidised under vigorous conditions, i.e. strong oxidising agents and at elevated temperatures.

Their oxidation involves carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



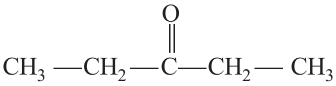
$$R\overset{1}{C}H_2 — \underset{\underset{O}{\|}}{\overset{2}{C}} — \overset{3}{C}H_2 R' \xrightarrow{[O]} R — COOH + R'— CH_2COOH$$

(by cleavage of $C_1 – C_2$ bond)

$$+ R — CH_2COOH + R'— COOH$$

(by cleavage of $C_2 – C_3$ bond)

49. (*c*) Since, the compound *X* yeilds phenyl hydrazone and gives negative response to the iodoform test and Tollen's test, it must contain a $>C = O$ group but is neither a methyl ketone nor an aldehyde. The structure of *X* could be



$$CH_3 — CH_2 — \overset{\overset{O}{\|}}{C} — CH_2 — CH_3$$

3-pentanone

having molecular formula $C_5H_{10}O$.

50. (*a*) Fehling solution *A* is aqueous copper sulphate and Fehling solution *B* is alkaline sodium potassium tartarate.

51. (*b*) On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

Aldehydes are oxidised to corresponding carboxylate anion.

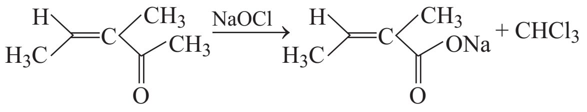
$$R\text{CHO} + 2\text{Cu}^{2+} + 5\text{OH} \longrightarrow R\text{COO}^- + \underset{\substack{\text{Red brown}\\\text{ppt.}}}{\text{Cu}_2\text{O}\downarrow} + 3\text{H}_2\text{O}$$

52. (*a*) Aromatic aldehydes and ketones do not give the positive Fehling test.

53. (*d*) Aldehydes and ketones having atleast one methyl group linked to the carbonyl C-atom are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acid.

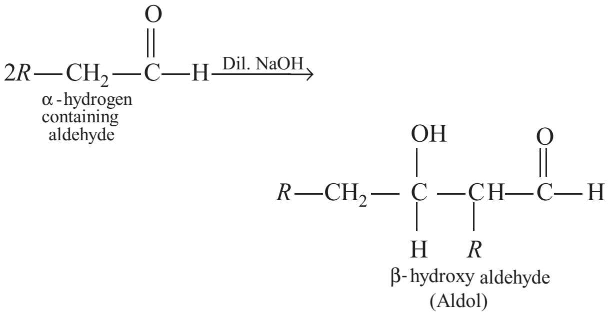
This is known as haloform reaction.

54. (*c*)



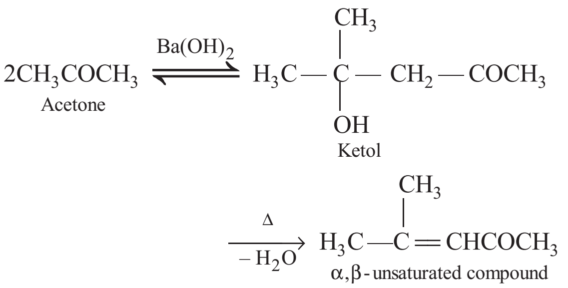
This oxidation does not affect the carbon-carbon double bond, if present in the molecule.

55. (*c*) Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as aldol reaction.



$$\underset{\substack{\alpha\text{-hydrogen}\\\text{containing}\\\text{aldehyde}}}{2R\text{—CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H}} \xrightarrow{\text{Dil. NaOH}} \underset{\substack{\beta\text{-hydroxy aldehyde}\\\text{(Aldol)}}}{R\text{—CH}_2\text{—}\overset{\overset{\text{OH}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—}\underset{\underset{R}{|}}{\text{CH}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H}}$$

56. (*b*)

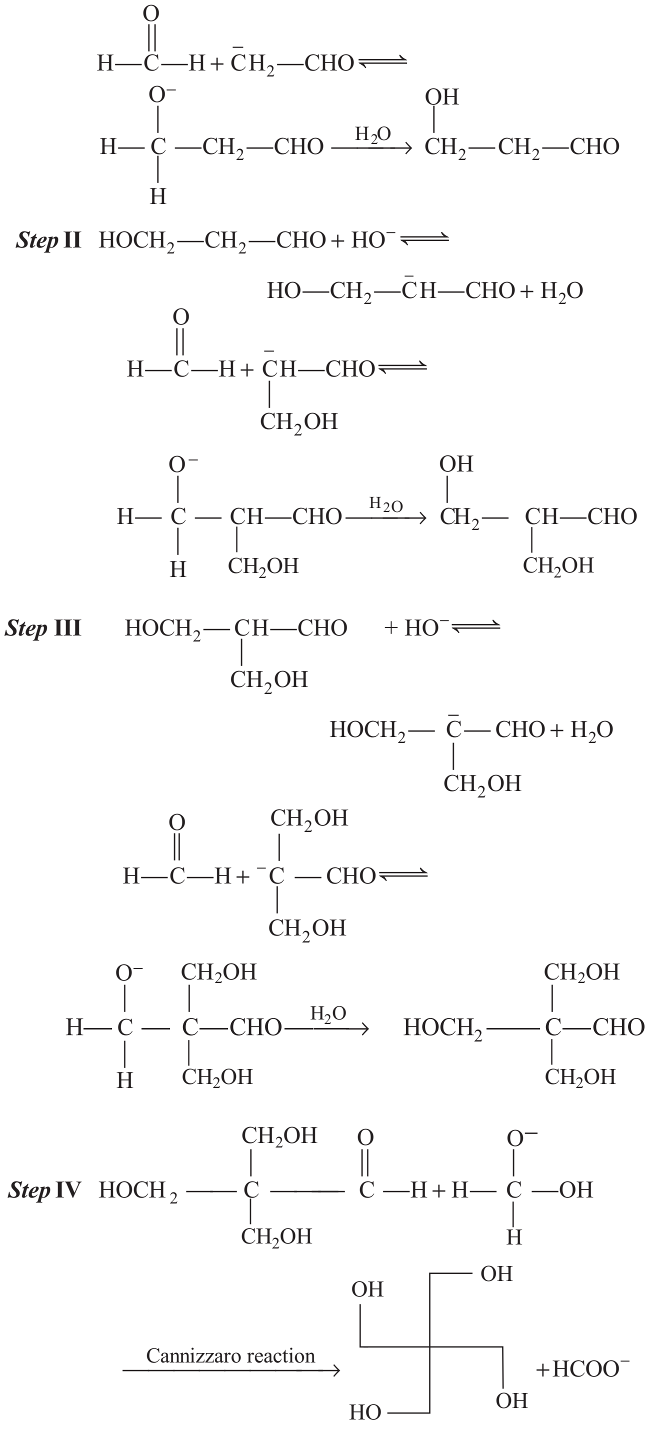


$$\underset{\text{Acetone}}{2\text{CH}_3\text{COCH}_3} \xrightleftharpoons{\text{Ba(OH)}_2} \underset{\text{Ketol}}{\text{H}_3\text{C—}\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{OH}}{|}}{\text{C}}}\text{— CH}_2\text{—COCH}_3}$$

$$\xrightarrow[-\text{H}_2\text{O}]{\Delta} \underset{\alpha,\beta\text{-unsaturated compound}}{\text{H}_3\text{C—}\overset{\overset{\text{CH}_3}{|}}{\text{C}}\text{=CHCOCH}_3}$$

57. (*c*) The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.

Step **I** $\text{CH}_3\text{CHO} + \text{OH}^- \longrightarrow \bar{\text{C}}\text{H}_2\text{—CHO} + \text{H}_2\text{O}$



$$\text{H—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H} + \bar{\text{C}}\text{H}_2\text{—CHO} \rightleftharpoons$$

$$\text{H—}\overset{\overset{\text{O}^-}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—CH}_2\text{—CHO} \xrightarrow{\text{H}_2\text{O}} \overset{\overset{\text{OH}}{|}}{\text{CH}_2}\text{—CH}_2\text{—CHO}$$

Step **II** $\text{HOCH}_2\text{—CH}_2\text{—CHO} + \text{HO}^- \rightleftharpoons$

$$\text{HO—CH}_2\text{—}\bar{\text{C}}\text{H—CHO} + \text{H}_2\text{O}$$

$$\text{H—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H} + \underset{\underset{\text{CH}_2\text{OH}}{|}}{\bar{\text{C}}\text{H}}\text{—CHO} \rightleftharpoons$$

$$\text{H—}\overset{\overset{\text{O}^-}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—}\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{CH}}\text{—CHO} \xrightarrow{\text{H}_2\text{O}} \overset{\overset{\text{OH}}{|}}{\text{CH}_2}\text{—}\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{CH}}\text{—CHO}$$

Step **III**

$$\text{HOCH}_2\text{—}\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{CH}}\text{—CHO} + \text{HO}^- \rightleftharpoons$$

$$\text{HOCH}_2\text{—}\underset{\underset{\text{CH}_2\text{OH}}{|}}{\bar{\text{C}}}\text{—CHO} + \text{H}_2\text{O}$$

$$\text{H—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H} + {}^-\overset{\overset{\text{CH}_2\text{OH}}{|}}{\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{C}}}\text{—CHO} \rightleftharpoons$$

$$\text{H—}\overset{\overset{\text{O}^-}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—}\overset{\overset{\text{CH}_2\text{OH}}{|}}{\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{C}}}\text{—CHO} \xrightarrow{\text{H}_2\text{O}} \text{HOCH}_2\text{—}\overset{\overset{\text{CH}_2\text{OH}}{|}}{\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{C}}}\text{—CHO}$$

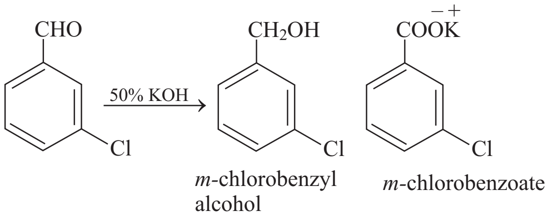
Step **IV**

$$\text{HOCH}_2\text{—}\overset{\overset{\text{CH}_2\text{OH}}{|}}{\underset{\underset{\text{CH}_2\text{OH}}{|}}{\text{C}}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—H} + \text{H—}\overset{\overset{\text{O}^-}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—OH}$$

$$\xrightarrow{\text{Cannizzaro reaction}} \text{C(CH}_2\text{OH)}_4 + \text{HCOO}^-$$

In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

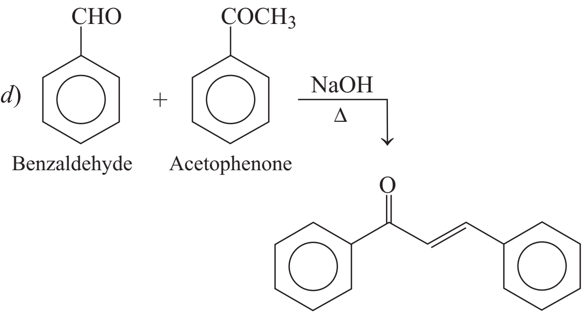
58. (*c*) When benzaldehyde is treated with 50% alkali, it undergoes oxidation to give an acid salt as well as reduction to give an alcohol. This reaction is called Cannizzaro's reaction.



59. (*c*) The C-atom of the carbonyl group of benzaldehyde is less electrophilic than C-atom of the carbonyl group present in propanal due to resonance. Hence, it is less reactive than propanal towards nucleophilic addition reaction.

60. (*c*) **Cannizzaro reaction** Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali.

61. (*d*)



62. (*c*) $>C=O \xrightarrow{I_2+NaOH} -COOH$

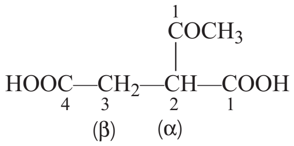
e.g. $H_3C-CH=CH-CH_2-COCH_3 \xrightarrow{I_2 + NaOH\ solution} CH_3-CH=CH-CH_2-COOH$

63. (*c*) Formaldehyde is known as formalin (40%) solution. It is used to preserve biological specimen.

64. (*d*) All are correct statement.

65. (*a*) Some higher members of aliphatic carboxylic acids contains ($C_{12}-C_{18}$) known as fatty acids, occur in natural fats as esters of glycerol.

66. (*a*)

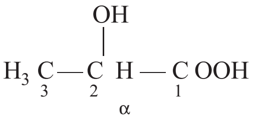


$$\underset{4}{HOOC}-\underset{3\,(\beta)}{CH_2}-\underset{2\,(\alpha)}{\overset{\overset{1}{COCH_3}}{\overset{|}{CH}}}-\underset{1}{COOH}$$

Common name → α-acetylsuccinic acid.

IUPAC name → 2- (1-oxoethyl) butane-1, 4-dioic acid. 3

67. (*c*)

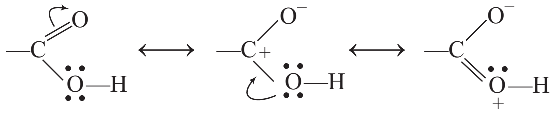


$$\underset{3}{H_3C}-\underset{\substack{2\\ \alpha}}{\overset{\overset{OH}{|}}{C}H}-\underset{1}{C}OOH$$

Common name → Lactic acid or α-hydroxy propanoic acid.

IUPAC → 2-hydroxypropanoic acid.

68. (*a*) The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonating structure shown below.

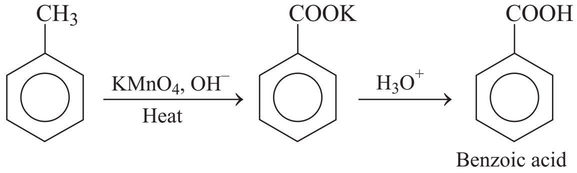


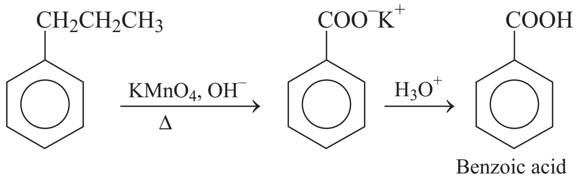
69. (*d*) Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as $KMnO_4$ in neutral, acidic or alkaline medium or by $K_2Cr_2O_7$ and CrO_3 in acidic medium.

$$CH_3(CH_2)_8CH_2OH \xrightarrow[\text{or } CrO_3\text{-}H_2SO_4]{\text{Alk. } KMnO_4,\ H_3O^+} CH_3(CH_2)_8COOH$$

70. (*b*) Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or alkaline potassium permanganate.

The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.





71. (*d*) Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

$$R-CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} RCONH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$$

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.

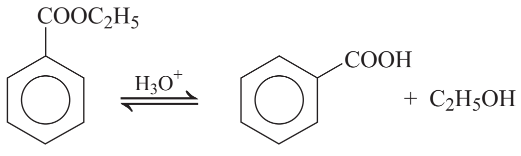
$$R-MgX + CO_2 \xrightarrow[\text{ether}]{\text{Dry}} R-COO^-MgX \xrightarrow{H_3O^+} RCOOH$$

72. (*c*) Formic acid cannot be prepared by Grignard reagent.

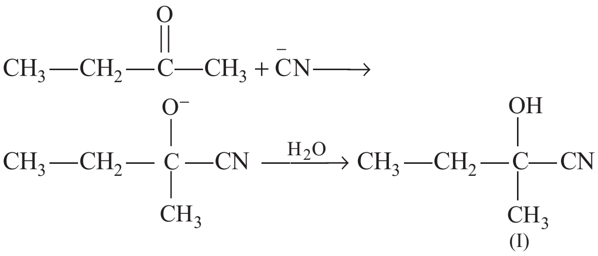
73. (*b*) $\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\substack{\text{Benzoic acid}\\(I)}}{2C_6H_5-COOH}$

$$\underset{\substack{\text{Benzoyl ethanoic}\\ \text{anhydride}}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\substack{\text{Benzoic acid}\\(II)}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

74. (*a*) Acidic hydrolysis of esters directly give carboxylic acids while basic hydrolysis of esters gives carboxylates, which on acidification give corresponding carboxylic acids.



75. (*a*) The first step is cyanohydrin reaction,

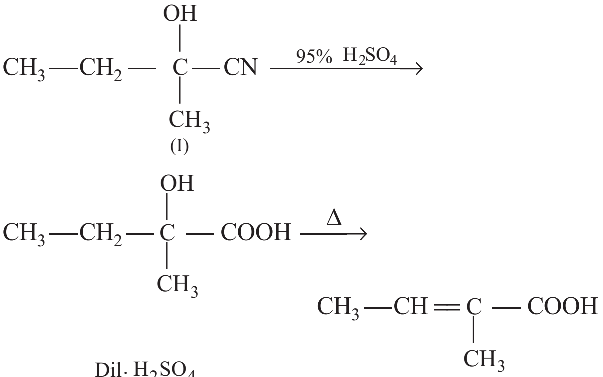


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3+\overset{-}{C}N\longrightarrow$$

$$CH_3-CH_2-\underset{CH_3}{\overset{O^-}{C}}-CN\xrightarrow{H_2O}CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-CN$$

(I)

In the second step the —CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc. H_2SO_4.



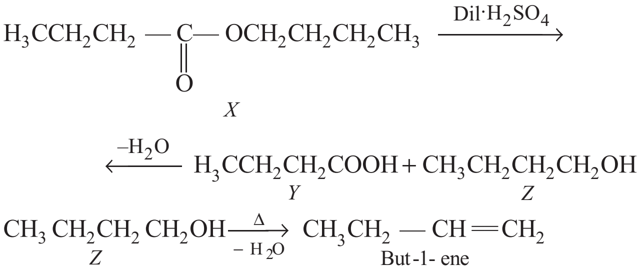
$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-CN\xrightarrow{95\%\ H_2SO_4}$$

(I)

$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-COOH\xrightarrow{\Delta}$$

$$CH_3-CH=\underset{CH_3}{C}-COOH$$

76. (*c*) $X \xrightarrow{Dil \cdot H_2SO_4} Y + Z$

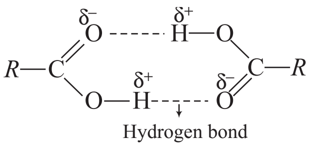


$$\underset{X}{H_3CCH_2CH_2-\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3}\xrightarrow{Dil \cdot H_2SO_4}$$

$$\xleftarrow{-H_2O}\underset{Y}{H_3CCH_2CH_2COOH}+\underset{Z}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{Z}{CH_3\,CH_2CH_2\,CH_2OH}\xrightarrow[-H_2O]{\Delta}\underset{\text{But-1-ene}}{CH_3CH_2-CH=CH_2}$$

77. (*a*) Carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



78. (*d*) Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature. Other option are correct.

79. (*c*) The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogen carbonates to evolve CO_2.

$$2RCOOH + 2Na \longrightarrow \underset{\text{Sodium carbonate}}{2RCOO^-Na^+} + \underset{X}{H_2\uparrow}$$

$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + \underset{Y}{CO_2\uparrow}$$

80. (*a*) Smaller the pK_a stronger is the acid. Hence, correct order is

$$I < II < III < IV$$

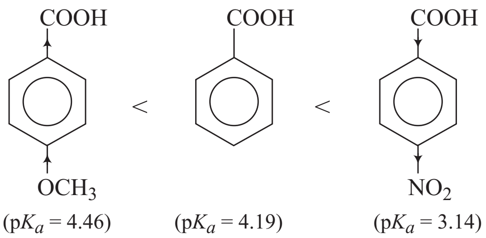
81. (*b*) Carboxylic acids are weaker than mineral acids but they are stronger acids than alcohols and many simple phenols (pK_a is ~ 16 for ethanol and 10 for phenol).

82. (*b*) I → $CHCl_2COOH$

II → HCOOH

III → CH_3COOH

83. (*a*) The presence of electron withdrawing group on the benzene ring of aromatic carboxylic acid increases their acidity, while electron donating group decreases their acidity.



84. (*a*) Acidity increases as the electronegativity of the C-atom directly attached to —COOH group increases or the hybridisation of the C-atom directly attached to COOH changes from $sp^3 \rightarrow sp^2 \rightarrow sp$.

The acidic strength decrease in the order

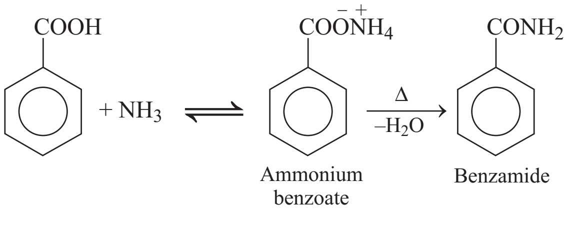
$$I > II > III > IV$$

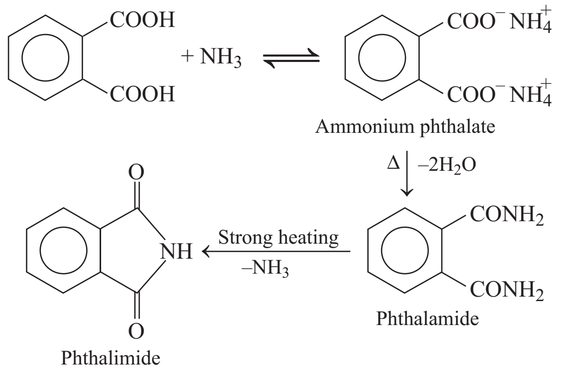
85. (*d*) The acidity of halogenated acid increases with increase in electronegativity of the halogen present. The correct order is

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$$

86. (*c*) Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.

87. (*d*) Carboxylic acids react with ammonia to give ammonium salt, which on further heating at high temperature give amides.





88. (*a*) Diborane does not easily reduce functional groups such as ester, nitro, halo etc. Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane.

89. (*c*) Sodalime is the mixture of NaOH and CaO in the ratio of 3 : 1.

90. (*d*) Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime. The reaction is known as decarboxylation.

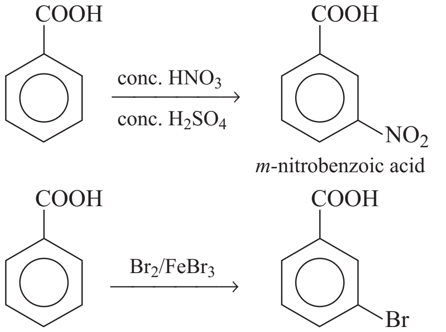
$$R-COONa \xrightarrow[\text{Heat}]{\text{NaOH and CaO}} RH + Na_2CO_3$$

91. (*a*) Alkali metal salts of carboxylic acids undergo decarboxylation on electrolysis of their aqueous solution and form hydrocarbons having twice the number of C-atoms present in the alkyl group of the C-atoms present in the alkyl group of the acid. The reaction is known as Kolbe electrolysis.

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

93. (*b*) Aromatic carboxylic acids do not undergo Friedel-Crafts' reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid)gets bonded to the carboxyl group, which facilitate the reaction at *ortho* and *para*-position.

94. (*d*)

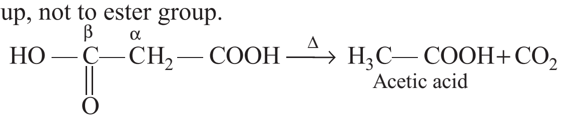


m-nitrobenzoic acid

m-bromobenzoic acid

95. (*d*) $NaBH_4$ is a reducing agent but it only reduce carbonyl group, not to ester group.

96. (*a*)



$$HO-\overset{\beta}{\underset{\underset{O}{\|}}{C}}-\overset{\alpha}{C}H_2-COOH \xrightarrow{\Delta} \underset{\text{Acetic acid}}{H_3C-COOH}+CO_2$$

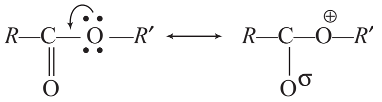
Malonic acid

97. (*a*) The order of reactivity is explained in the terms of the relative basic strength of the leaving groups. The relative basic strength decrease in the order

$$NH_2^- > RO^- > R'COO^- > Cl^-$$

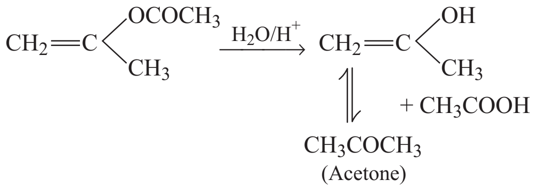
Hence, the correct order of reactivity is acid chlorides > anhydrides > ester > amide.

98. (*a*) (I) oxygen is more basic than (II) oxygen because lone pair of (II) oxygen is involved in the resonance.

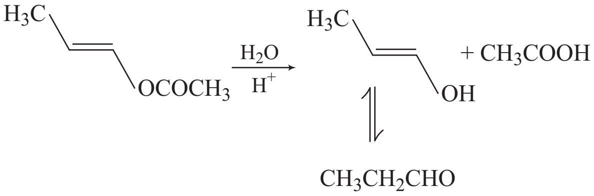


$$R-\underset{\underset{O}{\|}}{C}-\ddot{O}-R' \longleftrightarrow R-\underset{\underset{O^{\sigma}}{|}}{C}-\overset{\oplus}{O}-R'$$

99. (*c*)

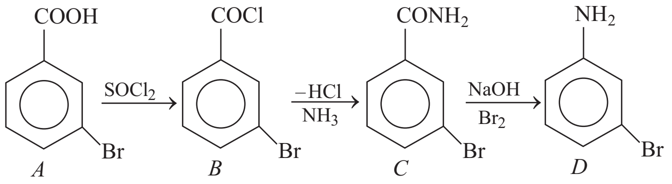


Fehling's solution does not reduce the acetone.



Fehling's solution can reduce the aldehyde.

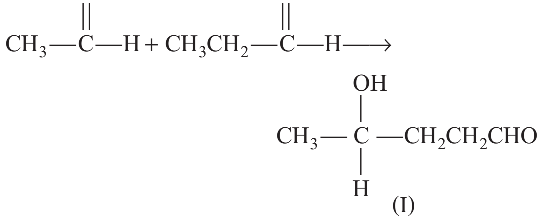
100. (*d*)



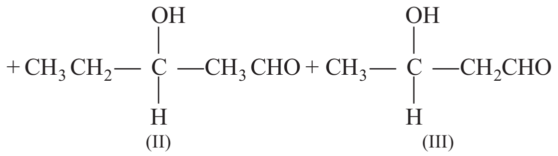
101. (*c*) Methanoic acid is used in rubber, textile, dye, leather and electroplating industries.

103. (*c*)
- (a) Aromatic aldehyde and ketones are meta-directive by nature.
- (b) They are not of oval shapes.
- (c) Yes, many of the aldehydes and ketones are well known for their odour and flavour.
- (d) Aldehydes only oxidised by mild (or weak) oxidising agents like Tollen's reagent, Fehling solution etc.

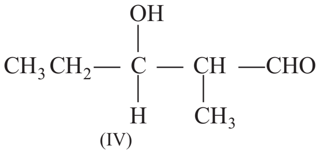
104. (*a,c,d*)
- (a) Due to absence of α-hydrogen, CCl_3CHO does not exhibit aldol condensation.
- (b)



$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3CH_2-\overset{\overset{O}{\|}}{C}-H \longrightarrow \underset{\text{(I)}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_2CHO}$$

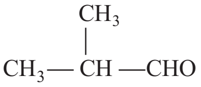


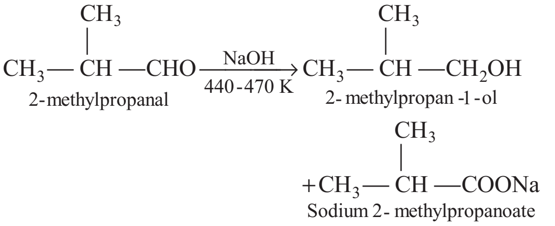
$$\underset{(II)}{+CH_3CH_2-\underset{H}{\overset{OH}{C}}-CH_3CHO} + \underset{(III)}{CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO}$$



$$\underset{(IV)}{CH_3CH_2-\underset{H}{\overset{OH}{C}}-\underset{CH_3}{CH}-CHO}$$

(c) $HCHO + CH_3CHO \xrightarrow[\text{condensation}]{\text{Cross aldol}} \text{Aldol products}$

(d)  $CH_3-\overset{CH_3}{CH}-CHO$ undergoes Cannizzaro reaction apart from having α-H-atom. It is due to the formation of less stable carbanion.



$$\underset{\text{2-methylpropanal}}{CH_3-\overset{CH_3}{CH}-CHO} \xrightarrow[440\text{-}470\ K]{NaOH} \underset{\text{2-methylpropan-1-ol}}{CH_3-\overset{CH_3}{CH}-CH_2OH} + \underset{\text{Sodium 2-methylpropanoate}}{CH_3-\overset{CH_3}{CH}-COONa}$$

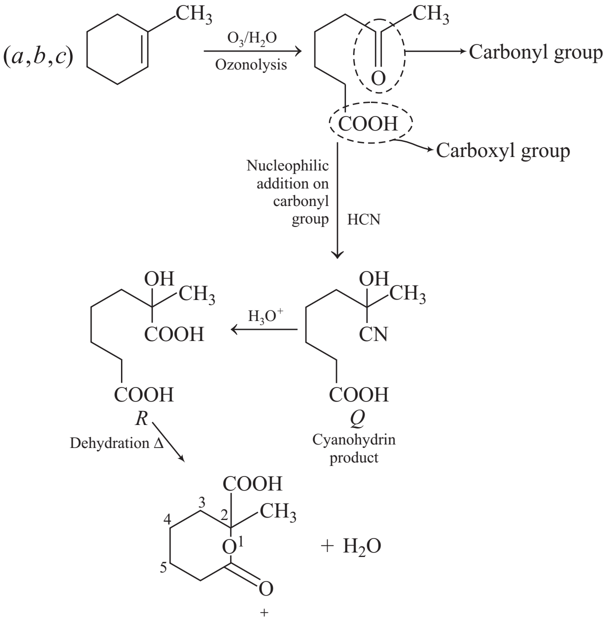
105. (*a,c,d*) *a,c,d* are incorrect. Only (b) is correct, i.e.

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{I_2/NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[NH_3]{H^+}$$

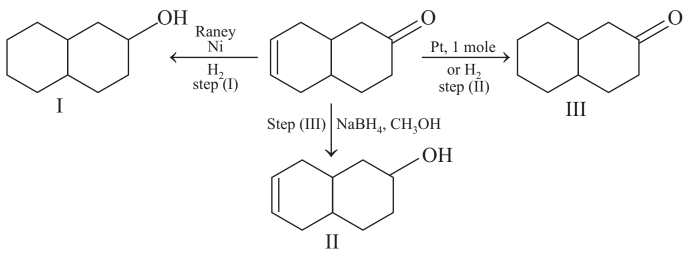
$$\underset{\text{Acetamide}}{CH_3CONH_2} \xleftarrow{\Delta} \underset{\text{Ammonium acetate}}{CH_3CO\overset{-}{O}\overset{+}{N}H_4}$$

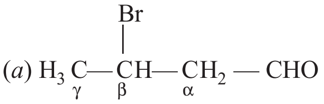
106. (*a,b,d*) Only (c) is incorrect as both ethanal and propanal will give silver mirror test and red precipitate with Fehling's solution. They can be distinguished by iodoform test.

107. (*a,b,c*)



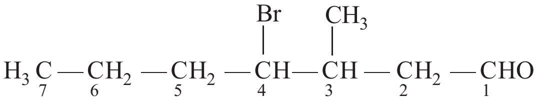
108. (*a,b,c,d*)



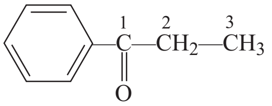
109. (*a*)  $H_3\underset{\gamma}{C}-\underset{\beta}{\overset{Br}{CH}}-\underset{\alpha}{CH_2}-CHO$

β- bromobutyraldehyde.

The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ etc. The α-carbon being the one directly linked to the aldehyde group, β-carbon the next and so on.

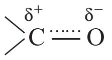
110. (*d*)  $H_3\underset{7}{C}-\underset{6}{CH_2}-\underset{5}{CH_2}-\underset{4}{\overset{Br}{CH}}-\underset{3}{\overset{CH_3}{CH}}-\underset{2}{CH_2}-\underset{1}{CHO}$

4-bromo-3-methylheptanal

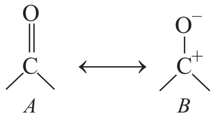


1-phenylpropan-1-one

111. (*d*) The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. The carbonyl carbon is an electrophilic (Lewis acid) and the carbonyl oxygen is a nucleophilic (Lewis base) centre.



112. (*a*) Carbonyl compounds have substantial dipole moments thus, they are polar. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (*A*) and a dipolar (*B*) structures as shown.



113. (*d*) The dipole moment of aldehydes and ketones (2.3 – 2.8 D) is much higher than that of alcohols (1.6 – 1.8 D).

114. (*d*) π-electron of the carbonyl bond is unsymmetrical because the O-atom in the carbonyl group is far more electronegative than C-atom. As the result, the O-atom tends to attract the electron cloud of the π-bond towards itself.

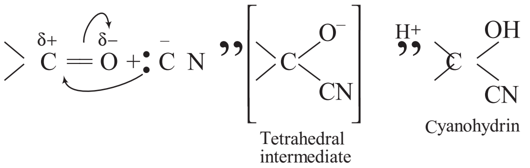
115. (*d*) Formaldehyde cannot be prepared by the Rosenmund reduction since formylchloride, HCOCl, is unstable at room temperature.

116. (*d*) The boiling points of aldehydes and ketones are greater than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

117. (*c*) Aldehydes and ketones react with hydrogen cyanide to yield cyanohydrins. This reaction occurs very slowly with pure HCN.

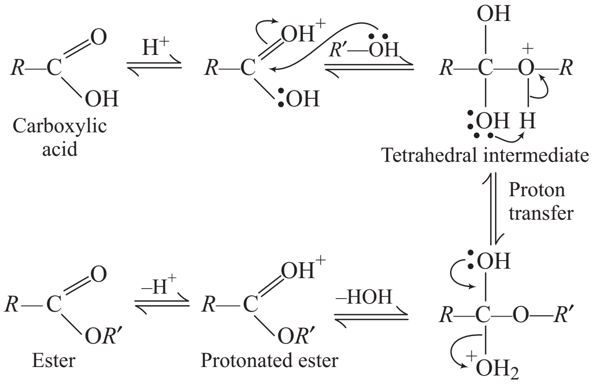
Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

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



118. (*a*) The hydrogen sulphite adduct is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for the separation and purification of aldehydes.

119. (*c*) Protonation of the carboxyl oxygen activates the carbonyl group toward nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-\overset{\oplus}{O}H_2$ group which being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



120. (*c*) $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$3RCOOH + PCl_5 \longrightarrow 3RCOCl + H_3PO_3$

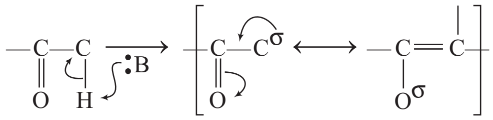
$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

Thionyl chloride is preferred because the other two products are gaseous and escape from the reaction mixture making the purification of the products easier.

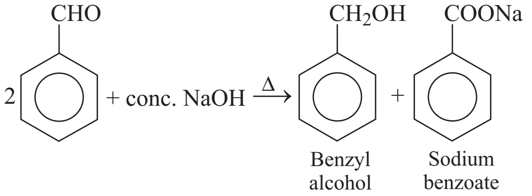
121. (*a*) On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

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

122. (*c*) The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



123. (*d*)



Benzaldehyde does not have α-hydrogen. On reaction with alkali it undergoes Cannizzaro reaction.

124. (*d*) Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.

125. (*d*) The IUPAC name of $CH_3CH_2CH_2COOH$ is butanoic acid. In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending '-e' in the name of the corresponding alkane with -oic acid.

126. (*a*) IUPAC name of $HOOC\ (CH_2)_2\ COOH$ is butanedioic acid. For naming compounds containing more than one carboxyl group, the ending -e of the alkane is retained. The number of carboxyl groups are indicated by adding the multiplicative prefix, di, tri etc., to the term 'oic'.

127. (*a*) Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

128. (*a*) The molecular mass of acetic acid in benzene is 120 instead of 60 because the carboxylic acid exists as cyclic dimers in which two molecules of the acid are held together by two strong hydrogen bonds.

129. (*d*) The melting points and boiling points of aromatic acids are usually higher than those of aliphatic acids of comparable molecular masses.

This is due to the planar benzene ring in the aromatic acids which can fit more closely in the crystal lattice than *zig-zag* structure of aliphatic acids.

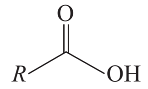
130. (*c*) Carboxylate ion is more stable than phenoxide ion due to two equivalent resonating structures in which negative charge is at the O-atom. In phenoxide ion, negative charge is at the less-electronegative carbon atom.

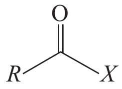
Therefore, corresponding acid of the carboxylate ion, i.e. carboxylic acid is more acidic than phenol.

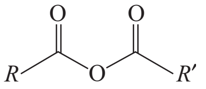
131. (*d*) Ester hydrolysis is slow in the beginning and becomes fast after sometime because a small amount of dilute sulphuric acid is added in the begining to start the reaction.

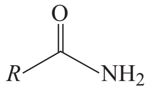
As the reaction proceeds, *R*COOH is produced. The rate of ester hydrolysis increases with the increase in the amount of carboxylic acid produced.

132. (*b*) A →2, B → 1, C → 4, D → 3.

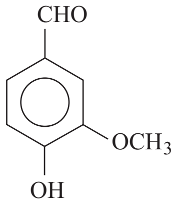

Carboxylic acid

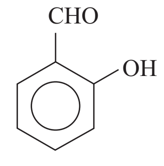

Acyl halide

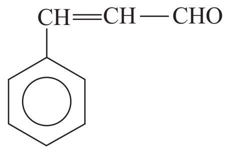

Acid anhydride


Amide

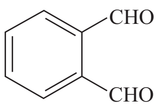
133. (*d*) A → 3, B → 1, C → 2


Vanillin
(from vanilla beans)


Salicylaldehyde
(from meadow sweets)


Cinnamaldehyde (from cinnamon)

134. (*d*) A → 4, B → 1 C → 3, D → 2.

Structure	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1, 2-dicarbaldehyde

135. (*c*) A → 1, B → 3, C → 2.

$$\text{Hexan-1-ol} \xrightarrow{PCC} \text{Hexanal}$$

$$\text{Cyclohexanol} \xrightarrow[CrO_3]{K_2Cr_2O_7\text{ (acidic)}} \text{Cyclohexanone}$$

$$p\text{-fluorotoluene} \xrightarrow[(CH_3COO)_2O]{CrO_3} p\text{-fluorobenzaldehyde}$$

136. (*c*) A → 2, B → 3, C → 1.

$$\underset{\text{Ethane nitrile}}{CH_3-C\equiv N} \xrightarrow{\text{DIBAL-H}} \underset{\text{Ethanal}}{CH_3CHO}$$

$$\underset{\text{Allyl alcohol}}{CH_2=CH-CH_2OH} \xrightarrow{PCC} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

$$\underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3} \xrightarrow[\text{Zn dust}]{O_3/H_2O} \underset{\text{Ethanal}}{2CH_3CHO}$$

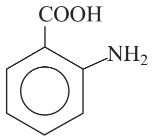
137. (*d*) A → 2, B → 4, C → 1, D → 3.

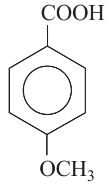
Formaldehyde is used to prepare bakelite. Acetaldehyde is used primarily as starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate. Benzaldehyde is used in perfume and in dye industries. Butyraldehyde, vanillin, acetophenone, camphor are well known for their odours and flavour.

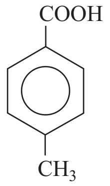
138. (*b*) A → 4,B → 3,C → 1, D → 2

Structure	Common name	IUPAC name
HOOC—COOH	Oxalic acid	Ethane-1, 2-dioic acid
$HOOC-(CH_2)_2COOH$	Succinic acid	Butane-1, 4-dioic acid
$HOOC-(CH_2)_3COOH$	Glutaric. acid	Pentane-1, 5-dioic acid
$HOOC-(CH_2)_4COOH$	Adipic acid	Hexane-1, 6-dioic acid

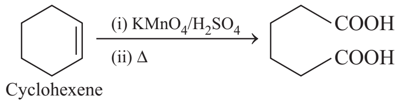
139. (*a*) A → 2,B → 1,C → 3


: Anthranilic acid

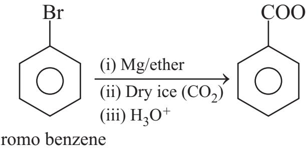

: Anisic acid


: Toluic acid

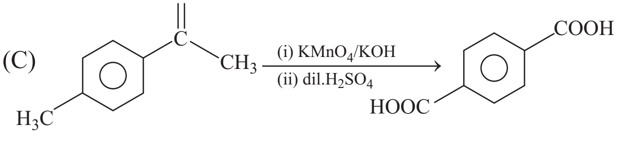
140. (*b*) A → 3, B → 1,C → 2

(A)


Cyclohexene

(B)


Bromo benzene

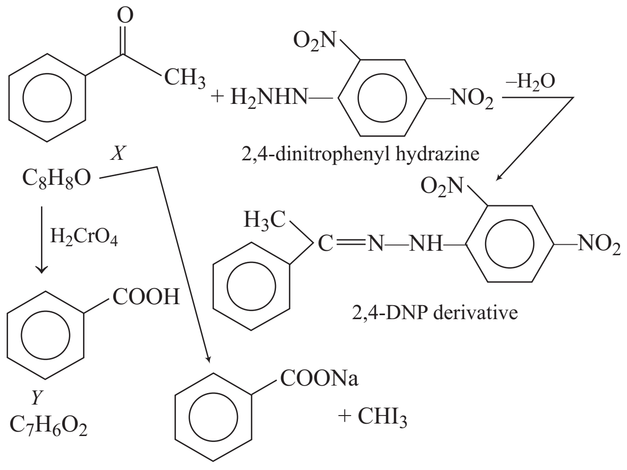
(C)


141. (*a*) A → 4, B → 2, C → 3, D → 1.

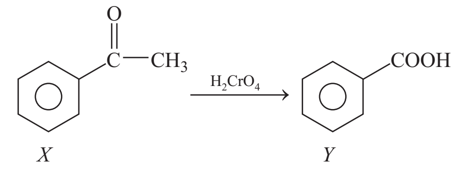
Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6,6. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

142. (*a*) (*X*) forms 2, 4-DNP derivative so it is an aldehyde or ketone. (*X*) must be ketone as it does not reduce Tollen's or Fehling reagent. (*X*) must be methylketone as it responds to iodoform test. (*X*) do not decolourise bromine water.

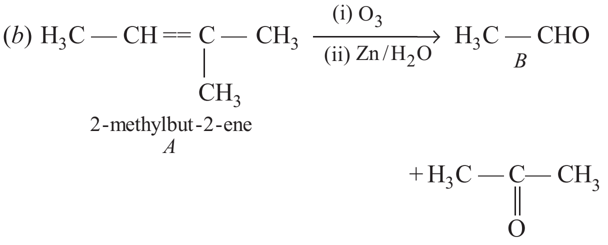
Which suggests the presence of unsaturation due to an aromatic ring. Compound (*Y*) should be benzoic acid according to the molecular formula of (*Y*). The compound (*X*) must be monosubstituted aromatic methyl ketone.



143. (*b*)



144. (*b*)

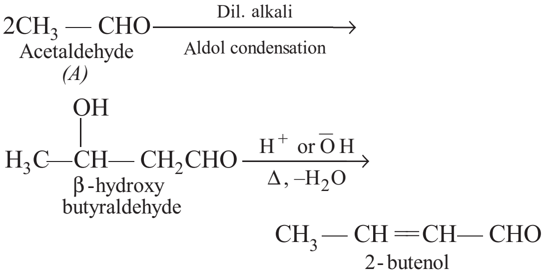


$$H_3C-CH=\underset{\underset{CH_3}{|}}{C}-CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} \underset{B}{H_3C-CHO} + \underset{C}{H_3C-\underset{\underset{O}{\|}}{C}-CH_3}$$

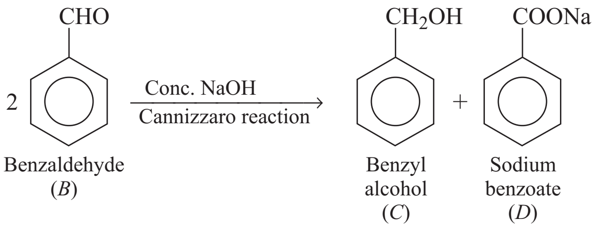
2-methylbut-2-ene
A

145. (*a*) $(B) \rightarrow CH_3CHO$; $(C) \rightarrow H_3CCOCH_3$

146. (*b*)

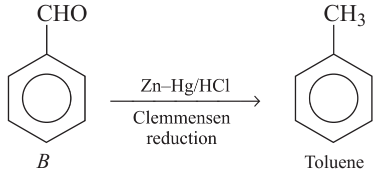


$$2\underset{\substack{\text{Acetaldehyde}\\(A)}}{CH_3-CHO} \xrightarrow[\text{Aldol condensation}]{\text{Dil. alkali}} \underset{\substack{\beta\text{-hydroxy}\\\text{butyraldehyde}}}{H_3C-\overset{\overset{OH}{|}}{C}H-CH_2CHO} \xrightarrow[\Delta,\,-H_2O]{H^+ \text{ or } \bar{O}H} \underset{\text{2-butenol}}{CH_3-CH=CH-CHO}$$

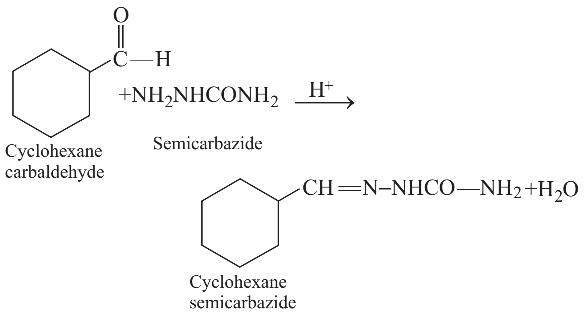


147. (*b*) The reactions occur in the given information are aldol condensation and Cannizzaro out of which Cannizzaro reaction occurs in the last stage.

148. (*a*)



149. (*a*)



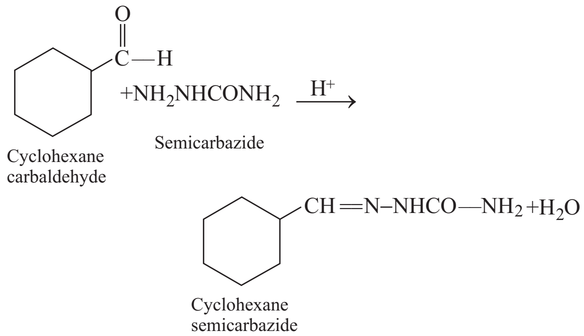
150. (*b*)

(i) The compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, so it is an aldehyde.

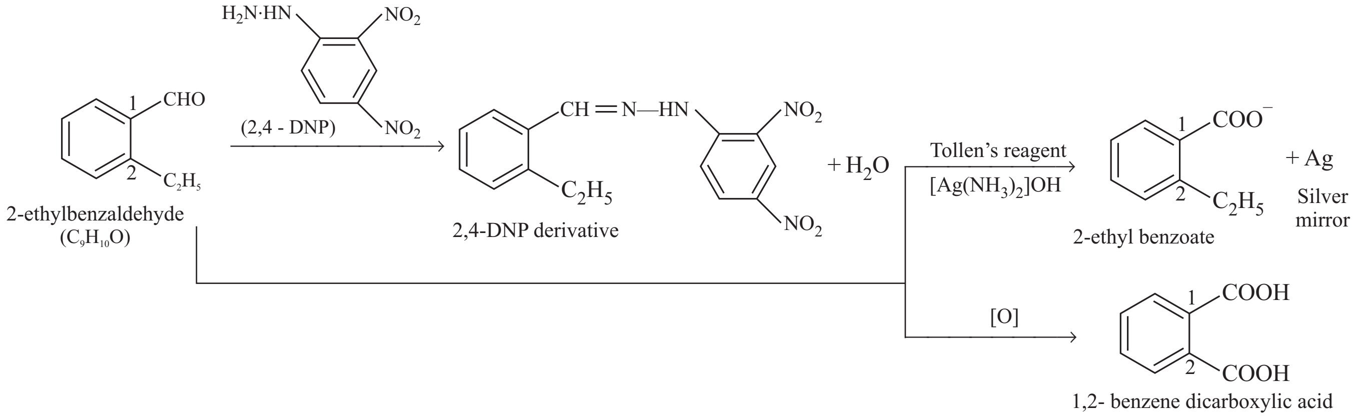
(ii) It undergoes Cannizzaro reaction, so the aldehyde group should be directly attached to the benzene ring.

(iii) On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid, so it should be an *ortho* substituted benzaldehyde.

For molecular formula $C_9H_{10}O$, the possibility is only *o*-ethylbenzaldehyde.



(iv) The equations for all the reactions are given below :



151. (*a*) The reactivity of a compound depends on the steric hindrance due to the groups present around the carbonyl group. Greater the steric hindrance, less will be the reactivity of the compound. Reactivity towards HCN is in following order:

Di-tertiary butyl ketone < methyl tertiary butyl ketone < acetone < acetaldehyde

152. (*a*) **Step I** To determine the molecular formula of the compound.

Element	Percentage	Atomic mass	Number of moles	Simplest molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.81$	$\frac{5.81}{1.16} = 5$
H	11.63	1	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10$
O	$(100 - 69.77 - 11.63) = 18.60$	16	$\frac{18.60}{16} = 1.16$	$\frac{1.16}{1.16} = 1$

Empirical formula of the given organic compound = $C_5H_{10}O$.

$$\text{Molecular formula} = n \times (\text{empirical formula}) \quad \text{where, } n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$

Given, molecular mass = 86

Empirical formula mass of $C_5H_{10}O = (12 \times 5) + (10 \times 1) + (16) = 60 + 10 + 16 \Rightarrow n = \frac{86}{86} = 1$

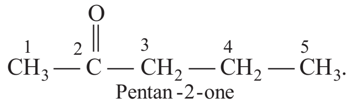
Molecular formula = $1 \times C_5H_{10}O = C_5H_{10}O$

Step II Predicting the structure of the compound.

Criteria : 1. Formation of addition compound with $NaHSO_3$ depicts the presence of aldehyde or ketone.

2. The given compound does not reduce Tollen's reagent but gives positive iodoform test, so it is a methyl ketone.

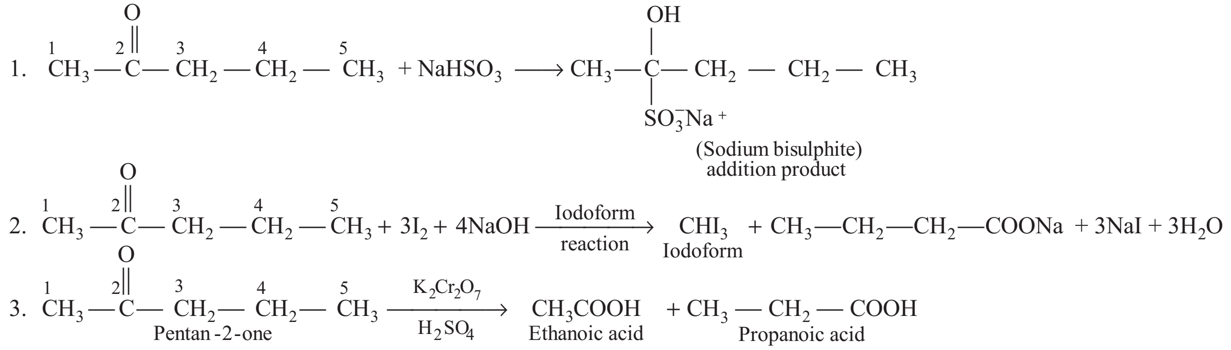
3. On oxidation, the compound forms a mixture of ethanoic and propanoic acid, so it is



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

Pentan-2-one

Step III Chemical equations



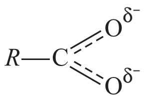
$$1.\quad \overset{1}{CH_3}—\overset{\overset{O}{\|}}{\underset{2}{C}}—\overset{3}{CH_2}—\overset{4}{CH_2}—\overset{5}{CH_3} + NaHSO_3 \longrightarrow CH_3—\underset{SO_3^-Na^+}{\overset{OH}{C}}—CH_2—CH_2—CH_3$$

(Sodium bisulphite) addition product

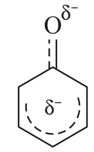
$$2.\quad \overset{1}{CH_3}—\overset{\overset{O}{\|}}{\underset{2}{C}}—\overset{3}{CH_2}—\overset{4}{CH_2}—\overset{5}{CH_3} + 3I_2 + 4NaOH \xrightarrow[\text{reaction}]{\text{Iodoform}} \underset{\text{Iodoform}}{CHI_3} + CH_3—CH_2—CH_2—COONa + 3NaI + 3H_2O$$

$$3.\quad \underset{\text{Pentan-2-one}}{\overset{1}{CH_3}—\overset{\overset{O}{\|}}{\underset{2}{C}}—\overset{3}{CH_2}—\overset{4}{CH_2}—\overset{5}{CH_3}} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{CH_3—CH_2—COOH}$$

153. (*b*) Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the less electronegative C-atom. The negative charge is delocalised over two electronegative O-atoms in carboxylate ion whereas in phenoxide ion the negative charge less effectively delocalised over one oxygen atom and less electronegative O-atoms.



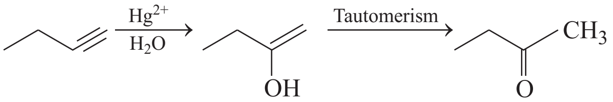
Carboxylate ion



Phenoxide ion

154. (*b*) But-1-yne on reaction with water in presence of Hg^{2+} ions as a catalyst produces butan-2-one.

Mechanism



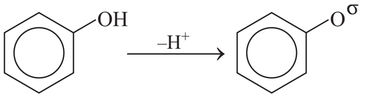
155. (*a*) Reactivity of carbonyl compounds can be decided by two factors:

(i) **Steric factor** Lesser the steric factor greater will be its reactivity.

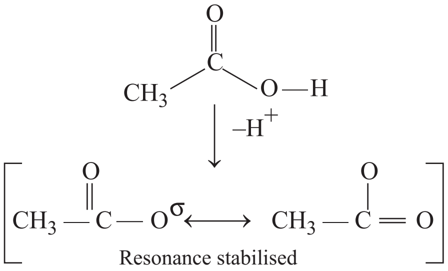
(ii) **Electronic factor** Greater the number of alkyl group lesser will be its electrophilicity.

Hence, $CH_3—CHO$ is most reactive towards nucleophilic addition reaction.

156. (*c*) Phenol is more stable than alcohol due to formation of more stable conjugate base after removal of H^+ from phenol.

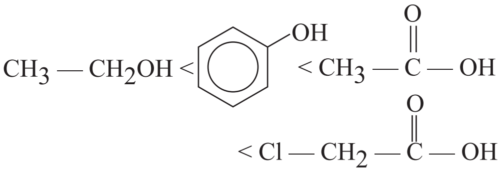


On the other hand, carboxylic acid is more acidic than phenol due to formation of more stable conjugate base after removal of H^+ as compared to phenol.

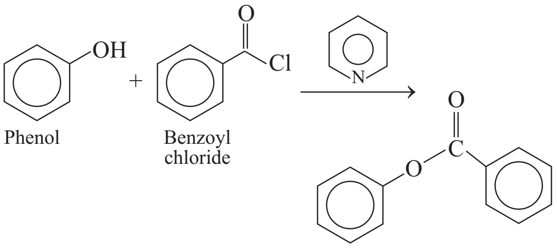


Chloroacetic acid is more acidic than acetic acid due to the presence of electron withdrawing chlorine group attached to α-carbon of carboxylic acid.

Hence, correct choice is (c).



157. (*b*) Compound Ph—COO—Ph can be prepared like this.

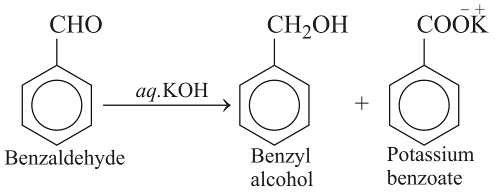


This is an example of Schotten-Baumann reaction.

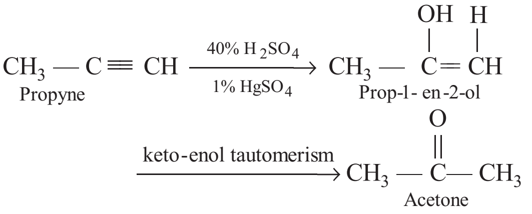
158. (*c*) Acetone and benzaldehyde both do not react with Fehling's solution. Fehling's solution react with ketone as acetone while benzaldehyde is an aromatic aldehyde having no α-hydrogen.

159. (*d*) Necessary condition for Cannizzaro reaction is absence of α-hydrogen atom. So, CH_3CHO will not give Cannizzaro reaction while other three compounds have no α-hydrogen. Hence, they will give Cannizzaro reaction.

160. (*b*) Benzaldehyde is an aromatic aldehyde having no α-hydrogen. So, on reaction, with aq. KOH solution it undergoes Cannizzaro reaction to produce benzyl alcohol and potassium benzoate.



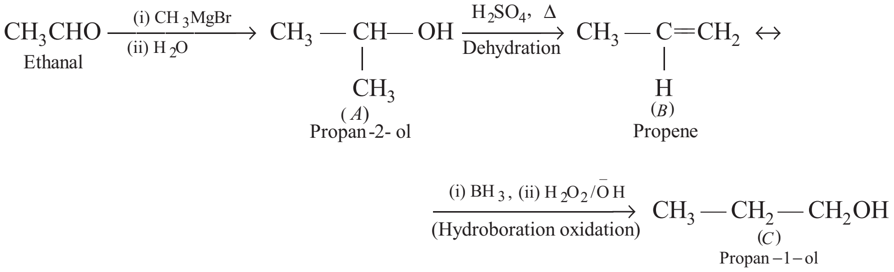
161. (*d*) Chemical reaction can be shown as



$$\underset{\text{Propyne}}{CH_3—C\equiv CH} \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Prop-1-en-2-ol}}{CH_3—\overset{\overset{OH}{|}}{C}=\overset{\overset{H}{|}}{CH}} \xrightarrow{\text{keto-enol tautomerism}} \underset{\text{Acetone}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_3}$$

A is prop-1-en-2-ol, which undergoes tautomerism to form acetone.

162. (*b*) Chemical reaction can be shown as



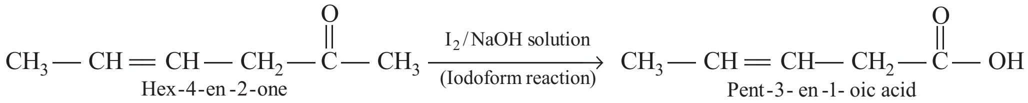
$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} \underset{\substack{(A)\\ \text{Propan-2-ol}}}{CH_3 - \underset{\substack{|\\ CH_3}}{CH} - OH} \xrightarrow[\text{Dehydration}]{H_2SO_4,\ \Delta} \underset{\substack{(B)\\ \text{Propene}}}{CH_3 - \underset{\substack{|\\ H}}{C} = CH_2} \leftrightarrow$$

$$\xrightarrow[\text{(Hydroboration oxidation)}]{\text{(i) } BH_3,\ \text{(ii) } H_2O_2/\bar{O}H} \underset{\substack{(C)\\ \text{Propan}-1-\text{ol}}}{CH_3 - CH_2 - CH_2OH}$$

Thus, $CH_3\,\underset{\substack{|\\ CH_3}}{CH} - OH$ and $CH_3 - CH_2 - CH_2OH$ are positional isomers.

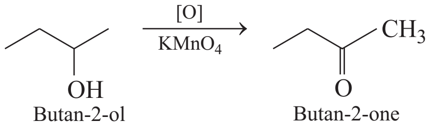
163. (*c*) Iodoform test is used to predict the presence of $-COCH_3$ group which is converted into $-COOH$ group.

The reaction is shown as

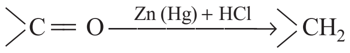


$$\underset{\text{Hex-4-en-2-one}}{CH_3 - CH = CH - CH_2 - \overset{\substack{O\\ \|}}{C} - CH_3} \xrightarrow[\text{(Iodoform reaction)}]{I_2/\text{NaOH solution}} \underset{\text{Pent-3-en-1-oic acid}}{CH_3 - CH = CH - CH_2 - \overset{\substack{O\\ \|}}{C} - OH}$$

164. (*b*) Butan-2-ol on oxidation with alk. $KMnO_4$ solution produces butanone as follows:



165. (*a*) Clemmensen reduction is used to convert carbonyl group to CH_2 group as follows



$$>C = O \xrightarrow{\text{Zn (Hg)} + \text{HCl}} >CH_2$$

Zinc amalgam and HCl act as reagent in this reaction.