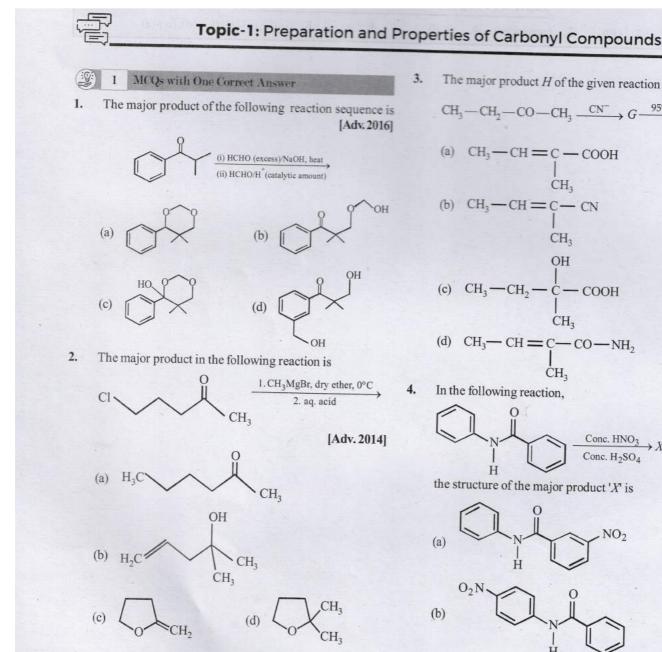
Chapter Aldehydes Ketones and Carboxylic Acids



The major product H of the given reaction sequence is $CH_3 - CH_2 - CO - CH_3 \xrightarrow{CN^-} G$ [2012 - II] (a) $CH_3 - CH = C - COOH$ CH, In the following reaction the structure of the major product 'X' is [2007]

$$(d) \quad O_2N \qquad \begin{matrix} O \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \end{matrix} \begin{matrix} \\ \\ \end{matrix} \begin{matrix} \\ \\ \end{matrix} \end{matrix}$$

5. MeO
$$\leftarrow$$
 CHO + (X) $\frac{\text{CH}_3\text{COONa}}{\text{H}_3\text{O}^+}$

The compound (X) is

[2005S]

- (a) CH₃COOH
- (b) BrCH2-COOH
- (c) (CH₃CO)₂O
- (d) CHO-COOH
- 6. How will you convert butan-2-one to propanoic acid?

[2005S]

- (a) Tollen's reagent
- (b) Fehling's solution
- (c) NaOH/I₂/H⁺
- (d) NaOH/NaI/H+
- 7. The correct order of reactivity of PhMgBr with [20045]

- (a) (I)>(II)>(III)
- (b) (III) > (II) > (I)
- (c) (II)>(III)>(I)
- (d) (l)>(lll)>(ll)

Major product is:

[2003S]

The product of acid hydrolysis of P and Q can be distinguished by [2003S]

$$P = H_2C$$
 \longrightarrow $OCOCH_3$ $Q =$ \bigcirc $OCOCH_3$

- (a) Lucas Reagent
- (b) 2,4-DNP
- (c) Fehling's Solution
- (d) NaHSO₃
- 10. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives [2001S]
 - (a) benzyl alcohol and sodium formate
 - (b) sodium benzoate and methyl alcohol
 - (c) sodium benzoate and sodium formate
 - (d) benzyl alcohol and methyl alcohol
 - The appropriate reagent for the following transformation is O [2000S]

- (a) Zn(Hg), HCl
- (b) NH,NH,/OH
- (c) H₂/Ni
- (d) NaBH,

(d) $CD_2 = C - CD_3$

12. Which one of the following will most readily be dehydrated in acidic condition? [2000S]

$$(a) \qquad \begin{matrix} O & OH \\ \hline \\ (b) & \begin{matrix} OH \\ \hline \\ OH \end{matrix} \\ (c) & \begin{matrix} OH \\ \hline \\ OH \end{matrix} \\ OH \\ \end{matrix}$$

13. The enol form of acetone, after treatment with D₂O, gives.

[1999 - 2 Marks]

OD O
(a)
$$CH_3 - C = CH_2$$
 (b) $CD_3 - C - CD$
OH OD

(c) $CH_2 = C - CH_2D$

14. In the Cannizzaro reaction given below, [1996 - 1 Mark] $2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^-$

the slowest step is

- (a) the attack of OH at the carbonyl group,
- (b) the transfer of hydride to the carbonyl group,
- (c) the abstraction of proton from the carboxylic acid,
- (d) the deprotonation of PhCH, OH.
- 15. m-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives [1991 - 1 Mark]
 - (a) potassium m-chlorobenzoate and m-hydroxybenzaldehyde
 - (b) m-hydroxybenzaldehyde and m-chlorobenzyl alcohol
 - (c) m-chlorobenzyl alcohol and m-hydroxybenzyl alcohol
 - (d) potassium m-chlorobenzoate and m-chlorobenzyl alcohol.
- 16. The enolic form of acetone contains [1990 - 1 Mark]
 - (a) 9 sigma bonds, 1 pi-bond and 2 lone pairs
 - (b) 8 sigma bonds, 2 pi-bonds and 2 lone pairs
 - (c) 10 sigma bonds, 1 pi-bond and 1 lone pair
 - (d) 9 sigma bonds, 2 pi-bonds and 1 lone pair
- Polarisation of electrons in acrolein may be written as

[1988 - 1 Mark]

(a) $CH_2 = CH - CH = O$ CH2=CH-CH=O

(c) $CH_2 = CH - CH = O$ (d) CH₂=CH-CH=O

- 18. The compound that will not give iodoform on treatment with alkali and iodine is: [1985 - 1 Mark]
 - (a) acetone
- (b) ethanol
- (c) diethyl ketone
- (d) isopropyl alcohol
- 19. The Cannizzaro reaction is not given by [1983 1 Mark]
 - (a) trimethylacetaldehye
- (b) acetaldehyde
- (c) benzaldehyde
- (d) formaldehyde
- 20. When acetaldehyde is heated with Fehling's solution it gives a precipitate of [1983 - 1 Mark]
- (a) Cu
- (b) CuO
- (c) Cu₂O
- (d) $Cu + Cu_2O + CuO$
- 21. A compound that gives a positive iodoform test is

[1982 - 1 Mark]

- (a) 1-pentanol
- (b) 2-pentanone
- (c) 3-pentanone
- (d) pentanal
- The reagent with which both acetaldehyde and acetone react easily is [1981 - 1 Mark]
 - (a) Fehling's reagent
- (b) Grignard reagent
- (c) Schiff's reagent
- (d) Tollen's reagent

Integer Value Answer

An organic compound Phaving molecular formula C6H6O3 gives ferric chloride test and does not have intramolecular hydrogen bond. The compound P reacts with 3 equivalents of NH2OH to produce oxime Q. Treatment of P with excess methyl iodide in the presence of KOH produces

compound R as the major product. Reaction of R with excess iso-butylmagnesium bromide followed by treatment with H₃O⁺ gives compound S as the major product.

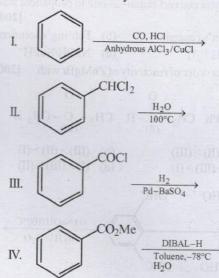
[Adv. 2024]

The total number of methyl (-CH3) group(s) in compound

- 24. Complete reaction of acetaldehyde with excess formaldehyde, upon heating with conc. NaOH solution, gives P and Q. Compound P does not give Tollens' test, whereas Q on acidification gives positive Tollens' test. Treatment of P with excess cyclohexanone in the presence of catalytic amount of p-toluenesulfonic acid (PTSA) gives product R. Sum of the number of methylene groups (-CH₂-) and oxygen atoms in **R** is _____. [Adv. 2024]
- In the reaction given below, the total number of atoms having sp2 hybridization in the major product P is

$$\frac{1. O_3 \text{ (excess)}}{\text{then Zn/H}_20} P$$
[Adv. 2021]

Among the following, the number of reaction(s) that produce(s) benzaldehyde is [Adv. 2015]



- 27. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with NaBH4 (NOTE: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are [Adv. 2014]
- In the scheme given below, the total number of intramolecular aldol condensation products formed from Y'is

$$\frac{1. O_3}{2. Zn, H_2O} Y \xrightarrow{1. NaOH (aq)}$$
[2010]

Fill in the Blanks

29. The structure of the enol form of CH3-CO-CH2-CO-CH3 with intramolecular hydrogen bonding is

[1993 - 1 Mark]



[1992 - 1 Mark]

- 32. Each item from (i) to (x) given below indicates a reaction type, a process or a homologue. Match each of these items with the related phrase by writing the correct phrase in the corresponding vacant space given under each. The correct phrase must be picked only from those given below within brackets:

(Bayer's process, Nucleophilic addition, Free radical substitution, Ostwald's process, Homologous pair, Cyanamide process, Electrophilic substitution, Homolytic addition, Thermite process, Nucleophilic substitution)

 $[1981 - 1 \times 10 = 10 \text{ Marks}]$

- (i) Cyclopropane, chlorine and light
- (ii) Welding
- (iii) Propanone and sodium bisulphite

......

.....

- (iv) Production of ammonia
- (v) Chloromethane and methanol
- (vi) Ore purification
- (vii) Ethanal and methanal
- (viii)Benzene, nitric acid and sulphuric acid
- (ix) Production of nitric acid
- (x) Propene, hydrogen bromide and a peroxide catalyst

5 True / False

 The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol.

[1987 - 1 Mark]

- 34. The yield of ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized. [1983 1 Mark]
- Benzaldehyde undergoes aldol condensation in an alkaline medium. [1982 - 1 Mark]

6 MCQs with One or More than One Correct Answer

36. The option(s) with correct sequence of reagents for the conversion of P to Q is(are): [Adv. 2024]

$$O \longrightarrow CO_2Et \xrightarrow{reagents}$$

$$H_3C \longrightarrow \overline{P}$$

- (a) (i) Lindlar's catalyst, H₂; (ii) SnCl₂/HCl; (iii) NaBH₄;(iv) H₃O⁺
- (b) (i) Lindlar's catalyst, $\rm H_2$; (ii) $\rm H_3O^+$; (iii) $\rm SnCl_2/HCl$; (iv) $\rm NaBH_4$
- (c) (i) NaBH₄; (ii) SnCl₂/HCl; (iii) H₃O⁺; (iv) Lindlar's catalyst, H₂
- (d) (i) Lindlar's catalyst, H_2 ; (ii) NaBH₄; (iii) SnCl₂/HCl; (iv) H_3O^+
- 37. Reaction of iso-propylbenzene with O₂ followed by the treatment with H₃O⁺ forms phenol and a by-product P. Reaction of P with 3 equivalents of Cl₂ gives compound Q. Treatment of Q with Ca(OH)₂ produces compound R and calcium salt S. The correct statement(s) regarding P, Q, R and S is(are) [Adv. 2024]
 - (a) Reaction of **P** with **R** in the presence of KOH followed by acidification gives

- (b) Reaction of R with O₂ in the presence of light gives phosgene gas
- (c) Q reacts with aqueous NaOH to produce Cl₃CCH₂OH and Cl₃CCOONa
- (d) S on heating gives P
- 38. In the following reactions, P, Q, R and S are the major products. [Adv. 2023]

$$\text{CH}_{3}\text{CH}_{2}\text{CH}\left(\text{CH}_{3}\right)\text{CH}_{2}\text{CN} \xrightarrow{\text{(i) PhMgBr, then H}_{3}\text{O}^{\oplus}} \text{P}$$

Ph – H + CH₃CCl
$$\xrightarrow{\text{(i) anhyd. AlCl}_3}$$
 Q

$$CH_{3}CH_{2}CCI \xrightarrow{(i)\frac{1}{2}(PhCH_{2})_{2}Cd} R$$

$$\begin{array}{c} \text{PhCH}_2\text{CHO} & \xrightarrow{(i) \text{PhMgBr}, \text{then H}_2\text{O}} \\ \xrightarrow{(ii) \text{CrO}_3, \text{dil}, \text{H}_2\text{SO}_4} & \\ \xrightarrow{(iii) \text{HCN}} \\ \text{(iv) H}_2\text{SO}_4, \Delta & \\ \end{array} \\ \Rightarrow S$$

The correct statement(s) about P, Q, R and S is(are)



- (a) Both P and Q have asymmetric carbon(s).
- (b) Both Q and R have asymmetric carbon(s).
- (c) Both P and R have asymmetric carbon(s).
- (d) P has asymmetric carbon(s), S does not have any asymmetric carbon.
- Considering the following reaction sequence, the correct statement(s) is(are) [Adv. 2022]

$$O \longrightarrow O \longrightarrow O$$

$$AlCl_3 \longrightarrow P \xrightarrow{Zn/Hg, HCl} Q \xrightarrow{SOCl_2} R$$

$$a \text{ hydrocarbon} \xleftarrow{Zn/Hg, HCl} S$$

- (a) Compounds P and Q are carboxylic acids.
- (b) Compound S decolorizes bromine water.
- (c) Compounds P and S react with hydroxylamine to give the corresponding oximes.
- (d) Compound R reacts with dialkylcadmium to give the corresponding tertiary alcohol.
- In the reaction scheme shown below, Q, R, and S are the major products. [Adv. 2020]

$$\xrightarrow{ \text{(i) Zn-Hg/HCl} } \mathbf{R} \xrightarrow{ \text{(ii) H}_3 \text{O}^+ } \mathbf{S}$$

The correct structure of

(a) S is
$$H_3C$$
 CH_3 H_3C CH_3 CH_3

(c)
$$\mathbf{R}$$
 is $\mathbf{H}_3\mathbf{C}$ \mathbf{CH}_3 $\mathbf{H}_3\mathbf{C}$ \mathbf{CH}_3 \mathbf{CH}_3

(d) S is
$$H_3C$$
 CH_3 H_3C CH_3 H_3C CH_3

41. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C₈H₈O. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction

(i)
$$P \xrightarrow{\text{i)O}_3/\text{CH}_2\text{Cl}_2} Q$$

 $Q \xrightarrow{\text{ii)Zn/H}_2\text{O}} Q$

(ii)
$$R \xrightarrow{i)O_3/CH_2Cl_2} S$$

 $ii)Zn/H_2O \xrightarrow{} S$
 (C_8H_8O)

The option(s) with suitable combination of P and R, respectively, is (are) [Adv. 2017]

(a)
$$H_3C$$
 and CH_3

(b)
$$H_3C$$
 CH_3 and CH_3

(c)
$$CH_3$$
 and CH_3 CH_3 CH_3

42. The correct statement(s) about the following reaction sequence is (are) [Adv. 2016]

$$\text{Cumene}(C_9H_{12}) \xrightarrow{\text{(i)}O_2} \mathbf{P} \xrightarrow{\text{CHCl}_3/\text{NaOH}}$$

Q (major) + R (minor)

$$\mathbf{Q} \xrightarrow{\text{NaOH}} \mathbf{S}$$



- (a) R is steam volatile
- Q gives dark violet coloration with 1% aqueous FeCl₃ solution
- (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
- (d) S gives dark violet coloration with 1% aqueous FeCl₃ solution
- 43. Positive Tollen's test is observed for

[Adv. 2016]

44. The major product of the following reaction is

[Adv. 2015]

ii.
$$H^+$$
, heat

CH₃

(a)

CH₃

O

CH₃

O

CH₃

O

CH₃

O

CH₃

O

CH₃

45. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are) [Adv. 2013]

$$H_3C$$
 P
 CH_2Br
 H_3C
 Q
 CBr_3
 Br_3C
 R
 CBr_3

$$BrH_2C$$
 S
 CH_2Br
 H_3C
 T
 ONa
 $CHBr_3$
 U

(a) Reaction I: P and Reaction II: P

(b) Reaction I: U, acetone and Reaction II: Q, acetone

(c) Reaction I: T, U, acetone and Reaction II: P

(d) Reaction I: R, acetone and Reaction II: S, acetone

6. In the following reaction, the product(s) formed is (are)

[Adv. 2013]

$$\begin{array}{c}
\text{OH} \\
\hline
\text{CHCI}_3 \\
\text{OH}^-
\end{array}?$$

OHC
$$CHO$$
 CHO CHO $CHCl_2$ Q

(a) P(major)

(b) Q(minor)

(c) R (minor)

(d) S(major)

47. The smallest ketone and its next homologue are reacted with NH₂OH to form oxime [2006 - 5M, -1]

(a) Two different oximes are formed

(b) Three different oximes are formed

(c) Two oximes formed are optically active

(d) All oximes formed are optically active

48.
$$\begin{array}{c} + \text{Cl} - \text{CH}_2\text{CH}_2\text{CH}_3 \\ \xrightarrow{\text{AlCl}_3} P \xrightarrow{\text{(i) O}_2/\Delta} Q + \text{Phenol} \end{array}$$

The major products P and Q are

[2006 - 5M, -1]

	N	
(b)		and CH ₃ COCH ₃
(c)		and CH ₃ COCH ₃
(d)	J	and CH ₃ CH ₂ CHO

- 49. Which of the following will undergo aldol condensation?
 - [1998 2 Marks]
 - (a) acetaldehyde
 - (b) propanaldehyde
 - (c) benzaldehyde
 - (d) trideuteroacetaldehyde
- 50. Which of the following will react with water?

[1998 - 2 Marks]

- (a) CHCl₃
- (b) Cl₂CCHO
- (c) CCl₄
- (d) CICH,CH,Cl
- 51. A new carbon-carbon bond formation is possible in
 - (a) Cannizzaro reaction
- [1998 2 Marks]
- (b) Friedel-Craft alkylation
- (c) Clemmensen reduction
- (d) Reimer-Tiemann reaction
- 52. Which of the following are examples of aldol condensation?

 [1989 1 Mark]
 - (a) 2CH₃CHO dil. NaOH → CH₃CHOHCH₂CHO
 - (b) 2CH₃COCH₃ dil. NaOH

CH3COH(CH3)CH3COCH3

- (c) 2HCHO $\xrightarrow{\text{dil. NaOH}}$ CH₃OH
- (d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$
- 53. Keto-enol tautomerism is observed in [1988 1 Mark]
 - (a) H_5C_6-C-H
- (b) H₅C₆-C-CH₃
- (c) H₅C₆-C-C₆H
- (d) H₅C₆-C-CH₇-CH₃
- 54. Base catalysed aldol condensation occurs with:
 - (a) propionaldehyde
- [1984 1 Mark]
- (b) benzaldehyde
- (c) 2-methylpropionaldehyde
- (d) 2, 2-dimethylpropionaldehyde

Match the Following

55. The major products obtained from the reactions in List-II are the reactants for the named reactions mentioned in List-I. Match List-I with List-II and choose the correct option.

[Adv. 2023]

List-II List-II

- Etard reaction (1) Acetophenone Zn-Hg, HCl
- (Q) Gattermann (2) Toluene $(i) \text{KMnO}_4, \text{KOH}, \Delta \longrightarrow$ reaction
- (R) Gattermann— (3) Benzene CH₃Cl anhyd.AlCl₃ → Koch reaction
- (S) Rosenmund (4) Aniline $\xrightarrow{\text{NaNO}_2/\text{HCl}}$ reduction

(5) Phenol $\xrightarrow{Zn, \Delta}$

- (a) $P \rightarrow 2$; $Q \rightarrow 4$; $R \rightarrow 1$; $S \rightarrow 3$
- (b) $P \rightarrow 1$; $Q \rightarrow 3$; $R \rightarrow 5$; $S \rightarrow 2$
- (c) $P \rightarrow 3$; $Q \rightarrow 2$; $R \rightarrow 1$; $S \rightarrow 4$
- (d) $P \rightarrow 3$; $Q \rightarrow 4$; $R \rightarrow 5$; $S \rightarrow 2$
- 56. Match the entries in Column I with the correctly related quantum number(s) in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS [2008]

Column I

Column II

- (A) $H_2N NH_3CI$
- (p) sodium fusion
 extract of the
 compound
 gives Prussian
 blue colour
 with FeSO₄
- (q) gives positive FeCl₃ test
- (r) gives white precipitate with AgNO₃
- (D) O_2N NH NH_3Br (s) reacts with aldehydes to form the
 - reacts with aldehydes to form the corresponding hydrazone derivative

8 Comprehension/Passage Based Questions

Paragraph-I

An organic compound P with molecular formula $C_9H_{18}O_2$ decolorizes bromine water and also shows positive iodoform test. P on ozonolysis followed by treatment with H_2O_2 gives Q and R. While compound Q shows positive iodoform test, compound R does not give positive iodoform test. Q and R on oxidation with pyridinium chlorochromate (PCC) followed by heating give S and T, respectively. Both S and T show positive iodoform test.

Complete copolymerization of 500 moles of Q and 500 moles of R gives one mole of a single acyclic copolymer U.

[Given, atomic mass: H=1, C=12, O=16]



57. Sum of number of oxygen atoms in S and T is

[Adv. 2024]

58. The molecular weight of U is _____

[Adv. 2024]

Passage-I

In the following reactions

[Adv. 2015]

$$\begin{array}{l} C_8H_6 \xrightarrow{Pd-BaSO_4} C_8H_8 \xrightarrow{(i) B_2H_6} X \\ H_2O \\ HgSO_4, H_2SO_4 \\ C_8H_8O \xrightarrow{(i) EtMgBr, H_2O} Y \end{array}$$

59. Compound X is

60. The major compound Y is

Passage-II

Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below. [2010]

61. The compounds P and Q respectively are:

(c)
$$H_3C$$
 CH_2 H H_3C H CH_3 CH_3 CH_3 CH_4 CH_3 CH_4 CH_5 $CH_$

(d)
$$CH_3$$
 CH_2 H and H H

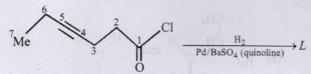
62. The compound R is:

63. The compound S is:

Passage-III

In the following reaction sequence, products I, J and L are formed. K represents a reagent. [2008]

Hex
$$-3$$
 - ynal $\xrightarrow{1.\text{NaBH}_4} I$ $\xrightarrow{1.\text{Mg/ether}} J$ $\xrightarrow{K} J$



64. The structure of the product *I* is –

65. The structures of compounds J and K, respectively, are

66. The structure of product L is

Passage-IV

A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and compound L, whereas K on reaction with KOH gives only M.

12008

$$M = H_3C$$
 Ph

67. Compound H is formed by the reaction of

(b)
$$Ph$$
 CH_3 + $PhCH_2MgBr$

(c)
$$Ph$$
 + $PhCH_2MgBr$

$$(d) \underbrace{\stackrel{O}{\underset{Ph}{\longleftarrow}}}_{H} + \underbrace{\stackrel{O}{\underset{Ph}{\longleftarrow}}}_{MgBr}$$

68. The structure of compound I is

(a)
$$\stackrel{Ph}{\underset{H}{\longleftarrow}} \stackrel{CH_3}{\underset{CH_2Ph}{\longleftarrow}} \stackrel{(b)}{\underset{(d)}{\longleftarrow}} \stackrel{H_3C}{\underset{Ph}{\longleftarrow}} \stackrel{Ph}{\underset{H}{\longleftarrow}} \stackrel{Ph}{\underset{H}{\longleftarrow}} \stackrel{CH_3}{\underset{H}{\longleftarrow}} \stackrel{CH_3}{\underset{H}{\longleftarrow}}$$

69. The structure of compounds J, K and L respectively, are –

- (a) PhCOCH₃, PhCH₂COCH₃ and PhCH₂COO⁻K⁺
- (b) PhCHO, PhCH, CHO and PhCOO-K+
- (c) PhCOCH₃, PhCH₂CHO and CH₃COO⁻K⁺
- (d) PhCHO, PhCOCH3 and PhCOO-K+

9 Assertion and Reason Type Questions

Each question contains **STATEMENT-1** (Assertion) and **STATEMENT-2** (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is incorrect.
- (d) If Statement -1 is incorrect but Statement -2 is correct.
- 70. Statement-1: Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.

Statement-2: It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. [2001S]

(Q:)

10 Subjective Problems

- 71. A monomer of a polymer on ozonolysis gives two moles of CH₂O and one mole of CH₃COCHO. Write the structure of monomer and write all 'cis' configuration of polymer chain. [2005 2 Marks]
- 72. $A(C_6H_{12}) \xrightarrow{HCl} B+C_{(C_6H_{13}Cl)}$ [2003 4 Marks]

 $B \xrightarrow{\text{alc. KOH}} D$ (isomer of A)

 $D \xrightarrow{\text{ozonolysis}} E$ (it gives negative test with Fehling solution but responds to iodoform test).

 $A \xrightarrow{\text{Ozonolysis}} F + G$ (both gives positive Tollen's test but do not give iodoform test).

 $F+G \xrightarrow{\text{conc. NaOH}} \text{HCOONa} + A \text{ primary alochol.}$ Identify from A to G.

- 73. Compound 'A' of molecular formula C₉H₇O₂Cl exists in keto form and predominantly in enolic form 'B'. On oxidation with KMnO₄, 'A' gives m-chlorobenzoic acid. Identify 'A' and 'B'. [2003 2 Marks]
- 74. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures: [2001 5 Marks]

$$\xrightarrow{\text{Br}_2/\text{CCl}_4} (A) \xrightarrow{\text{NaNH}_2} (B)$$

$$\xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} (C) \xrightarrow{\text{NH}_2\text{NHCONH}_2} (D)$$

- $[C] \xrightarrow{\text{NaOD/D}_2\text{O(excess)}} (E)$
- 75. An organic compound **A**, C₆H₁₀O on reaction with CH₃MgBr followed by acid treatment gives compound **B**. The compound **B** on ozonolysis gives compound **C**, which in presence of a base gives 1-acetylcyclopentene **D**. The compound **B** on reaction with HBr gives compound **E**. Write the structures of **A**, **B**, **C** and **E**. Show how **D** is formed from **C**?

 [2000 5 Marks]
- 76. Write the structural formula of the main organic product formed when:
 - (i) Identify A, B, C and give their structures.

$$CH_{3} \xrightarrow{Br_{2}} (A) + (B)$$

$$L_{3} \xrightarrow{NaOH} (A) + (B)$$

$$L_{4} \xrightarrow{H^{+}} (C) C_{7}H_{12}C$$

$$[2000 - 3 Marks]$$

(ii)
$$\xrightarrow{\text{base}}$$
 [2000 - 1 Mark]

(iii)
$$H_3CCOCOC_6H_5 + NaOH/H_3O^{\oplus} \longrightarrow ---$$
[1997 - 1 Mark]

(iv) $CICH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow ----$

[1997 - 1 Mark]

(v)
$$R - C = C - R + HClO_4 \longrightarrow ----$$

$$\begin{bmatrix} C \\ R = n-Pr \end{bmatrix}$$

[1997 - 1 Mark]

$$(vi) \qquad \bigoplus_{O} + Ph_3P = CH_2 \longrightarrow -\frac{E}{---}$$

[1997 - 1 Mark]

(vii) Complete the following reaction with appropriate structure. [1996 - 1 Mark]

$$CH_3CH_2$$
 $C=O \xrightarrow{1.KCN/H_2SO_4} D$

[1992 - 1 Mark]

- (ix) propanal $\xrightarrow{\text{NaOH}}$ [1985 1 Mark]
- (x) methanal reacts with ammonia [1981 ½ Mark]
- 77. Complete the following reaction with appropriate structures of products/reagents: [1998 2 + 2 Marks]

78. Write the intermediate steps for the following reaction.

$$C_6H_5CH(OH)C \equiv CH \xrightarrow{H_3O^+} C_6H_5CH = CHCHO$$
[1998 - 2 Marks]

79. An aldehyde A (C₁₁H₈O), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B.

[1998 - 2 Marks]

80. Suggest appropriate structures for the missing compounds.

(The number of carbon atoms remains the same throughout the reactions.)

[1996 - 3 Marks]

$$CH_{3} \xrightarrow{\text{dil. KMnO}_{4} \to A} \xrightarrow{\text{HIO}_{4} \to B} \xrightarrow{\text{OH}^{-} \to C}$$

81. An organic compound A, C₈H₆, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A. [1994 - 3 Marks]

- Arrange the following in increasing order of expected enol [1992 - 1 Mark]
- Complete the following reactions:

(i)
$$H_3C-CHO \xrightarrow{CH_3MgBr} ? \xrightarrow{?} H_3C-\overset{OH}{C-C-CH_3}$$

[1988 - 1 Mark]

(ii)
$$2CH_3CCH_3 \xrightarrow{\text{base catalyst}} ? \xrightarrow{\text{acid catalyst}} ?$$
[1988 - 1 Mark

(iii)
$$\stackrel{\text{SO}_3\text{H}}{\longrightarrow}$$
 $\stackrel{\text{OH}}{\longrightarrow}$ $\stackrel{\text{CHCl}_3/\text{NaOH}}{\longrightarrow}$?

[1988 - 1 Mark]

- An unknown compound of carbon, hydrogen and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures for the unknown compound? [1987 - 5 Marks]
- A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula C₆H₁₃Cl. Compound (A) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes (B) and (C), having formula C_6H_{12} . The mixture of (B) and (C), on ozonolysis, furnished four compounds:

[1986 - 4 Marks]

- (i) CH,CHO;
- (ii) C2H2CHO;
- (iii) CH₃COCH₃ and
- (iv) H3C-CH-CHO

What are the structures of (A), (B) and (C)?

- Give a chemical test/suggest a reagent to distinguish between acetaldehyde from acetone. [1987 - 1 Mark]
- 87. Arrange the following in: Increasing reactivity towards HCN [1985] CH3CHO, CH3COCH3, HCHO, C3H5COCH3
- 88. Give reasons for the following:
 - Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid. [1999 - 2 Marks]
 - In acylium ion, the structure $R C \equiv O^+$ is more stable than $R - C^+ = O$. [1994 - 1 Mark]
 - (iii) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion. [1991 - 1 Mark]
 - Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. [1986 - 1 Mark]
 - Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water.

[1985 - 2 Marks]

- 89. Outline the reaction sequence for the conversion of
 - Carry out the following transformation in not more than three steps. [1999 - 3 Marks]

$$CH_3 - CH_2 - C \equiv C - H \rightarrow CH_3 - CH_2 - CH_2 - C - CH_3$$

- (ii) acetylene to acetone [1985 - 1 Mark]
- (iii) methanal to ethanal (the number of steps should not be more than three). [1981 - 2 Marks]

Topic-2: Preparation and Properties of Carboxylic Acids and its Derivatives

MCQs with One Correct Answer

The correct order of acid strength of the following [Adv. 2019]

- (a) I>II>III>IV
- (b) II>I>IV>III
- (c) I>III>II>IV
- (d) III>II>IV
- The correct order of acidity for the following compounds

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

The compound that does NOT liberate CO2, on treatment with aqueous sodium bicarbonate solution, is

[Adv. 2013]

- (a) Benzoic acid
- (b) Benzenesulphonic acid
- (c) Salicylic acid
- (d) Carbolic acid (Phenol)
- The compound that undergoes decarboxylation most readily under mild condition is [2012]

(a)
$$COOH$$
 CH_2COOH (b) CH_2COOH (c) $COOH$ CH_2COOH $COOH$ $COOH$

5. The carboxyl functional group (-COOH) is present in

- (a) picric acid
- (b) barbituric acid
- (c) ascorbic acid
- (d) aspirin
- The major product of the following reaction is [2011]

- (a) a hemiacetal
- (b) an acetal
- (c) an ether
- (d) an ester
- In the reaction

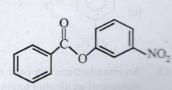
the structure of the product T is:

[2010]

The compounds P, Q and S

were separately subjected to nitration using HNO₃/H₂SO₄ mixture. The major product formed in each case

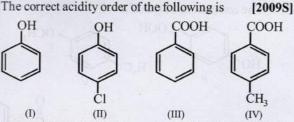
(c)
$$HO \longrightarrow NO_2$$
 $H_3C \longrightarrow NO_2$ NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2





OH

The correct acidity order of the following is



- (a) (III) > (IV) > (II) > (I)
- (b) (IV)>(III)>(I)>(II) (d) (II) > (III) > (IV) > (I)
- (c) (III)>(II)>(IV)In the following reaction sequence, the correct structures of E, F and G are

$$\begin{array}{c}
O & O \\
Ph & * \\
Ph & * \\
F] \xrightarrow{\text{Heat}} [E] \xrightarrow{\text{I}_2} [F] + [G] \\
\text{[* implies 13C labelled carbon)}
\end{array}$$
[2008]

(a)
$$E = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{CH}_3}^{O} F = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{O Na } G = \text{CHI}_3}^{O}$$

(b)
$$E = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{CH}_3}^{*} F = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{O Na } G = \text{CHI}_3}^{O}$$

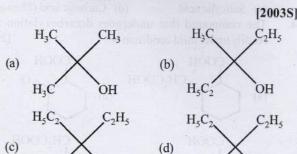
(c)
$$E = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{CH}_3}^{*} F = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{O Na } G}^{\oplus} \bigoplus_{\text{CHI}}^{*}$$

(d)
$$E = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{CH}_3}^{*} F = \bigvee_{\text{Ph}}^{O} \bigvee_{\text{O Na } G^{\stackrel{*}{=}} \text{CH}_3 \text{I}}^{O}$$

4-Methylbenzenesulphonic acid reacts with sodium acetate to give [2005S]

An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be [2003S]

- (a) Optically active mixture (b) Pure enantiomer
- Meso compound
- (d) Racemic mixture
- Ethyl ester $\rightarrow P$. The product P will be



- 14. Benzoyl chloride is prepared from benzoic acid by [20008]
 - Cl_2, hv
- (b) SO₂Cl₂
- (c) SOCI,
- (d) Cl2, H2O

H₇C₃

- When propionic acid is treated with aqueous sodium bicarbonate, CO2 is liberated. The 'C' of CO2 comes from [1999 - 2 Marks]
 - (a) methyl group
- (b) carboxylic acid group
- (c) methylene group
- (d) bicarbonate
- The organic product formed in the reaction

$$C_6H_5COOH \xrightarrow{I LiAlH_4} II H_3O^+$$

- (b) C₆H₅COOH & CH₄
- C6H5CH3 & CH3OH
- C6H5CH3 & CH4

Integer Value Answer

17. In the following reaction sequence, the major product P is formed. [Adv. 2024]

H
$$CO_{2}Et \xrightarrow{(i) Hg^{2^{+}}, H_{3}O^{+}} P$$

$$(ii) Zn-Hg/HCI$$

$$(iii) H_{3}O^{+}, \Delta \rightarrow P$$

Glycerol reacts completely with excess P in the presence of an acid catalyst to form Q. Reaction of Q with excess NaOH followed by the treatment with CaCl, yields Casoap R, quantitatively. Starting with one mole of Q, the amount of R produced in gram is [Given, atomic weight: H=1, C=12, N=14, O=16, Na=23,C1 = 35, Ca = 40

18. The total number of carboxylic acid groups in the product [Adv. 2013]

CH₃

19. Amongst the following, the total number of compounds soluble in aqueous NaOH is

Numeric / New Stem Based Questions

In the following reaction, compound Q is obtained from compound P via an ionic intermediate. [Adv. 2020]

$$C_6H_5$$
 C_6H_5
 C_6H_5

What is the degree of unsaturation of Q?

Fill in the Blanks

Formic acid when heated with conc. H₂SO₄ produces [1983 - 1 Mark]

5 True / False

The boiling point of propionic acid is less than that of n-butyl alcohol, an alcohol of comparable molecular weight.

[1991 - 1 Mark]

Hydrolysis of an ester in presence of a dilute acid is known [1983 - 1 Mark] as saponification.

MCQs with One or More than One Correct Answer

In the following reactions, P, Q, R, and S are the major [Adv. 2023] products.

$$(i)KMnO_4, KOH, \Delta \rightarrow P$$

$$H_3CH_2C$$

$$(ii)H_3O^{\oplus}$$

$$(ii)NaOH, H_2O$$

$$(ii)H_3O^{\oplus}$$

$$Q$$

COOMe
$$\frac{(i)H_3O^{\oplus}, \Delta}{(ii)H_2CrO_4} R$$

$$\frac{(i)M_3O^{\oplus}, \Delta}{(ii)H_2CrO_4} R$$

$$\frac{(i)M_3O^{\oplus}, \Delta}{(ii)H_3O^{\oplus}, \Delta} R$$

$$\frac{(i)M_3O^{\oplus}, \Delta}{(ii)H_3O^{\oplus}, \Delta} R$$

$$\frac{(i)M_3O^{\oplus}, \Delta}{(ii)H_3O^{\oplus}, \Delta} R$$

The correct statement(s) about P, Q, R, and S is(are)

- P and Q are monomers of polymers dacron and glyptal, respectively.
- P, Q, and R are dicarboxylic acids.
- Compounds Q and R are the same.
- R does not undergo aldol condensation and S does not undergo Cannizzaro reaction.
- Consider the following reaction scheme and choose the

correct option(s) for the major products Q, R and S.

Styrene
$$(i)B_2H_6$$
 $(ii)CrO_3,H_2SO_4$ $(ii)CrO_3,H_2SO_4$ $(iii)Cl_2,Red phosphorus$ Q $(iii)H_2O$ $(ii$

SO,H

NH,

26. Choose the correct option(s) for the following reaction sequence [Adv. 2019]

MeO
$$(i) \operatorname{Hg}^{2+}, \operatorname{dil. H}_{2}\operatorname{SO}_{4}$$

$$(ii) \operatorname{AgNO}_{3}, \operatorname{NH}_{4}\operatorname{OH}$$

$$(iii) \operatorname{Zn-Hg, conc. HCl} \to Q$$

$$(i) \operatorname{SOCl}_{2} \operatorname{pyridine} \longrightarrow R \xrightarrow{Zn-\operatorname{Hg conc. HCl}} S$$

Consider Q, R and S as major products.

27. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) [Adv. 2018]

(a)
$$Conc. H_2SO_4$$
 Δ

(b) Me H heated iron tube

873 K

(c) CHO

CHO

 CHO
 CHO

28. Reagent(s) which can be used to bring about the following transformation is (are) [Adv. 2016]

$$COOH$$
 $COOH$ $COOH$

(a) LiAlH₄ in $(C_2H_5)_2O$

(b) BH₃ in THF

(c) NaBH₄ in C₂H₅OH

(d) Raney Ni/H, in THF

29. With reference to the scheme given below, which of the given statement(s) about *T*, *U*, *V* and *W* is (are) correct?

$$H_{3}C$$

$$T$$

$$LiAlH_{4}$$

$$excess$$

$$U$$

$$CrO_{3}/H^{\oplus}$$

$$U$$

$$CrO_{3}/H^{\oplus}$$

$$U$$

$$CrO_{3}/H^{\oplus}$$

$$U$$

$$V \leftarrow CrO_{3}/H^{\oplus}$$

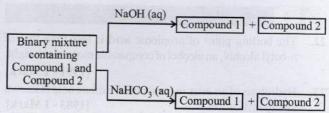
(a) T is soluble in hot aqueous NaOH

(b) U is optically active

(c) Molecular formula of W is $C_{10}H_{18}O_4$

(d) V gives effervescences on treatment with aqueous NaHCO₂.

30. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction as shown in the given scheme. [2012]



(a) C₆H₅OH and C₆H₅COOH

(b) C_6H_5COOH and $C_6H_5CH_2OH$

(c) $C_6H_5CH_2OH$ and C_6H_5OH

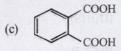
(d) C₆H₅CH₂OH and C₆H₅CH₂COOH

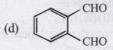
31. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? [2006 - 5M, -1]

(a)
$$COOCH_3$$
 (b) $COOCH_3$ COOCH CHO

Aldehydes, Ketones and Carboxylic Acids

B83



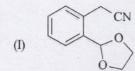


- Which of the following compounds will react with ethanolic 32. [1984 - 1 Mark]
- (a) ethyl chloride
- (b) acetyl chloride
- chlorobenzene (c)
- (d) benzaldehyde
- Which of the following compounds will give a yellow 33. precipitate with iodine and alkali? [1984 - 1 Mark]
 - 2-Hydroxypropane (b) acetophenone
- - methyl acetate (d) acetamide

Match the Following

Directions [Qs. 34-35]: Answer the following by appropriately matching the lists based on the information given in the paragraph. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.

List-I List-II



(i) DIBAL-H (ii) dil. HCl (iii) NaBH₄ (iv) conc. H2SO4

CHO CO,H

(II)
$$\begin{array}{c} \text{(i) O}_3 \\ \text{(ii) Zn, H}_2\text{O} \\ \text{(iii) NaBH}_4 \\ \text{(iv) conc. H}_2\text{SO}_4 \end{array}$$

OH (Q) OH

(III) Cl (ii) KCN (ii)
$$H_3O^{\dagger}, \Delta$$
 (iii) $LiA\ell H_4$ (iv) conc. H_2SO_4

(IV)
$$CO_2Me$$
 (i) LiA/H₄ (ii) conc. H₂SO₄

- .OH (S) CO,H
- CO,H (T) CO₂H
- (U)
- 34. Which of the following options has correct combination considering List-I and List-II?
 - (a) (I), (S), (Q), (R)
- (b) (II), (P), (S), (U)
- (c) (I), (Q), (T), (U)
- (II), (P), (S), (T)(d)
- 35. Which of the following options has correct combination considering List I and List -II?
- (b) (IV), (Q), (U)
- (c) (III), (S), (R)
- (d) (III), (T), (U)

Directions [Qs. 36-38]: By appropriately matching the information given in the three columns of the following table. Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. [Adv. 2017]

Column 1

Column 2

Column 3

(I) Toluene (i) NaOH/Br, (P) Condensation

- Acetophenone (II) (III) Benzaldehyde
- (ii) Br₂/hv (CH₃CO)₂O/CH₃COOK (iii)
- (Q) Carboxylation (R) Substitution

(IV) Phenol

NaOH/CO, (iv)

- (S) Haloform
- For the synthesis of benzoic acid, the only CORRECT combination is
 - (a) (II) (i) (S)
- (b) (IV)(ii)(P)
- (c) (I) (iv) (Q)
- (d) (III) (iv) (R)

- 37. The only CORRECT combination that gives two different carboxylic acids is
 - (a) (II) (iv) (R)
- (b) (IV)(iii)(Q)
- (c) (III) (iii) (P)
- (d) (I)(i)(S)
- 38. The only CORRECT combination in which the reaction proceeds through radical mechanism is
- (a) (III) (ii) (P)
- (b) (IV)(i)(Q)
- (c) (II)(iii)(R)
- (d) (I)(ii)(R)
- 39. Different possible thermal decomposition pathways for peroxy esters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists. [Adv. 2014]

$$\begin{array}{c}
\stackrel{\bullet}{\text{P}} & \stackrel{\bullet}{\text{R}} + \text{R'} \stackrel{\bullet}{\text{O}} \\
\stackrel{\bullet}{\text{P}} & \stackrel{\bullet}{\text{CO}}_{2} \uparrow \\
\stackrel{\bullet}{\text{R}} & \stackrel{\bullet}{\text{RCO}}_{2} + \text{R'} \stackrel{\bullet}{\text{O}} \xrightarrow{-\text{CO}_{2} \uparrow} \stackrel{\bullet}{\text{R}} + \stackrel{\bullet}{\text{X'}} + \text{carbonyl compound} \\
\stackrel{\bullet}{\text{S}} & \stackrel{\bullet}{\text{RCO}}_{2} + \text{R'} \stackrel{\bullet}{\text{O}} \xrightarrow{-\text{CO}_{2} \uparrow} \stackrel{\bullet}{\text{R}} + \text{R'} \stackrel{\bullet}{\text{O}}
\end{array}$$

List-I

List-II

P. Pathway P

1. C₆H₅CH₂ O CH

Q. Pathway Q

2. C₆H₅ O CH₃

R. Pathway R

S. Pathway S

4. C_6H_5 O C_6H_3 C_6H_5

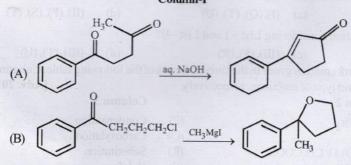
Code:

P Q R S (a) 1 3 4 2 (b) 2 4 3 1

- P Q R S (c) 4 1 2 3 (d) 3 2 1 4
- Match the reactions in Column-I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column-II.

Column-I

Column-II



- (p) Nucleophilic substitution
- (q) Electrophilic substitution

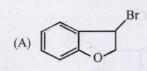
(C)
$$CH_2CH_2CH_2OH \xrightarrow{H_2SO_4}$$

(r) Dehydration

- (D) $CH_2CH_2CH_2C(CH_3)_2$ OH H_2SO_4 H_3C CH_3
- (s) Nucleophilic addition
- (t) Carbanion
- 41. Match each of the compounds given in Column-I with the reaction(s), that they can undergo, given in Column-II.

[2009]

Column-I



Column-II

- (p) Nucleophilic substitution
- (q) Elimination
- (r) Nucleophilic addition
- (s) Esterification with acetic anhydride
- (t) Dehydrogenation
- 42. Match the compounds/ions in Column-I with their properties/reactions in Column-II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. [2007]

Column-I

- (A) C_6H_5CHO
- (B) CH₃C≡CH
- (C) CN
- (D) I

Column-II

- (p) gives precipitate with 2, 4-dinitrophenylhydrazine
- (q) gives precipitate with AgNO₃
- (r) is a nucleophile
- (s) is involved in cyanohydrin formation

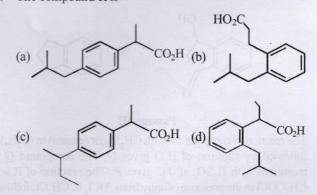
(19) 8 Comprehension/Passage Based Questions

Passage-I

An organic acid $P(C_{11}H_{12}O_2)$ can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S. [Adv. 2018]

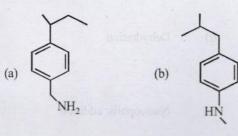
$$\begin{array}{c} \begin{array}{c} 1) \, H_2/Pd\text{-}C \\ 2) \, NH_3/\Delta \\ S \stackrel{(3)}{\leftarrow} Br_2/NaOH \\ 4) \, CHCl_3, \, KOH, \, \Delta \\ 5) \, H_2/Pd\text{-}C \end{array} \begin{array}{c} 1) \, H_2/Pd\text{-}C \\ P \stackrel{(2)}{\rightarrow} SOCl_2 \\ 3) \, MeMgBr, \, CdCl_2 \end{array} \\ \begin{array}{c} Q \stackrel{(1)}{\rightarrow} HCl \\ 2) \, Mg/Et_2O \\ \hline 3) \, CO_2 \, (dry \, ice) \\ 4) \, NaBH_4 \end{array} \longrightarrow R$$

43. The compound R is



[Adv. 2017]

44. The compound S is



(c)
$$NH_2$$
 (d) H

Passage-II

Treatment of benzene with CO/HCl in the presence of anhydrous AlCl₃/CuCl followed by reaction with Ac₂O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br₂/Na₂CO₃, followed by heating at 473 K with alc. KOH furnishes **Y** as the major product. Reaction of **X** with H₂/Pd-C, followed by H₃PO₄ treatment gives **Z** as the major product.

[Adv. 2018]

[Adv. 2018]

45. The compound Y is

(a)
$$COBr$$
 (b) HO OH Br $COBr$ (c) (d) Br $COBr$

46. The compound Z is

Passage-III

The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives Q. The compound Q on treatment with H_2SO_4 at $0^{\circ}C$ gives R. The reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed

by treatment with H_2O produces compound S. [Et in compound P is ethyl group]

$$(H_3C)_3C$$
 $CO_2Et \longrightarrow Q \longrightarrow R \longrightarrow S$

47. The product S is

(d)
$$(H_3C)_3C$$
 O CH_3 $COCH_3$

48. The reactions, Q to R and R to S, are

- (a) Dehydration and Friedel-Craft's acylation
- (b) Aromatic sulfonation and Friedel-Craft's acylation
- (c) Friedel-Craft's alkylation, dehydration and Friedel-Craft's acylation
- (d) Friedel-Craft's alkylation and Friedel-Craft's acylation

Passage-IV

P and **Q** are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O . On heating, **P** forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, **P** as well as **Q** could produce one or more than one from **S**, **T** and **U**.

- 49. Compounds formed from P and Q are, respectively
 - (a) Optically active S and optically active pair [T, U]
 - (b) Optically inactive S and optically inactive pair [T, U]
 - (c) Optically active pair [T, U] and optically active S
 - (d) Optically inactive pair [T, U] and optically inactive S
- 50. In the following reaction sequences V and W are respectively

$$Q \xrightarrow{\text{H}_2/\text{Ni}} V$$

$$+ V \xrightarrow{\text{A1Cl}_3 \text{ (anhydrous)}} \xrightarrow{\text{1. Zn-Hg/HCl}} W$$

(b)
$$CH_2OH \\ CH_2OH \\ V$$
 and W

Passage-V

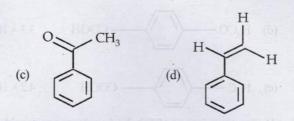
In the following reaction sequence, the compound J is an intermediate.

$$\mathbf{I} \xrightarrow{\text{(CH}_3\text{COO})_2\text{O}} \mathbf{J} \xrightarrow{\text{(i) H}_2,\text{Pd/C}} \mathbf{K}$$

$$\xrightarrow{\text{(ii) SOCl}_2} (\text{iii) anhyd. AlCl}_3$$

J (C₉H₈O₂) gives effervescences on treatment with NaHCO₃ and also give positive Baeyer's test. [2012]

51. The compound I is



52. The compound K is

9 Assertion and Reason Type Questions

Each question contains **STATEMENT-1** (Assertion) and **STATEMENT-2** (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is incorrect.
- (d) If Statement -1 is incorrect but Statement -2 is correct.
- 53. Statement-1: p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.
 Statement-2: o-Hydroxybenzoic acid has intramolecular

hydrogen bonding. [2007]

54. Statement-1: Acetic acid does not undergo haloform reaction.Statement-2: Acetic acid has no alpha hydrogens.

[1998 - 2 Marks]
55. Statement-1: Acetate ion is more basic than the methoxide

ion.

Statement-2: The acetate ion is resonance stabilized

[1994 - 2 Marks]

	10	Subjective Problems	
56.		ch the K_a values	[2003] Ka
	(a) (b)	Benzoic acid O ₂ N——COOH	6.4×10^{-5} 30.6×10^{-5}
	(c)	СІ СООН	10.2 × 10 ⁻⁵



(d)
$$H_3CO$$
 — COOH 3.3×10^{-5} (e) H_3C — COOH 4.2×10^{-5}

57. A racemic mixture of (±) 2-phenylpropanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of the two esters produced.

[2003 - 2 Marks]

58. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures.

Ba*CO₃ + H₂SO₄
$$\longrightarrow$$
 (X) gas [C* denotes C¹⁴]
CH₂ = CH - Br $\xrightarrow{\text{(i) Mg/ether}}$ (Y) $\xrightarrow{\text{LiAlH}_4}$ (Z)

[2001 - 5 Marks]

Explain the formation of labelled formaldehyde (H₂C*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

59. An organic compound A, C₈H₄O₃, in dry benzene in the presence of anhydrous AlCl3 gives compound B. The compound B on treatment with PCl5, followed by reaction with H₂/Pd (BaSO₄) gives compound C, which on reaction with hydrazine gives a cyclic compound $D(C_{14}H_{10}N_2)$. Identify A, B, C and D. Explain the formation of D from C.

[2000 - 5 Marks]

- 60. Write the structural formula of the main organic product formed when:
 - Write the structures of the products A and B.

CH₃ — C —
18
OC₂H₅ $\xrightarrow{\text{H}_3\text{O}^+}$ $A+B$

[2000 - 2 Marks]

(ii)
$$(COOH)_2 + (CH_2OH)_2 + Conc.H_2SO_4$$

(iii)
$$o - HOOC - C_6H_4 - CH_2 - C_6H_5$$

$$\xrightarrow{SOCl_2} - \xrightarrow{G} - \xrightarrow{anhydrous} - \xrightarrow{H} - \cdots$$

$$H \xrightarrow{Zn-Hg} I$$
 [1995 - 2 Marks]

(iv)
$$C_6H_5 - CHO + CH_3 - COOC_2H_5$$

$$\frac{\text{NaOC}_2\text{H}_5 \text{ in absolute}}{\text{C}_2\text{H}_5 \text{ OH and heat}} - \frac{\mathbf{D}}{\text{--}}$$

[1995 - 1 Mark]

(v)
$$CH_3 - CH_2 - COOH \xrightarrow{P \text{ and bromine}} - \xrightarrow{A}$$

$$\xrightarrow{1. \text{ alcoholic KOH(excess)}} - \xrightarrow{B}$$
2. H^+

$$(vi) \quad \text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{CH}_3 \xrightarrow{\quad (i)\text{CH}_3\text{MgBr}(\text{excess}) \\ \quad (ii)\text{ H}^+} \rightarrow$$

[1994 - 1 Mark]

(vii)
$$C_6H_5COOH + CH_3MgI \rightarrow ? + ?$$

[1993 - 2 Marks]

ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water. [1981 - 1/2 Mark]

Explain briefly the formation of the products giving the structures of the intermediates.

$$\begin{array}{c|c} O & & & & & & & \\ O & & & & & & & \\ C & -OC_2H_5 & & & & & \\ CH_2 & & & & & & \\ C & -OC_2H_5 & & & & \\ & & & & & \\ O & & & & & \\ \end{array}$$

- 62. An ester A (C₄H₈O₂), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved. [1998 - 6 Marks]
- 63. Give reasons for the following:
 - Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why?

[1997 - 2 Marks]

(ii) Formic acid is a stronger acid than acetic acid;

[1985 - 1 Mark]

(iii) Acetic acid can be halogenated in the presence of red P and Cl2 but formic acid cannot be halogenated [1983 - 1 Mark] in the same way.



- Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly. [1995-2 Marks]
 - (i) C₆H₅-CO-CH₂-COOH
 - (ii) C₆H₅-CO-COOH
 - (iii) C₆H₅ CH COOH | OH
 - (iv) C₆H₅ CH COOH | NH₂
- 65. An organic compound A, C₈H₆, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A.
 [1994 3 Marks]
- 66. In the following reactions identify the compounds A, B, C and D. [1994 1 × 4 = 4 Marks]

- 67. An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with KMnO₄ also gives 'B'. 'B' on heating with Ca(OH)₂ gives 'E' (molecular formula, C₃H₆O). 'E' does not give Tollen's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenylhydrazone. Identify 'A', 'B', 'C', 'D' and 'E'. [1992 3 Marks]
- 68. Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br₂ and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO₂ to give ethanol. Suggest structures for 'X', 'Y' and 'Z'. [1992 1 Mark]
- 69. Arrange the following in:
 Increasing order of acid strength:

 (I) CICH₂COOH, (II) CH₃CH₂COOH,

 (III) CICH₂CH₂COOH, (IV) (CH₃)₂CHCOOH,

 (V) CH₃COOH
- 70. (i) $C_6H_5COOH \xrightarrow{PCl_5} C \xrightarrow{NH_3}$ $D \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} E;$ Identify C, D and E. [1991 2 Marks]

(ii)
$$H_3C-CH=CH-CHO \xrightarrow{NaBH_4} F$$

$$\xrightarrow{HCI} G \xrightarrow{KCN} H;$$

Identify F, G and H. [1991 - 2 Marks]

- 71. Compound A (C₆H₁₂O₂) on reduction with LiAlH₄ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave C. The compound D was oxidized further to give F which was found to be a monobasic acid (molecular weight = 60.0). Deduce the structures of A, B, C, D and E. [1990 4 Marks]
- 72. The sodium salt of a carboxylic acid, A, was produced by passing a gas, B, into an aqueous solution of caustic alkali at an elevated temperature and pressure. A, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, C. A sample of 0.4 g of acid C, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid C weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B and C. [1990 5 Marks]
- 73. Outline the reaction sequence for the conversion of
 - (i) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. [1990 2Marks]
 - (ii) Ethanal to 2-hydroxy-3-butenoic acid.

[1990 - 2 Marks]

(iii) acetic acid to tertiary-butyl alcohol.

[1989 - 11/2 Marks]

74. Complete the following reactions:

$$CH_3COOH \xrightarrow{?} CICH_2COOH \xrightarrow{excess ammonia} ?$$

[1988 - 1 Mark]

75. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B), (A) on mild oxidation gives (C), (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D), (D) with phosphorus pentachloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid.
Identify the compounds A, B, C, D and E.

[1987 - 5 Marks]

- 76. Complete the following with appropriate structures:
 - (i) $(CH_3CO)_2O \xrightarrow{C_2H_3OH} CH_3COOH + ?$ [1986 1 Mark]
 - (ii) ? $\xrightarrow{\text{NaOH}}$ \longrightarrow CH=CH-CHO [1986-1 Mark]

- 77. A liquid (X), having a molecular formula C₆H₁₂O₂ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are the structures of (X), (Y) and (Z)? [1986 3 Marks]
- 78. Arrange the following in increasing ease of hydrolysis CH₃COOC₂H₅, CH₃COCl, (CH₃CO)₂O, CH₃CONH₅.
- 79. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis: Propionic anhydride from propionaldehyde [AgNO₃/NH₄OH, P₂O₅]. [1984 2 Marks]
- [AgNO₃/NH₄OH, P₂O₅]. [1984 2 Marks] 80. State the conditions under which the following preparations are carried out. Give the necessary equations which need not be balanced.
 - (i) Ethanol from acetylene
- [1983 1 Mark]
- (ii) Acetic acid from methyl iodide [1983 1 Mark]

- 81. An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid (B). When B is treated with bromine in presence of phosphorus, it yields a compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D. [1982 2 Marks]
- 82. Outline the accepted mechanism of the following reaction.

 Show the various steps including the charged intermediates.

 [1981 3 Marks]

$$\bigcirc + CH_3 - C - CI \xrightarrow{AlCl_3} \bigcirc C - CH_3 + HCI$$

83. Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified. [1981 - 2 Marks]

?

Answer Key

			To I	opic	-1 : Pre	para	ation	and I	rope	rties	s of Ca	rboi	nyl Co	mpo	unds				
1.	(a)		(d)	3.	(a)	4.	(b)	5.	(c)	6.	(c)	7.	(c)	8.	(b)	9	(c)	10	(a)
11.	(b)		(a)	13.	(b)	14.	(b)	15.	(d)	16.					(c)		(b)	20.	
21.	(b)		(b)		(12)	24.	(18)	25.	(12)	26.	(4)		(5)	28.			(0)	20.	(0)
30.	C ₆ H ₅ C	H(O	COCH ₃)	benz	ylidene	acetate	-010	31.	(sodia		otassiur				(False)	34	(True	135	(Foloo
36.	(a,c,d)	37.	(a,b,d)	38.	(c, d)		(a, c)		(b, d)	41.	(a, b)	42.	(b, c)		(a, b, c)			45.	
46.			(b, c)	48.	(c)	49.	(a, b,		(b)		(b, d)						(a, c)		0.00
56.	(A) - r	s; (E	B) - p, q; ((C) -	p, q, r; (I	D) - p,	S		(2)				(4,0)		The state of the s	60.	3320		10.15(b) (10.00)
62.	(a)		(d)		(d)	65.		66.			(b)	68.	(a)			70.		61.	(0)
		To	pic-2:	Pre	parati	on ar	d Pro	pert	ies of	Car	boxyli	c Aci	ids ar						
1.	(a)		(a)		(d)				(d)		(b)	1000		No. in Case of	(c)		_	10.	(c)
11.	(a)	12.			(a)			15.	(d)				(909)			19.	10000		(18.00)
21.	(CO)	22.	(False)	23.	(False)	24.	(c, d)	25.	(b)	1232	(a, d)						(a, c,		(10.00)
	(b, d)	31.	(d) 32	2.(a, l				33.	(a, b)	127	(b)	35.		36.		37.		38.	(4)
30.	(a)	40.	A-r, s,	t;B	-p, s;C	- r, s;	D-q,	r							(C)-r			30.	(u)
30. 39.	(a)			an install	/1	11 -		12	(2)		(b)	45.				47.			
	(A) - p	q, s;	(B) - q; ((C) - $($	q, r, s; (L	7 - 4,		47.	(a)	77.	101		101	40	(2)	41	(2)	48.	(0)



Hints & Solutions



Topic-1: Preparation and Properties of Carbonyl Compounds

1. (a

2. (d) Cl
$$\frac{\delta_{-} \delta_{+}}{\text{(i) CH}_{3} \text{MgBr}}$$
 Cl $\frac{\delta_{-} \delta_{+}}{\text{(ii) aq. acid}}$ (nucleophilic addition)

5-Keto-2-methylhexanal

3. (a)
$$CH_3 - CH_2 - C - CH_3 \xrightarrow{CN}$$

O

 $CH_3CH_2 - C - CH_3 \xrightarrow{95\%} CH_3CH_2 - C - CH_3$
 CN
 CN
 $COOH$

$$COOH$$

$$COOH$$

 $\stackrel{\triangle}{\longrightarrow} CH_3CH = C - CH$ $\downarrow COOH$

4. **(b)** The ring to which –NH group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which –C = O is attached is deactivated. Hence, the electrophile NO₂⁺ would go to the *para*-position of the activated ring.

(c) This reaction is an example of "Perkin reaction".
 The compound X should be (CH₃CO)₂O.

 In this step the carbanion is obtained by removal of an α-H atom from a molecule of an acid anhydride, the anion

α-H atom from a molecule of an acid anhydride, the anion of the corresponding acid acting as a necessary base.

6. (c) H₃C - C - CH₂CH₃
$$\frac{I_2/OH^-}{\text{(haloform reaction)}}$$

 (c) Reaction of PhMgBr with carbonyl compounds is an example of nucleophilic addition on carbonyl group which increases with the increase in electron-deficiency of carbonyl carbon.

Thus the decreasing order should be

$$\begin{array}{c|c} O & O & O \\ \parallel & \parallel & \parallel \\ CH_3 \longrightarrow C-H > CH_3 \longrightarrow C \longleftarrow CH_3 > C_6H_5 - C - C_6H_5 \\ \text{(II)} & \text{(III)} & \text{(III)} & \text{(I)} \\ \text{Carbonyl C is most} & \text{electron deficient} \\ \text{due to only one} & \text{tree present} & e \text{ deficient because} \\ +1(-CH_3) \text{ group} & \text{care supplied by two} \\ -C_6H_5 \text{ gps. due to} \\ +M \text{ effect} & \text{the present} \\ \end{array}$$

8. (b)

COOH HOH₂C

$$H^*/H_2O$$
 $CH_2OH HOOC$

 (c) Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.

$$P \xrightarrow{\text{H}_2\text{O/H}^+} \text{H}_2\text{C} \xrightarrow{\text{OH}} \text{CH}_3 \xrightarrow{\text{C} = 0} \text{CH}_3 \xrightarrow{\text{C} = 0} \text{CH}_3$$

$$Q \xrightarrow{\text{H}_2\text{O/H}^+} \text{H}_3\text{C} \xrightarrow{\text{OH}} \text{OH} \xrightarrow{\text{C} + 0} \text{CHO}$$

10. (a) Both compounds do not contain α-hydrogen hence

undergo Crossed Cannizzaro reaction.

Initially OH⁻ attacks at the carbonyl carbon of HCHO than that of PhCHO because carbonyl carbon of HCHO is

(i) more electrophilic than that of C₆H₅CHO

(ii) less sterically hindered

to give hydroxymethoxide which acts as hydride donor in next step to give sodium formate.

Carboxyl carbon less electrons deficient

11. **(b)** Zn(Hg), HCl cannot be used when acid sensitive group like –OH is present, but NH₂NH₂, OH⁻ can be used.

Due to $\pi - \sigma - \pi$ conjugation, this dehydrated product will be most stable.

 (b) This is a type of deuterium exchange reaction. Mechanism

$$\begin{bmatrix} CH_3 - C - CH_3 & \longrightarrow CH_3 - C = CH_2 \\ O & :OH \end{bmatrix} + O$$
(keto form) (enol form)

$$CH_{3}-C=CH_{2}\xrightarrow{OD^{-}}CH_{3}-C=CH_{2}$$

$$D-O_{\oplus}-H\longleftarrow CH_{2}\longrightarrow CH_{3}-C=CH_{2}$$

$$CH_{3}-C-CH_{2}D\rightarrow D$$

$$(keto form)$$

$$CH_{3}-C-CH_{2}D\rightarrow D$$

$$(keto form)$$

$$CH_{3}-C-CH_{2}D\rightarrow CH_{3}-C=CD_{2}$$

$$OH$$

$$CH_{3}-C-CH_{2}D\rightarrow CH_{3}-C=CD_{2}$$

$$OH$$

This reaction is fast in basic conditions where all $\alpha-H$ will replace by D.

14. (b) The possible mechanism is

(i)
$$Ph - C = O + OH - \longrightarrow Ph - C - O - OH$$

2nd molecule

The slowest step is the transfer of hydride to the carbonyl group as shown in step (ii).

15. (d) *m*-Chlobenzaldehyde does not contains α-H atom and thus undergoes conc. KOH. Cannizzaro reaction with

16. (a)
$$CH_3 - C - CH_3$$
 $CH_3 - C = CH_2$

keto form

enolic form

No. of σ bonds in enolic form : 3 + 1 + 1 + 1 + 1 + 2 = 9

No. of π bonds in enolic form: 1

No. of lone pairs of electrons in enolic form = 2

 (d) -CHO withdraws electrons from the double bond or from a conjugated system towards itself.

$$CH_2 = CH - C = 0$$
 or $CH_2 = CH - CH = 0$

- 18. (c) Iodoform test is given by compounds having -COCH₃, CHOHCH₃ and CH₃CH₂OH. Thus diethyl ketone does not give this test.
- (b) The compound containing α-H atom (CH₃CHO) does not undergo Cannizzaro's reaction. The other three reaction α-hydrogen.
- 20. (c) $CH_3CHO + 2Cu^{2+} + OH^- \rightarrow CH_3COOH + Cu_2O \downarrow$ Fehling solution (red)
- 21. (b) Compounds having $-C CH_3$ groups, show

positive iodoform test.

Hence,
$$CH_3 - CH_2 - CH_2 - CH_3$$

(pentanone-2) gives this test. O

- 22. (b) Fehling solution, Schiff's reagent & Tollen's reagent react only with aldehydes, but Grignard reagents react both with aldehydes and ketones.
- (12)P gives FeCl₃ test and there are no intramolecular H-bonds.

Thus, P wil be a trihydric phenol.

Number of CH₃ groups = 12

24. (18) Reactions taking place as:

$$\begin{array}{c|c}
O \\
| & \\
CH_3 - C - H + HCHO \\
\hline
(Acetaldehyde) & (excess) \\
\hline
\end{array}$$
NaOH
$$\Delta$$

Number of CH_2 groups in R = 14Number of O-atoms = 4 Required Answer = 14 + 4 = 18

12)
$$\bigcirc O_3 \text{ (excess)}$$
 then Zn/H_2O

$$\stackrel{\text{OH HO:}}{\underset{N}{\text{NH}_2\text{OH}}} \stackrel{\text{OH OH}}{\underset{N}{\text{NN}}} \stackrel{\text{OH OH}}{\underset{N}{\text{NN}}} \stackrel{\text{OH}}{\underset{N}{\text{NN}}} \stackrel{\text{OH}}{\underset{N}} \stackrel{\text{OH}}{\underset{N}} \stackrel{\text{OH}}{\underset{N}} \stackrel{\text{OH}}{\underset{N}{\text{NN}}} \stackrel{\text{OH}}{\underset{N}} \stackrel{\text{OH}}{\underset{N}}$$

So, total 12 atoms are sp² hybridised (4 C atoms, 4 N atoms and 4 O atoms)

27. (5) General molecular formula for ketones is $C_nH_{2n}O$

$$C_n H_{2n} O = 100 \text{ or } 12n + 2n + 16 = 100, n = 6$$

Possible isomeric ketones with 6 carbon atoms are

Note that only isomer (III) has a chiral carbon so on reduction with $NaBH_4$ it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

For example:

$$\begin{array}{c} O \\ | \\ CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{\text{NaBH}_4} CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{\text{$(\pm$ racemic mixture)}$} H \end{array}$$

Due to presence of one chiral carbon, the alcohol can be on both optically active forms and the compound will be racemic mixture.

$$\begin{array}{c} \text{CH}_{3} \text{ O} \\ \text{CH}_{3} - \text{CH}_{2} - *\text{CH} - \text{C} - \text{CH}_{3} \\ \text{(III)} \\ + \\ \text{CH}_{3} \text{ O} \\ \text{CH}_{3} - \text{CH}_{2} - *\text{C} + \text{C} - \text{CH}_{3} \\ \text{CH}_{3} - \text{CH}_{2} - *\text{C} - \text{CH}_{3} + \text{CH}_{3} - \text{CH}_{2} - *\text{C} - *\text{C} - \text{CH}_{3} \\ \text{H} & \text{H} & \text{H} & \text{OH} \\ \text{(2S, 3R)} \\ \end{array}$$

A pair of diastereomers from R-isomer of ketone

A pair of diastereomers from S-isomer of ketone Note: All stereoisomers are reacted separately.

28.

$$\begin{array}{c}
1. O_{3} \\
\hline
2. Zn, H_{2}O
\end{array}$$

$$\begin{array}{c}
OH \\
\hline
-H_{2}O
\end{array}$$
NaOH(aq)

The number of intra molecular aldol condensation products $(\alpha, \beta$ –unsaturated carbonyl compound formed from Y is 1.

29.
$$CH_3 - C = CH - C - CH_3$$

C₆H₅CH(OCOCH₃)₂ benzylidene acetate;

$$CH_3 + CrO_3 + (CH_3CO)_2O \longrightarrow CH_3(OCOCH_3)_2 \xrightarrow{H^+/H_2O} CHO$$

sodium potassium tartarate.

(i) Free radical substitution

(ii) Thermite process

(iii) Nucleophilic addition

(iv) Cyanamide process;

(v) Nucleophilic substitution (vi) Bayer's process

(vii) Homologous pair

(viii) Electrophilic substitution (ix) Ostwald's process

(x) Homolytic addition.

33. False. Grignard reagents react with ketones to form teralcohols; hence here, ter-butanol will be formed.

True: Aldehydes (from primary alchols) may further be oxidised easily to acids as compared to ketones (from secondary alcohols).

35. False: Benzaldehyde has no α-hydrogen atom, hence, it does not undergo aldol condensation but undergoes Cannizzaro reaction.

36. (a, c, d)

(a)
$$COOEt \xrightarrow{(i) \text{ Lindlar's catalyst}}$$
 H_2 $COOEt \xrightarrow{(P)}$

$$O \longrightarrow COOEt \longrightarrow CN$$

$$H_3C$$

$$O \longrightarrow CN$$

$$O \longrightarrow$$

$$O \longrightarrow COOEt$$

$$O \longrightarrow CH = NH$$

$$H_3C$$

$$\begin{array}{c}
\text{NaBH}_4 \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}$$

$$\begin{array}{c}
\text{OH} \\
\text{COOEt} \\
\text{CH = NH} \\
\text{H}_3C$$

$$\xrightarrow{\text{H}_3\text{O}^+} \xrightarrow{\text{OH}} \xrightarrow{\text{COOH}} \xrightarrow{\text{CHO}}$$

(c) (P)
$$\xrightarrow{\text{NaBH}_4}$$
 $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{COOEt}}$ $\xrightarrow{\text{CN}}$

$$\begin{array}{c} \text{SnCl}_2 \\ \text{HCl} \end{array} \begin{array}{c} \text{OH} \\ \text{COOEt} \\ \text{H}_3 \text{C} \end{array}$$

OH COOH Linder's catalyst
$$H_2$$
 H_2 $COOH$ CHO

(i) Lindlar's catalyst, H2, (ii) NaBH₄,

(iii) SnCl2/HCl, (iv) H3O+ (d) Similarly, (P)

Hydrolysis of - CN gives - COOH and thus option (b) is not correct.



37. (a, b, d)

$$CH_{3}-CH-CH_{3} CH_{3}-C-CH_{3} OH$$

$$O_{2} O_{2} O_{2} OH$$

$$O_{3} OH OH$$

$$O_{4} OH OH$$

$$O_{5} OH OH$$

$$O_{7} OH OH$$

$$OH OH$$

$$\begin{array}{ccc}
\text{CHCl}_3 + (\text{CH}_3 - \text{COO})_2 & \text{Ca} & \xrightarrow{\text{Ca}(\text{OH})_2} & \text{CH}_3 - \text{C} - \text{CCl}_3 \\
\text{(R)} & \text{(S)} & \text{(Q)}
\end{array}$$

(a)
$$CH_3 - CH_3 + CHCl_3 \xrightarrow{(i)KOH} CH - CCl_3$$
(P) (R) (ii) H^+ $CH - CCl_3$

(b)
$$CHCl_3 + O_2 \xrightarrow{hv} COCl_2$$

Phosgene gas

(c)
$$CH_3 - C - CCl_3 \xrightarrow{aq.NaOH} CH_3 - C - O^- + CHCl_3$$

(d)
$$(CH_3 - COO)_2 Ca \xrightarrow{\Delta} CH_3 - C - CH_3$$

38. (c, d)

$$\begin{array}{c} CH_3-CH_2-CH-CH_2-CN \xrightarrow{\hspace*{0.5cm} (i) \ PhMgBr} \\ CH_3 \end{array} \xrightarrow{\hspace*{0.5cm} (i) \ PhMgBr} \\ CH_3 \end{array} \xrightarrow{\hspace*{0.5cm} (i) \ PhMgBr} \\ (ii) \ H_3O^* \\ OH \\ Asymmetric \\ carbon \end{array} \xrightarrow{\hspace*{0.5cm} (i) \ PhMgBr} \\ (ii) \ H_2O \\ Ph \\ (ii) \ H_2O \\ (iii) \ H_2O \\ (iiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiii) \ H_2O \\ (iiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiiii) \ H_2O \\ (iiii) \ H_2O$$

$$\begin{array}{c} O \\ & \\ & \\ \end{array} \\ + CH_3 - C - Cl \xrightarrow{anhy.AlCl_3} Ph - C - CH_3 \\ & \\ & \\ & \\ \end{array} \\ \begin{array}{c} (i) \ PhMgBr \\ (ii) \ H_2O \end{array}$$

(Q) No asymmetric carbon

$$\bigcap_{O} C - Cl + \frac{1}{2} (Ph - CH_2)_2 Cd \rightarrow \bigcap_{O} Ph$$

$$\downarrow_{(i)} PhMgBr$$

$$\downarrow_{(ii)} H_2O$$

$$Ph$$

$$\downarrow_{(ii)} H_2O$$

$$Ph$$

$$\downarrow_{OH}$$

$$carbon$$

$$(R)$$

$$\begin{array}{c} Ph-CH_2-C-H \xrightarrow{PhMgBr} Ph-CH_2-CH-Ph \\ OH \\ \downarrow CrO_3, dil.H_2SO_4 \\ \hline Ph-CH_2-C-Ph \\ OH \\ \hline \\ Ph-CH = C-Ph \xleftarrow{H_2SO_4} Ph-CH_2-C-Ph \\ COOH \\ (S) \\ No \ asymmetric \ carbon \end{array}$$

39. (a, c)

$$\begin{array}{c}
O & O & O \\
\hline
O & AlCl_3
\end{array}$$

$$\begin{array}{c}
O & O \\
\hline
O$$

$$\underbrace{\text{OOCl}_2}_{\text{(Q)}} \underbrace{\text{OH}}_{\text{(R)}} \underbrace{\text{Cl}}^{\text{AlCl}_3}$$

$$(S) \xrightarrow{Zn/Hg} HCl$$

$$\begin{array}{c} \text{CH}_{3} \\ \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} \\ \\ \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{CH}_{2} \\ \\ \text{CH}_{3} + \text{CH}_{3} - \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{CH}_{3} - \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} + \text{C} - \text{CH}_{3} + \text{C} - \text{CH}_{3} \\ \\ \text{CH}_{3} +$$

Q is steam volatile, but not R.

Q and R show positive test with 1% aqueous FeCl₃ solution but not S.

Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

(a, b, c) Aldehydes and α-Hydroxyketones show positive Tollen's test.

44. (a)

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c}$$

45. (c) Reaction I:

$$\begin{array}{c} O \\ H_{3}C \\ \end{array} \xrightarrow[H]{} + OH \xrightarrow{-H_{2}O} \end{array}$$

$$\begin{array}{c|c} Br & \stackrel{\Theta}{\longrightarrow} & \stackrel{\Theta}{\longrightarrow} & \\ O & & & \\ O & & & \\ \hline \\ H_3C & \stackrel{\Theta}{\longrightarrow} & \\ \hline \\ Br & & \\ \hline \\ Br & \\ \hline \\ (even more stable anion due to two -Br groups) \\ \end{array}$$

$$\begin{array}{c|c}
O \\
\hline
O \\
C \\
C \\
Br \\
Br \\
Br
\end{array}$$

$$H_3C$$
 $OH + \overrightarrow{CBr}_3$
 H_3C
 ON_3
 OON_3

The reaction starts with one mole each of Br₂ and acetone. In this reaction mechanism, we can see that consumption of bromine is more than that of acetone.

Thus, acetone will be left after completion of reaction. The reaction will not stop after forming P or Q, but continue till the product I is obtained.

Only option (c) matches with the result.

Reaction II:

$$H_3C$$
 C
 CH_3
 H_3C
 CH_2
 CH_2
 CH_2
 CH_2
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 $CH_$

Chemistry

Here, one mole of acetone reacts with one mole of Br_2 . This matches with the compound given in P.

46. (b,d)
$$CHCl_3$$
 OH CHO
 $CHCl_3$ OH
 OH
 $CHCl_3$ OH
 OH
 OH
 $CHCl_3$ OH
 OH

$$\begin{array}{c}
OH \\
O \\
CH_3
\end{array}
+ OH^{-} \xrightarrow{H_2O}
\begin{array}{c}
O \\
CH_3
\end{array}
+ H_2O$$

$$CH_3 \xrightarrow{C} CCl_2 \xrightarrow{C} CCl_2$$

$$CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3$$

$$OH \qquad OH$$

$$\begin{array}{ccc}
OH & OH \\
CHCl_2 & \hline
OH & CHO \\
\hline
CH_3 & CH_3 & CH_3 \\
\hline
(major) (S')
\end{array}$$

$$\begin{array}{c} (O) \\ (O) \\ (CH_3) \end{array} \xrightarrow{O} \begin{array}{c} (O) \\ (O) \\ (CH_2) \end{array} \xrightarrow{H_2O} \begin{array}{c} (O) \\ (O) \\ (CH_2) \end{array} \xrightarrow{H_2O} \begin{array}{c} (O) \\ (O) \\ (O) \end{array}$$

47. (b, c)

(same compound optically inactive) (methyl-methyl ketoxime)

48. (c)
$$+ CH_3CH_2CH_2Cl \xrightarrow{AlCl_3}$$
 Isopropylbenzene (cumene), (P)

$$\begin{array}{c|c}
O_2 & O - O - H \\
\hline
O_2 & O - O - H \\
\hline
Cumene \\
hydroperoxide
\end{array} \qquad \begin{array}{c}
OH \\
+ O \\
\hline
OH \\
Acetone (Q)
\end{array}$$

- (a, b, d) Carbonyl compounds having α H or α D undergo aldol condensation.
 - (a) $\overset{\alpha}{\text{CH}}_3$ CHO
- (b) CH₃ CH₂CHO
- (c) α CHO
- (d) $\stackrel{\alpha}{\text{CD}_3\text{CHO}}$ $(\alpha\text{-D present})$
- 50. (b) Three Cl of chloral makes its carbonyl carbon highly electron deficient, hence H₂O, a nucleophile easily adds on it forming chloral hydrate, CCl₃CH(OH)₂, which is quite stable due to intramolecular H-bonding between two OH groups.

$$Cl \xrightarrow{H} C + C = O \xrightarrow{H_2O} Cl_3C - C = O$$

$$Cl_3C - C = O$$

$$Cl_3C - C - OH$$

$$OH$$

51. (b,d)

(a) HCHO $\xrightarrow{\text{OH}^-}$ CH₃OH + HCOO (No new C - C bond is formed)

(b) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5 - CH_3$ (New C - C bond is formed)

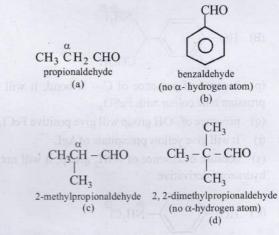
(c)
$$C = O \xrightarrow{Na/H_g} CH_2$$

(No new C - C bond is formed)

(d)
$$OH$$
 OH CHO

(New C - C bond is formed)

- (a,b) Aldehydes and ketones containing α-hydrogen atom undergo aldol condensation.
- 53. (b,d) Keto-enol tautomerism is shown in compounds having α-hydrogen on the C adjacent to the CO group.
- (a, c) Aldehydes having at least one α-hydrogen atom undergo aldol condensation.



55. (d) $P \rightarrow 3$, $Q \rightarrow 4$, $R \rightarrow 5$, $S \rightarrow 2$

(1)
$$Ph - C - CH_3 \xrightarrow{Zn - Hg/HCl} Ph - CH_2 - CH_3$$
Acetophenone

2)
$$CH_3$$
 $C-Cl$ CHO

(i) KMnO₄, KOH/Δ
(ii) SOCl₂ OHO

Toluene OHO
 OHO

(4)
$$NH_2$$
 $N_2 Cl$
 Cl
 Cu/HCl
 $Cu/$

(5)
$$CHO$$

$$CHO$$

$$CO/HCI$$

$$AlCI_3$$

$$Gattermann$$

$$Koch reaction$$

$$(R)$$

56. (A)-r, s; (B)-p, q; (C)-p, q, r; (D)-p, s

(A)
$$H_2N - NH_3Cl$$

- (p) does not have carbon thus, will not respond to (p).
- (r) because of presence of Cl[⊕] ion, it will give white precipitate of AgCl with AgNO₃.
- (s) because of -NH₂ group it will react with aldehydes to form hydrazone derivative.

- (p) because of presence of C-N bond, it will form prussian blue colour with $FeSO_4$.
- (q) presence of -OH group will give positive FeCl₃ test.
- (r) It will give yellow precipitate of AgI.
- (s) because of absence of $-\mathrm{NH}_2$ group, it will not give hydrazone derivative.

In the similar way, it will respond to p, q and r.

(D)
$$O_2N$$
 \longrightarrow $NH - \stackrel{\oplus}{NH_3Br}$

- (p) gives positive test with (p)
- (r) gives yellow precipitate of AgBr
- (s) it has a derivative of $NH_2 NH_2$, thus it will react with aldehyde to form hydrazone derivative.

57. (2)

$$(P)$$

$$C_9H_{18}O_2$$

$$(i) O_3$$

$$(ii) H_2O_2$$

$$(Q)$$

$$gives + ve iodoform$$

$$PCC$$

$$(R)$$

$$gives - ve iodoform$$

$$PCC$$

$$PCC$$

$$(S)$$

$$A$$

$$+ ve iodoform$$

$$+ ve iodoform$$

Sum of number of O-atoms in S and T = 1 + 1 = 2

58. (102018)

OH
$$(Q) + HOOC$$

$$OH$$

$$(R)$$

$$(V)$$

$$(PHBV)$$

$$(C_9H_14O_4)_n$$

$$(U)$$

Mol. Wt. of polymer = $[(104 \times 500) + (118 \times 500)]$ - (18×499) (no. of water molecules released) = (52000 + 59000) - 8982

 $=102018\,\mathrm{g}$

For 59-60. (Passage-I)

$$C \equiv CH$$

$$O(C_8H_6)$$

$$Pd\text{-BaSO}_4$$

$$O(C_8H_6)$$

$$O(C_$$

$$\begin{array}{c|c} & O \\ \hline \\ H_2O, HgSO_4, \\ \hline \\ H_2 \end{array} \\ \begin{array}{c} O \\ \hline \\ CH_3 \end{array} \\ \begin{array}{c} O \\ \hline \\ CH_3 \end{array} \\ \begin{array}{c} O \\ \hline \\ CH_2CH_3 \end{array} \\ \begin{array}{c} O \\ CH_2CH_3 \end{array} \\ \begin{array}{c}$$

59. (c) 60. (d) For 61-63. (Passage-II)

Let us summarize the given facts of the problem.

$$P + Q \xrightarrow{\text{aq.K}_2\text{CO}_3} R \xrightarrow{\text{HCN}} S \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{Heat}$$

Structures of P, Q, R and S can be established on going backward from the known final product.

$$H_3C$$
 H_3C
 H_3C

In the crossed aldol condensation product (R) from aldehydes (P) and (Q), dehydration will not occur readily because of formation of non-conjugated system.

61. (b) 62. (a) 63. (d) For 64-66 (Passage-III)

64. (d) 65. (a) 66. (c) For 67-69. (Passage-IV)

Before answering these question let us complete the sequence of reactions given in data.

The given compound (M) i.e.
$$H_3C$$
 Ph

is the only product formed by the action of KOH on compound K.

The compound
$$K$$
 is $Ph - C = O$

$$\begin{array}{ccc}
\text{CH}_{3} & & \text{O} \\
\text{II} & & \text{O} \\
\text{II} & & \text{CH}_{2}
\end{array}$$

$$\begin{array}{ccc}
\text{CH}_{3} & & \text{CH}_{3}
\end{array}$$

$$\begin{array}{cccc}
\text{CH}_{3} & & \text{CH}_{3}
\end{array}$$

Compound K (i.e. Ph-C=O) is one of the products of CH₃

ozonolysis of compound I. Therefore the compound I may be

$$C = C - Ph \xrightarrow{Ozonolysis} CO + Ph - C = CO$$

$$CH_3 CH_3 CH_3$$

$$(J) (K)$$

$$C = O \xrightarrow{KOH} Ph - CH_2 - OH$$

$$(J) Benzylalcohol$$

$$Corrected to be C. H. CHO and become Lie$$

Thus J seems to be C₆H₅CHO and hence I is

Now we will try to answer the questions.

67. (b) As can be seen from above reaction sequence compound (I) is Ph-CH = C-Ph and it is formed by CH₃

catalytic dehydration (acid catalysed) of a tertiary alcohol (compound *H*). Therefore, compound *H* is

$$\begin{array}{c} \text{OH} \\ \text{Ph}-\text{CH}_2-\text{C}-\text{Ph} \\ \text{CH}_3 \\ \\ \text{OH} \\ \text{Ph}-\text{CH}_2-\text{C}-\text{Ph} \xrightarrow{\text{H}^+} \text{-H}_2\text{O} \\ \text{CH}_3 \\ \end{array} \rightarrow \begin{array}{c} \text{OH} \\ \text{Ph}-\text{CH} = \text{C}-\text{Ph} \\ \text{CH}_3 \\ \end{array}$$

$$(H) \qquad \qquad (I) \\ \text{OH} \\ \text{OH}$$

(H) can be formed by the action of Ph CH₃ with PhCH₂MgBr as follows

Ph CH₃ + PhCH₂MgBr
$$\longrightarrow$$
 Ph CH₂-C-Ph + Mg $\stackrel{OMgBr}{\leftarrow}$ OH CH₃ $\stackrel{OH}{\leftarrow}$ CH₃ $\stackrel{OH}{\leftarrow}$ CH₃ $\stackrel{CH_3}{\leftarrow}$ $\stackrel{CH$

Therefore, the correct answer is option (b)

68. (a) As can be seen form the above sequence of reactions

Therefore, the correct answer is option (a).

(d) As can be seen from the above sequence of reactions the structures of compounds J, K and L respectively are

Ph - CHO, Ph - C = O and PhCOO
$$^-$$
K $^+$

$$(J) \qquad \qquad (L) \qquad \qquad (L)$$

$$CH_3 \qquad \qquad (K)$$

Thus, the correct answer is option (d),

70. (a) Ozonide can be reduced by $(CH_3)_2S$ to give carbonyl compounds and dimethyl sulphoxide.

$$R_2C$$
 CR_2
 CR_2
 CR_3
 CR_2
 CR_3
 CR_2
 CR_3
 CR_3

71.
$$H_2C = O + O = C - CH = O + O = CH_2$$

$$CH_3$$
 $H_2C = C - CH = CH_2$
Monomer

Thus, the possible polymer should be

$$\begin{array}{c}
CH_3 \\
nCH_2 = C - CH = CH_2 \longrightarrow \left\{ \begin{array}{c}
CH_3 \\
CH_2 - C = CH - CH_2
\end{array} \right\}_{n}$$
Structure of all *cis* configuration of the polymer.

$$\begin{pmatrix} CH_2 \\ H_3C \end{pmatrix} C = C \begin{pmatrix} CH_2 \\ H \end{pmatrix}_n$$

All cis form

- 72. (i) Formation of HCOONa and a primary alcohol due to Cannizzaro reaction of F and G indicate that either F or G should be HCHO. Thus, the alkene A should have $CH_2 =$ grouping. The remaining 5 C's of A should have grouping = HCC_4H_0 .
 - (ii) Formation of only E by the ozonolysis of D indicates that D (isomer of A, C_6H_{12}) should have following structure

$$\begin{array}{c} \operatorname{CH_3} & \operatorname{CH_3} \\ \operatorname{CH_3} - \operatorname{C} = \operatorname{C} - \operatorname{CH_3} & \xrightarrow{\operatorname{O_3}} \operatorname{2CH_3} \operatorname{C} = \operatorname{O} \\ \operatorname{CH_3} & \text{ (E) negative test with Fehling solution, but responds to iodoform reaction} \end{array}$$

Fehling's test is given by aldehydes and not ketones.

(iii) Since A is isomer of D, former should have following structure.

$$H_{2}C = CH - C - CH_{3}$$

$$CH_{3}$$

$$(A) (C_{6} H_{12}, alkene)$$

$$H_{3}C \xrightarrow{+}CH - C - CH_{3} \longrightarrow H_{3}C - CH - C - CH_{3}$$

$$CH_{3} \longrightarrow H_{3}C - CH - C - CH_{3} \longrightarrow H_{3}C - CH - C - CH_{3}$$

$$CH_{3} \longrightarrow H_{3}C - CH - C - CH_{3} \longrightarrow H_{3}C - CH - C - CH_{3}$$

$$\begin{array}{c}
Cl & CH_3 & CH_3 & CH_3 \\
 & \downarrow & \downarrow & CH_3CH - C - CH_3 + CH_3CH - C - CH_3 \\
 & \downarrow & CH_3 & Cl
\end{array}$$

$$\xrightarrow{B \text{ and } C}$$

$$\begin{array}{c} \text{CH}_{3} & \text{CH}_{3} \\ \text{H}_{2}\text{C} = \text{CH} - \text{C} - \text{CH}_{3} & \text{O}_{3} \\ \text{CH}_{3} & \text{CH}_{2}\text{O} + \text{OHC} - \text{C} - \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \end{array}$$

$$(A) & F \text{ and } G \\ \text{(Both give Fehling test, but not iodoform test)} \\ \text{CH}_{3} & \text{CH}_{2}\text{O} + \text{OHC} - \text{C} - \text{CH}_{3} & \text{conc. NaOH} \\ \text{(Cannizzaro reaction)} \end{array}$$

F and G

73.
$$C_9H_7O_2Cl \xrightarrow{KMnO_4} COOH$$

Hence, compound should have following part structure

or
$$C_3H_3O_2$$
 C_2H_3O C_2H_3O $C_3H_3O_2$ $C_3H_$

The enolic form of the compound is more stable than the keto form due to hydrogen bonding.

74.
$$CH = CH_2 \xrightarrow{Br_2/CCl_4} CH - CH_2Br_{(A)}$$

$$\begin{array}{c}
NaNH_{2} \\
\hline
(-2HBr)
\end{array}
\longrightarrow
\begin{array}{c}
C \equiv CH \\
(B)
\end{array}$$

$$\begin{array}{c}
HgSO_{4} \\
H_{2}SO_{4}
\end{array}
\longrightarrow
\begin{array}{c}
COCH_{3} \xrightarrow{NaOD/D_{2}O} \\
(Aldol condensation)
\end{array}$$

$$\begin{array}{c}
OD & O \\
C - CH_{2} - C
\end{array}
\longrightarrow
\begin{array}{c}
CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3}
\end{array}$$

$$\begin{array}{c}
N.NHCONH_{2} \\
C.CH_{3}
\end{array}$$

$$\begin{array}{c}
N.NHCONH_{2} \\
C.CH_{3}
\end{array}$$

75. The given reaction can be summarised as below:

Conclusions from the set of reactions

- (i) Carbon-hydrogen ratio in A indicates that it is a cyclic compound.
- (ii) Reaction of A with CH₃MgBr indicates that it should have a ketonic group.
- (iii) As B undergoes ozonolysis to form C, It must have a double bond, and C must have two carbonyl groups.
- (iv) Reaction of C (a dicarbonyl compound) with a base gives a cyclic compound, it indicates that intramolecular condensation have occurred during this conversion. Thus, A is cyclohexanone which explains all the given reactions.

The reaction is an example of benzil-benzilic acid type rearrangement.

CICH2CH2CH2COPh

$$\xrightarrow{-\text{HCI}} \text{CH}_2 \xrightarrow{\text{CH}} \text{CH}_2 \xrightarrow{\text{CH}} \text{CH}$$

(v)
$$R-C=C-R+HCIO_4 \longrightarrow R-C=C-R$$

$$C \qquad C \qquad CIO_4$$
OH

(vi)
$$O + Ph_3P = CH_2 \xrightarrow{\text{Wittig}} CH_2$$

(vii)
$$KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$$

$$CH_3CH_2$$
 $C = O \xrightarrow{(i) HCN} CH_3CH_2$
 $C \xrightarrow{(i) HCN} CH_3$
 $C \xrightarrow{(i) HCN} CH_4$
 $C \xrightarrow{(i) H$

$$(ii) \text{ H_2SO}_4 \xrightarrow{\text{CH}_3\text{CH}_2} \xrightarrow{\text{OH}} \xrightarrow{\text{C}} \xrightarrow{\text{OH}} \xrightarrow{\text{C}} \xrightarrow{\text{C$$

(ix)
$$CH_3 - CH_2 - C = O + HCH - CHO$$

H

 CH_3
 CH_3

$$\begin{array}{c}
OH \\
\xrightarrow{\text{NaOH}} CH_3CH_2 - C - CH - CHO \\
\downarrow \\
H CH_3
\end{array}$$

Hexamethylenetetramine (Urotropine)

77.
$$CHC_6H_5$$
 CHC_6H_5 CHC_6

LiAlH₄ reduces only ketonic group to 2° alcoholic group without affecting double bond. This dehydration occurs in acidic conditions.

78.

$$\xrightarrow{\text{tautomerises}} C_6H_5 - CH - CH - CH \xrightarrow{-H_2O}$$

$$C_6H_5-CH=CH-CHO$$

79. Following informations are provided by the problem.

(i) Since aldehyde A (C₁₁H₈O) gives C₆H₅CHO on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon (C₁₁-C₆=C₅), three hydrogen (H₈-H₅=H₃) and one oxygen atom, i.e., it should be C₅H₃O. Further the compound A has an aldehydic group, so the side chain can be written as C₄H₅CHO.

(ii) Formation of two moles of B from one mole of A by ozonolysis indicates that the side chain must possess two unsaturated linkages, one of which must be alkyne type, suggested by very low number of hydrogen atoms.

(iii) Further, since the aldehyde A does not undergo aldol condensation, α-hydrogen is absent and hence triple bond should be present between C₂ and C₃.

(iv) Thus the side chain C₄H₂CHO of A can be written as -CH=CH-C ≡ C-CHO.

(v) Thus compound A should possess following structure which explains all the given reactions.

$$\begin{array}{c|c} CH=CH-C\equiv C-CHO & CHO \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ \hline (ii) H_2O & & \\ \hline & & \\ \hline (ii) H_2O & & \\ \hline & & \\ \hline (CHO) & & \\ \hline & & \\ \hline (CHO) & & \\ \hline & & \\ \hline & & \\ \hline (CHO) & & \\ \hline & & \\ \hline (COOH) & & \\ \hline & & \\ \hline & & \\ \hline (OOOH) & & \\ \hline & & \\ \hline (OOOH) & & \\ \hline & & \\ \hline (OOOH) & & \\ \hline & & \\ \hline (OOOH) & & \\ \hline & & \\ \hline (OOOH) & & \\ (OOOH) & & \\ \hline (OOOH) & &$$

80.
$$\begin{array}{c} CH_{3} \\ CH_{3} \end{array} \xrightarrow{\text{dil KMnO}_{4}} CH_{3} \\ CH_{3} \end{array} \xrightarrow{\text{OH}} CH_{2} \xrightarrow{\text{CH}_{3}} CH_{2}$$

$$CH_{3} \xrightarrow{\text{CH}_{3}} CH_{2} \xrightarrow{\text{CH}_{3}} CH_{2}$$

$$CH_{3} \xrightarrow{\text{CH}_{3}} CH_{2} \xrightarrow{\text{CH}_{2}} CH_{2}$$

$$CH_{3} \xrightarrow{\text{CH}_{3}} CH_{2} \xrightarrow{\text{CH}_{2}} CH_{2}$$

The last step is intramolecular aldol condensation.

81.

$$\begin{array}{c} C_8H_6 & \xrightarrow{\text{dil. H}_2SO_4} B \xleftarrow{\text{anhydrous. AlCl}_3} RCOCl + C_6H_6 \\ (A) & \downarrow^{I_2, \text{ aq. KOH}} \end{array}$$

$$C + \text{Yellow compound (D)}$$

 (i) Formation of (B) from benzene and acid chloride in presence of anhydrous AlCl₃ (Friedel-Craft reaction) indicates that it is a ketone, C₆H₅COR.

(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction).
 This indicates that one of the alkyl groups in ketone (B) is -CH₃. Hence, (B) should be C₆H₅.CO.CH₃.

(iii) Since ketone (B) is also formed from the hydrocarbon $C_8H_6(A)$ by reaction with dil. H_2SO_4 and $HgSO_4$, the hydrocabon (A) must have an acetylenic hydrogen atom, i.e. $\equiv C - H$ grouping. Hence, (A) must be $C_6H_5C \equiv CH$.

Thus, compounds (A) to (D) are $C_6H_5.C \equiv CH \quad C_6H_5.CO.CH_3 \quad C_6H_5COOH \quad CHI_3$ (A)
(B)
(C)
(D)

Formation of (B) from (A)

OH

$$C_6H_5.C \equiv CH$$

Phenylacetylene (A)

 $C_6H_5.C \equiv CH$
 $C_6H_5.C \equiv CH_2$
 $C_6H_5.CO.CH_3$

Acetophenone (B)

82.
$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_2
 CH_3
 CH_3
 CH_3
 CH_2

The methyl group stabilizes the C = C in the enol form due to hyperconjugation.

However, the methyl group also stabilizes the carbonyl double bond in the keto form.

In fact, in simple carbonyl compounds, the methyl group stabilizes the carbonyl double bond much more than it stabilizes the enolic C = C bond.

Thus, a carbonyl in a ketone is slightly stronger than that in an aldehyde.

$$H_3C$$
 H
 H_2C
 H
 H_2C
 H

As a result, simple aldehydes generally have a higher enol content than simple ketones.

The two β -di carbonyl compounds have a much higher enol content than the two monocarbonyl compounds because of hydrogen bonding, conjugation and 6 membered cyclic form.

In fact, for these compounds, the enol form will be major form at equilibrium. Hence, the correct order of enol content is:

OH
(ii)
$$CH_3$$
- C - CH_2COCH_3 ; CH_3 - C - CH - $COCH_3$
 CH_3

(iii) (a) fuse with NaOH (b)
$$H^+$$
;

84. (i) Empirical formula can be calculated as

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.77	5.81	5
H	11.63	11.63	10
0	18.60	1.16	infact.

 \therefore Empirical formula of compound is $C_5H_{10}O$ and empirical formula wt. = 86.

Also molecular wt. = 86.

- ∴ Molecular formula of compound is C₅H₁₀O.
- (ii) Compound forms bisulphite addition compound and thus has carbonyl gp, i.e. aldehyde or ketone.
- (iii) It does not reduce Fehling solution and thus it is not an aldehyde but a ketone.
- (iv) It gives positive iodoform test and thus it has

(v) Above facts reveal that the compound is CH₃CH₂CH₂COCH₃ or (CH₃)₂CHCOCH₃ Pentan-2-one 3-Methylbutan-2-one 85. Let us summarise the given facts.

White ppt.
$$\leftarrow$$
 AgNO₃ (A) $\xrightarrow{\text{KOH}}$ (B) + (C) $\xrightarrow{\text{O}_2}$ (A) $\xrightarrow{\text{KOH}}$

$$(B) + (C) \xrightarrow{O_3}$$
(Isomeric alkenes, C_6H_{12})

With the help of structures of the four carbonyl compounds, (i) to (iv), we may write the structures of the two isomeric olefins (B) and (C). The two carbonyl compounds should be joined in such a way that the parent olefin has 6 carbon atoms. Two such possibilities are the combination of carbonyl compounds having (2+4) carbon atoms [i.e. (ii) + (iv)] and (3+3) carbon atom [i.e. (ii) + (ivi)].

combination of carbonyl compounds having
$$(2+4)$$
 carbon atoms $[i.e. (i) + (iv)]$ and $(3+3)$ carbon atom $[i.e. (ii) + (iii)]$.

CH₃CHO + OHC.CH(CH₃)₂ \leftarrow

CH₃CH = CH.CH(CH₃)₂

(i) (iv) Olefin B (C₆H₁₂)

$$C_2H_3CHO + OC(CH_3)_2 \leftarrow O_3 \qquad C_2H_5CH = C(CH_3)_2$$
(ii) (iii) Olefin (C_6H_{12})

Thus, the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.

86. Acetaldehyde can be distinguished from acetone by using Tollen's reagent or Fehling solution or Schiff's reagent. Only acetaldehyde responds to all these tests.

- 87. It is a case of nucleophilic addition reaction. More the electron deficiency of the carbonyl carbon, greater will be its reactivity towards nucleophilic addition.
- **88.** (*i*) *o*-Hydroxybenzaldehyde has intramolecular H-bonding while the *p*-isomer has intermolecular H-bonding.

Intramolecular H-bonding in o-isomer, low b.p.

$$--HO \longrightarrow C = O --- H-O \longrightarrow C = O ---$$

Intermolecular H-bonding in the p-isomer (association), high b.p.

(ii) In the acylium ion $(R-C \equiv O^+)$, each and every element has a complete octet, while in carbonium ion $(R-C^+ \equiv O)$, carbon bearing positive charge has incomplete octet which makes it more reactive than the acylium ion.

$$R:C:O^+: \longleftrightarrow R:C^+=O:$$

Acylium ion

Carbonium ion

(Carbon has only six electrons)

(iii) Hypoiodite (¬OI) is a strong base than iodide ion (I¬). (O is more electronegative thus easily accommodates negative charge than I in I¬). Haloform reaction is base-promoted reaction (the first step involves removal of acidic hydrogen atom of acetone by base). Hypoiodite ion being strong base than iodide ion, can easily remove acidic hydrogen atom.

(iv) In weakly acidic medium, carbonyl group is protonated to form conjugate acid.

$$C = O + H^{+} \longrightarrow Carbon becomes$$

In strongly acidic medium (pH < 3.5), the unshared pair of electrons of N of the reagent is protonated, with the result nucleophile (NH₂NH₂) is converted to an electrophile (NH₂NH₃) which cannot react.

$$H_2N - NH_2 \xrightarrow{H^+} H_2N + NH_3$$

Hence, in highly acidic medium, there is no protonation of the carbonyl group.

(v) Alcohols show hydrogen bonding.

The boiling points of carbonyl compounds are lower than the corresponding alcohols since former do not show intermolecular H-bonding like alcohols.

$$C_4H_9 - O - H$$
 $H - O - C_4H_9$

(H-bonding between two butanol molecules)

Solubility of butanal in water is due to hydrogen bonding between butanal and water molecules (similarity to butanol).

 $Ca(OH)_2 \rightarrow (CH_3COO)_2Ca \xrightarrow{distil} (CH_3)_2CO$

89. (i)
$$CH_3CH_2 - C = CH + Na^+ NH_2^-$$

$$\longrightarrow CH_3CH_2 - C = C^- : Na^+$$

$$\xrightarrow{CH_3I} CH_3CH_2 - C = C - CH_3$$

$$\xrightarrow{HgSO_4} CH_3CH_2CH_2 - C - CH_3$$
(ii) $CH = CH \xrightarrow{H_2SO_4} CH_3CHO \xrightarrow{KMnO_4} CH_3COOH$
Acetylene $Hg^{2+} CH_3CHO \xrightarrow{KMnO_4} CH_3COOH$

(iii) HCHO
$$\xrightarrow{[O]}$$
 HCOOH $\xrightarrow{\text{Ca (OH)}_2}$ Methanal

$$(HCOO)_2Ca \xrightarrow{(CH_3COO)_2 Ca} 2 CH_3CHO$$

Ethanal



Topic-2: Preparation and Properties of Carboxylic Acids and its Derivtives

 (a) Acidic strength depends upon the stability of anion formed higher the stability of the anion, higher will be acidic strength of the parent acid. Thus anion:

HC ° CCOO⁻>
$$H_2$$
C=CHCOO⁻> p -C₆ H_4 (OMe) COO⁻>
$$sp sp^2 H_3$$
CCH₂COO⁻

$$sp^3$$

2. (a)

∴ Acidity order is I > II > III > IV

 (d) Carbolic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO₂ on treatment with aq. NaHCO₃ solution.



4. (b) β-Ketoacids undergo decarboxylation easily. It is due to the stability of transition state formed after decarboxylation of β-keto acids. This is not possible in case of other acids.

$$\begin{array}{c}
O \\
C
\end{array}$$

$$\begin{array}{c}$$

5. (d)
$$O_2N$$
 O_2 O_2N O_2 O_2N O_3 O_4 O_4 O_5 O_6 O_7 O_8 O_8 O_8 O_9 O_9

8. (c)
$$\stackrel{CO_2H}{\longrightarrow}$$
 $\stackrel{CO_2H}{\longrightarrow}$ $\stackrel{CO_2H}{\longrightarrow}$ $\stackrel{NO_2}{\longrightarrow}$ $\stackrel{NO_2}{\longrightarrow}$

(OH group is strong activating and COOH group is weak deactivating group.)

$$\begin{array}{c}
OCH_3 \\
& \xrightarrow{HNO_3/H_2SO_4}
\end{array}$$

$$\begin{array}{c}
OCH_3 \\
CH_3 \\
CH_3
\end{array}$$

(OCH₃ group is more activating)

$$\begin{array}{c} & & & \\ & &$$

(Benzene ring having -O- is activated, benzene ring having -CO is deactivated)

(a) Carboxylic acid is stronger acid than phenol. The
presence of electron withdrawing group (e.g. Cl) increases
acidic strength, while presence of electron donating group
(e.g. CH₃) decreases acidic strength.

10. (c)
$$Ph$$

*
OH

Heat

 CH_3
 CH

11. (a) This is simply a displacement reaction.

$$SO_3H$$

$$+ CH_3COO^-Na^+$$

$$CH_3$$
Acid
$$Salt$$

$$SO_3^-Na^+$$

- **12.** (a) The optically active acid will react with d and l forms of alcohol present in the racemic mixture at different rates to form two diastereomers in unequal amounts leading to optical activity of the product.
- 13. (a) Recall that, esters react with excess of Grignard reagents to form 3° alcohols having at least two identical alkyl groups corresponding to Grignard reagent.

$$\begin{array}{ccc}
O & OH \\
R - C - OC_2H_5 + R"MgX \longrightarrow R - C - R" \\
R"
\end{array}$$

Since, here Grignard reagent is CH₃MgBr, the 3° alcohol should have at least two methyl groups. Hence, (a) is the correct choice.

14. (c)
$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$

15. (d)
$$C_2H_5COOH + NaHCO_3 \rightarrow$$

$$C_2H_5COONa + H_2O + CO_2$$

(a) LiAlH₄ is a reducing agent, it reduces –COOH group to –CH₂OH group.

17. (909) Reactions involves are:

$$H - C \equiv C - (CH_2)_{15} - CO - Et \xrightarrow{(i)Hg^{2+}} H_{3O^{+}}$$

$$\begin{array}{ccc}
O & O \\
\parallel & \parallel \\
CH_3 - C - (CH_2)_{15} - C - OEt
\end{array}$$
(ii) Zn-Hg/HC1

$$CH_3 - (CH_2) - (CH_2)_{15} - C - OEt \xrightarrow{H_3O^+} \Delta$$

$$CH_3 - (CH_2)_{16} - COOH$$

$$CH_3 - (CH_2)_{16} - COOH \xrightarrow{CH_2 - OH} \\ (excess) \xrightarrow{H^+}$$

$$\begin{array}{c|c}
CH_2 - O - C - (CH_2)_{16} - CH_3 \\
 & O \\
 & | CH_2 - O - C - (CH_2)_{16} - CH_3 \\
 & | O \\
 & CH_2 - O - C - (CH_2)_{16} - CH_3 \\
 & | CH_2 - O - C - (CH_2)_{16} - CH_3
\end{array}$$

$$\xrightarrow{\text{CaCl}_2} \frac{3}{2} (\text{CH}_3 - (\text{CH}_2)_{16} - \text{COO})_2 \text{Ca}$$
(R)

1 mole of Q will 1.5 mole of R. So, mass of R produced = $606 \text{ g} \times 1.5 = 909 \text{ g}$

19. (4) All carboxylic acids and phenols are soluble in aqueous NaOH. Thus, four compounds are soluble in aqueous NaOH. 20. (18.00)

$$\begin{array}{c|c} O & O & H \\ \parallel & \parallel & \parallel \\ C-OMe & & & & \\ Ph & & & & \\ \end{array}$$

DBE = 18 21. CO; HCOOH $\xrightarrow{\text{Conc.H}_2\text{SO}_4}$ CO + H₂O **22. False:** H-Bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.

$$R - C O - H - O C - R$$

23. False: Saponification is alkaline hydrolysis of esters.

$$\begin{array}{c} -\text{CO}_2 \downarrow \Delta \\ \text{O} \\ \text{C} - \text{OH} \\ \text{COOH} \\ \text{(R)} \end{array}$$

$$\begin{array}{c}
Mg \\
Dry \text{ ether}
\end{array}$$

$$\begin{array}{c}
O = C = O \\
C - OMgBr \xrightarrow{H_3O^+}
\end{array}$$

$$H - C$$

$$H -$$

25. (b)

CH=CH₂

$$(i)$$
 B₃H₆
 (ii) NaOH, H₂O₂, H₂O

 (P)
 $(CH_2 - CH_2 - CH)$
 (P)
 $(CH_2 - CH)$
 (P)
 (P)
 $(CH_2 - CH)$
 (P)
 (P)

Note: Primary alcohol on oxidation with CrO₃ in anhydrous medium give aldehyde. While with CrO₃, H₂SO₄, carboxylic acid is produced.

MeO

(a, d)
$$Hg^{2+}$$
, dil H_2SO_4 (hydration) O $AgNO_3$ NH_4OH

HOOC

27. (a, b, d)

(a)
$$Conc.H_2SO_4$$

$$\Delta$$
(b) $Me \longrightarrow H \xrightarrow{heated Fe tube}$

$$873 K$$
(c) $Chooled$

$$Chooled$$

$$Choled$$

$$Chooled$$

$$Chooled$$

$$Chooled$$

$$Chooled$$

$$Chooled$$

$$Chooled$$

28. (c, d)

 $LiAlH_4/(C_2H_5)_2O$: Reduces esters, carboxylic acids, epoxides and aldehydes and ketones.

(Clemmensen

reduction)

BH₃ in T.H.F: Reduces –COOH and aldehydes to alcohols but does not reduce esters and epoxides.

NaBH₄ in C₂H₅OH: Reduces only aldehydes and ketones to alcohols.

Raney Ni in T.H.F.: Does not reduce –COOH, –COOR and epoxides but it can reduce aldehydes to alcohols.

29. (a, c, d)

30. (b,d)

- (a) Both are soluble in NaOH. Hence, inseparable.
- (b) Only benzoic acid (C_6H_5COOH) is soluble in NaOH and NaHCO₃, while benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, **separable**.
- (c) Although NaOH can enable separation between benzyl alcohol ($C_6H_5CH_2OH$) and phenol (C_6H_5OH) as only the latter is soluble in NaOH. However, in NaHCO₃, both are insoluble. Hence, **inseparable**.
- (d) α-Phenylacetic acid (C₆H₅CH₂COOH) is soluble in NaOH and NaHCO₃, while benzyl alcohol (C₆H₅CH₂OH) is not. Hence, **separable**.

31. (d)

CHO
$$OH$$
intramolecular Cannizzaro reaction

CH2OH

 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH

32. (a, b, d) Ethyl chloride and acetyl chloride react with alc. KCN by nucleophilic substitution reaction while benzaldehyde undergoes benzoin condensation:

33. (a,b) Iodoform reaction is given by the compounds containing -COCH₃, -CH(OH)CH₃ group and also CH₃CH₂OH and CH₃CHO.

2-Hydroxypropane (CH₃CHOHCH₃) contains the grouping CH₃CHOH— and acetophenone (C₆H₅COCH₃) contains the grouping CH₃CO—.

34. (b)

$$\underbrace{\text{COOH}}^{\text{CH}_2} \xrightarrow{\text{i) O}_3} \underbrace{\text{COOH}}^{\text{O}}$$

35. (a)
$$Cl \xrightarrow{i) \text{ KCN}} CN \xrightarrow{ii) \text{ H}_3\text{O}^+, \Delta}$$

$$COOCH_3$$

$$(T) \xrightarrow{COOH} \xrightarrow{iii) \operatorname{LiAlH}_4} OH$$

$$\xrightarrow{\text{iv) conc. H}_2\text{SO}_4} \bigcirc \bigcirc$$

COOMe
$$(IV)$$
 (IV) $($

ii) conc.
$$H_2SO_4$$
 $=$ (R)

36. (a

$$\begin{array}{c|c}
 & \text{NaOH} \\
 & \text{Br}_2 \\
 & \text{(Haloform reaction)}
\end{array}$$
COOH
$$+ \text{CHBr}_3$$

37. (c) Perkin condensation of benzaldehyde with (CH₃CO)₂O/CH₃COOK yields cis and trans form of cinnamic acid.

$$C_6H_5CHO + (CH_3CO)_2O \frac{(i) CH_3COOK}{(ii) H^+}$$

Benzaldehyde Acetic anhydride

C₆H₅CH = CHCOOH Cinnamic acid cis and trans

38. (d) Alkylbenzenes when treated with Br₂ at high temperature, in the presence of sunlight and absence of halogen carrier undergo halogenation in the side chain via free radical formation.

$$\begin{array}{c|c} CH_3 & CH_2Br \\ \hline & Br_2/heat \\ \hline & light \end{array} \qquad \begin{array}{c|c} Br_2 \\ \hline & heat, light \end{array}$$

Toluene Benzyl chloride

Benzyl chloride Benzo trichloride
Free radical mechanism (Substitution reaction)

39. (a)

$$C_{6}H_{5}\dot{C}H_{2} + CO_{2} + CH_{3} + CO_{2} + CO_{2} + CO_{2} + CO_{2} + CO_{3} + CO_{2} + CO_{3} + CO_{3}$$

$$CH_3$$
 $CO_2 + C_6H_5\dot{C}H_2 + CH_3 - \dot{C}_5\dot{O}$
 $CH_2 - C_6H_5$
 $CH_2 - C_6H_5$

$$C_6H_5$$
 C_6H_5 C_6H_5 C_6H_5

$$C_{0}H_{5} \circ CH_{3} \rightarrow C_{0}H_{5} \circ C_{0}H_{5} + O = C = O + CH_{3} \circ O + CH_{3} \circ$$



41. (A) - p, q, t; (B) - p, s, t; (C) - r, s; (D) - p

$$(A) \begin{picture}(20,5) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

$$(B) \begin{picture}(20,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

(C)
$$CHO$$
OH
$$(CH_3CO)_2O$$

$$(S)$$

$$(CH_3CO)_2O$$

$$(SH_3CO)_2O$$

$$(SH_3CO)_$$

(D)
$$Nu$$
 Nu $+ Br$ Nu $+ Br$

42. (A)-p, q, s; (B)-q; (C)-q, r, s; (D)-q, r

(A) C₆H₅CHO forms ppt. of 2, 4 dibromophenylhydrazone

(p), forms silver mirror with ammonical silver nitrate – Tollen's reagent (q), forms cyanohydrin with CN⁻(s).

(B) $CH_3C \equiv CH$ gives ppt. with $AgNO_3$ (q)

(C) CN⁻ reacts with AgNO₃ to form ppt. of AgCN (q), it is a nucleophile (r) and forms cyanohydrin (s)

(D) I gives ppt. of AgI with AgNO₃ (q), and it is a nucleophile (r)

For 43-44 (Passage-I)

(i) The oxidation product (a dibasic acid) of the compound P reacts with ethylene glycol and gives polymer dacron (a very well known reaction) points out that the oxidation product i.e. the dibasic acid is terephthalic acid.

Dacron

(ii) Now since terephthalic acid is obtained by the oxidation of a carboxylic acid $P(C_{11}H_{12}O_2)$, P must have following partial structure $(C_{11}H_{12}O_2 - COOH - C_6H_4 = C_4H_7)$

COOH COOH

or

$$R$$
 P
 C_4H_7

(iii) The compound P undergoes reduction by means of H_2/Pd and also undergoes ozonolysis, it must have an unsaturated linkage. Further ozonolysis of P to form an aliphatic ketone indicates = $C(R_2)$ type of linkage for which

P should have following final structure, which

explains all the given reactions.

Glyoxal

Acetone

The above structure of P also explains other given reactions.





47. (a) 48. (a) For 49-50. (Passage-IV)

meso (S), optically inactive

P is in the cis-form, because it forms the cyclic anhydride.

(Racemic Mixture), optically inactive

50. (a) HOOC-CH=CH-COOH
$$\xrightarrow{\text{H}_2/\text{Ni}} \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$$
 Anhy.AlCl₃ $\bigcirc \bigcirc$ Q

$$\begin{array}{c}
O \\
O \\
O
\end{array}$$

$$\begin{array}{c}
OH \\
HCI
\end{array}$$

$$\begin{array}{c}
OH \\
H_3PO_4
\end{array}$$

$$\begin{array}{c}
OH \\
W
\end{array}$$

For 51-52 (Passage-V)

Reactions of compound J indicates that it has C = C linkage and -COOH group. Thus, J can be written as $C_6H_5CH = CH$ COOH. Since, J is unsaturated carboxylic acid and it is formed by the reaction of compound I with $(CH_3CO)_2O$ and CH_3COONa , compound I should be an aldehyde (recall Perkin reaction). Thus, the whole series of reactions can be written as below.

$$(I) \xrightarrow{\text{CHO}} \xrightarrow{\text{(CH}_3\text{CO)}_2\text{O}} \xrightarrow{\text{(J)}} \xrightarrow{\text{CH}} \xrightarrow{\text{CH}} \xrightarrow{\text{(i) H}_2-\text{Pd}} \xrightarrow{\text{(ii) H}_2-\text{Pd}} \xrightarrow{\text{CH}_2} \xrightarrow{\text{CH}_2} \xrightarrow{\text{anh.AlCl}_3} \xrightarrow{\text{CHC}_1} \xrightarrow{\text{COCl}} \xrightarrow{\text{CHC}_2} \xrightarrow{\text{CHC}_2} \xrightarrow{\text{CHC}_2} \xrightarrow{\text{CHC}_3\text{COONA}} \xrightarrow{\text{COCl}_3\text{COONA}} \xrightarrow{\text{COCNA}} \xrightarrow$$

51. (a) 52. (b)

53. (d) p-Hydroxybenzoic acid has higher boiling point than o-hydroxybenzoic acid due to intermolecular hydrogen bonding. Thus, statement-1 is false. o-Hydroxybezoic acid shows intramolecular H-bonding thus, statement-2 is true.

54. (c) Haloform reaction is shown by ketones having R-CO-CH₃ structure in which-CO-group is electron deficient, while

The – CO – in CH₃COOH is not electron deficient due to supply of electrons by the $-\ddot{O}H$ part-Acetic has three $\alpha-H$ atoms.

 (d) Acetate ion is reasonance stabilized while methoxide ion is not.

Hence, acetate ion is less basic than methoxide ion.

56. Higher the K_a value, more stronger is the acid. Correct order of acidic strength of the given acids is

Hence, the K_a values of the five acids will be in the order.

(b) (c) (a) (e) (d)

$$K_a$$
 value 30.6×10^{-5} 10.2×10^{-5} 6.4×10^{-5} 4.2×10^{-5} 3.3×10^{-5}

57. The two enantiomers of 2-phenylpropanoic acid in the racemic mixture react with (+) – alcohol to form two diastereomers.

COOH
$$H - C - Ph$$

$$CH_3$$

$$CH_3$$

$$Enantiomers$$

$$(+) - CH_3CH(OH)Et$$

$$COOCH(CH_3)Et$$

$$H - C - Ph$$

$$CH_3$$

$$(A)$$

$$COOCH$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

$$COOCH(CH_3)Et$$

(A) and (B) are diasteromers.

The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction.

- (+) Acid reacts with (+) –alcohol to give an (+)–(+)– ester, while (–) acid reacts with (+) alcohol to give (–)–(+)– ester. These two esters are diastereoisomers.
- (iv) Presence of electron withdrawing group increases the acidic character of the -COOH due to -I effect, Further the -I group (-Cl) from COOH group, weaker is the acid, thus III is weaker than I while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect. Thus,

58.
$$Ba\mathring{C}O_3 + H_2SO_4 \longrightarrow \mathring{C}O_2 \uparrow$$

$$CH_2 = CHBr \xrightarrow{(i)Mg} CH_2 = CHMgBr \xrightarrow{(ii)\mathring{C}O_2(X)} (ii)H_3O^+$$

$$CH_2 = CH \mathring{C}OOH \xrightarrow{LiAlH_4} CH_2 = CH.CH_2OH$$

Formation of CH2O from (Z)

$$CH_{2} = CH.\overset{*}{C}H_{2}OH \xrightarrow{H^{+}}$$

$$[CH_{2} = CH.\overset{*}{C}H_{2} \longleftrightarrow \overset{\oplus}{C}H_{2} - CH = \overset{*}{C}H_{2}]$$

$$\xrightarrow{Br^{-}} BrCH_{2}.CH = \overset{*}{C}H_{2} \xrightarrow{O_{3}} \overset{*}{C}H_{2} = O$$

60. (i)
$$CH_3 - \overset{O}{C} - \overset{18}{OC_2}H_5 \xrightarrow{H^+} \overset{O}{H_2O} \rightarrow CH_3 - \overset{O}{C} - OH + C_2H_5OH$$

(Ester hydrolysis involves acyl-oxygen fission)

(ii)
$$C$$
—OH C

(iii)

$$\begin{array}{c} \xrightarrow{\text{anhy.}} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

(iv) $C_6H_5CHO + CH_3COOC_2H_5$ $\frac{NaOC_2H_5 \text{ in}}{\text{absolute alcohol, heat}} C_6H_5CH = CHCOOC_2H_5$ (D)

(Claisen condensation)

(ν) CH₃CH₂COOH P and Br₂ HVZ reaction

(vi) Esters react with excess of RMgX to form 3° alcohols having two alkyl groups corresponding to R of RMgX. Thus,

$$C_6H_5CH_2COOCH_3 \xrightarrow{\quad (i) \ 2CH_3MgBr \quad} \xrightarrow{\quad (ii) \ H^+}$$

(vii) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COOMgI$

(ix)
$$CH_3 - C - OC_2H_5 + 2C_2H_5MgBr \longrightarrow$$

Ethyl acetate

$$CH_3 - C - C_2H_5 + Mg(Br)OC_2H_5 \xrightarrow{H^+}$$

$$C_2H_5$$

OH
$$CH_3 - C - C_2H_5$$

$$C_2H_5$$
Ethylbutanol-2

61.

62. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formates) or tertiary alcohols (from esters other than formates). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence, ester A (C₄H₈O₂) should be HCOOC₃H₇. Thus the various reactions and nature of compound B can be established as below.

$$\xrightarrow{\begin{array}{c} CH_3 \\ (i)CH_3MgBr \\ \hline \\ (ii)H_3O^+ \end{array} } CH_3 - C - OH \\ H \\ Isopropanol [B]$$

$$\begin{array}{c}
O \\
\downarrow | \\
\hline
\text{(haloform reaction)}
\end{array}
CH_3 - C - ONa \xrightarrow{H^+} CH_3COOH$$

63. (i) Both of the resonating structures of benzoate ion are equivalent, while it is not so in phenoxide ion.

Resonating structures of phenoxide ion

Resonating structures of benzoate ion

The benzoate ion is more stabilized because the negative charge on both structures is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms.

(ii)
$$H-C-OH \rightleftharpoons H-C-O^-+H^+$$
;
 $O O O$

$$CH_3-C-OH \rightleftharpoons CH_3-C-O^-+H^+$$

(iii) Presence of CH₃ gp in acetate ion shows +I effect and thereby intensifies charge on O⁻ of acetate ion which is thus destabilized. Thus formate ion is more stable than acetate ion or HCOOH loses proton more easily than CH₃COOH.

Formic acid has no alkyl group i.e no α – H atom, hence it does not undergo halogenation, while acetic acid has a methyl group (i.e three α – H atoms) on which halogenation takes place.

64. (i) β-Keto acids are unstable and undergo decarboxylation most readily. This is due to formation of 6-membered cyclic transition state.

65.
$$C_8H_6 \xrightarrow{\text{dil. H}_2SO_4} B \xleftarrow{\text{anhydrous. AlCl}_3} RCOCl + C_6H_6$$
(A) I_2 , aq. KOH
$$C + \text{Yellow compound (D)}$$

- Formation of (B) from benzene and acid chloride in presence of anhydrous AlCl₃ (Friedel-Craft reaction) indicates that it is a ketone, C₆H₅COR.
- (ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone (B) is -CH₃. Hence, (B) should be C₆H₅.CO.CH₃.
- (iii) Since ketone (B) is also formed from the hydrocarbon C₈H₆(A) by reaction with dil. H₂SO₄ and HgSO₄, the hydrocabon (A) must have an acetylenic hydrogen atom, i.e. ≡ C H grouping. Hence, (A) must be C₆H₅C ≡ CH.

Thus, compounds (A) to (D) are $C_6H_5.C \equiv CH \quad C_6H_5.CO.CH_3 \quad C_6H_5COOH \quad CHI_3$ (A)
(B)
(C)
(D)

Formation of (B) from (A)

OH
$$C_{6}H_{5}.C \equiv CH \xrightarrow{\text{dil.H}_{2}SO_{4}} [C_{6}H_{5}-C = CH_{2}]$$
Phenylacetylene (A)
$$\xrightarrow{\text{rearranges}} C_{6}H_{5}.CO.CH_{3}$$
Acetophenone (B)

66. $PCl_5 + SO_2 \longrightarrow SOCl_2 + POCl_3$ (A)
(B)

$$\begin{array}{c} 2\text{CH}_3\text{COCl+}(\text{CH}_3)_2\text{Cd} \longrightarrow 2\text{CH}_3 - \begin{array}{c} \text{CO-CH}_3 + \text{CdCl}_2 \\ (D) \end{array}$$

A
$$\xrightarrow{C_2H_5OH}$$
 B + C

Carboxylic acid

$$E \xrightarrow{(C_3H_6O)}$$
B + D

(i) Since, 'E' (C₃H₆O) forms a 2, 4-dinitrophenylhydrazone but does not reduce Tollen's reagent and Fehling solution, it must be a ketone, CH₃.CO.CH₃.

- (ii) The compound 'E' (established as ketone) is obtained by heating compound 'B' with Ca(OH)₂, 'B' must be CH₃COOH.
- (iii) Compound 'B' is obtained by the oxidation of 'D', the latter must be ethyl alcohol, C₂H₅OH and hence 'C' must be ethyl acetate, CH₃COOC₂H₅.
- (iv) Since, compound 'A' when treated with ethyl alcohol gives acetic acid 'B' and ethyl acetate 'C', it must be acetic anhydride.

$$\begin{array}{c} \text{CH}_3\text{CO.O.COCH}_3 + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{COOC}_2\text{H}_5 \\ \text{(A)} & \text{(B)} & \text{(C)} \\ \\ \text{CH}_3\text{COCH}_3 & \xrightarrow[\text{heat}]{\text{Ca(OH)}_2} & \text{CH}_3\text{COOH} & + & \text{C}_2\text{H}_5\text{OH} \\ \text{(E)} & & \text{(B)} & \text{(D)} \\ \\ & & & \text{oxidation} \\ \end{array}$$

68. For empirical formula of (Y)

Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.10	3
H	9.59	9.59	7
N	19.18	1.37	1
0	21.92	1.37	1 For

:. Empirical formula of (Y) is C₃H₇NO.

(Y) reacts with Br₂ and NaOH to give (Z) and (Z) reacts with HNO₂ to give ethanol and thus (Y) seems to have — CONH₂ group.

$$CH_3CH_2CONH_2 + Br_2 + 4NaOH \longrightarrow (Y)$$

$$\begin{array}{c} \mathrm{CH_{3}CH_{2}NH_{2}} \xrightarrow{\quad \mathrm{HNO_{2}} \quad \mathrm{CH_{3}CH_{2}OH} \\ \mathrm{(Z)\ basic} \quad \quad \mathrm{Ethanol} \end{array}$$

(Y) is formed from (X) having Cl on treatment with NH₃ and So, (X) is CH₃CH₂COCl i.e., propanoyl chloride.
CH₃CH₂COCl + NH₃ → CH₃CH₂CONH₂

69. Presence of electron withdrawing group increases the acidic character of the -COOH due to -I effect, Further the -I group (-Cl) from - COOH group, weaker is the acid, thus III is weaker than I while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect. Thus,

70. (i)
$$C_6H_5COOH \xrightarrow{PCI_5} C_6H_5COCI \xrightarrow{NH_3} C_6H_5COCI$$

(ii)
$$H_3CCH = CHCHO \xrightarrow{NaBH_4} CH_3CH = CH-CH_2OH$$

$$\xrightarrow{(F)} CH_3CH = CHCH_2CI$$

$$\xrightarrow{(G)} CH_3CH = CHCH_2COOH$$

$$\xrightarrow{(H)} CH_3CH = CHCH_2COOH$$

71.
$$C_6H_{12}O_2$$

Reduction
by LiAlH₄

B + C

The state of the st

Molecular weight of the monobasic acid (RCOOH) indicates that the R- should be CH₃-*i.e.*, acid F should be acetic acid (CH₃COOH, mol. wt. 60). Thus, compound D must be acetaldehyde CH₃CHO, and compound B which on oxidation gives CH₃CHO must be ethanol, CH₃CH₂OH. Acetaldehyde (D) on treating with aqueous alkali will undergo aldol condensation.

$$2CH_3CHO \xrightarrow{OH^-} CH_3CHCH_2CHO \xrightarrow{heat}$$

$$(D)$$

$$CH_3CH = CHCHO$$
 $\xrightarrow{H_2/}$ $CH_3CH_2CH_2CH_2OH$
Crotonaldehyde, (E) Butanol-1, (C)

Nature of A. Thus it is evident that reduction of A with LiAlH₄ gives two alcohols; B (ethanol) and C (butanol). Hence, A must be an ester i.e., ethyl butanoate $(CH_3CH_2COOC_2H_5)$.

Ethyl butanoate, A

$$CH_3CH_2CH_2CH_2OH + C_2H_5OH$$

Butanol, C Ethanol, B

72. The given set of reactions can be represented as below:

Aq. NaOH
$$\xrightarrow{\text{Gas B}}$$
 Sod. salt of acid A pressure

$$(i) \text{ NaOH (heat)} \rightarrow \text{Dibasic acid, } C$$

Calculation of molecular formula of C

% of H =
$$\frac{2}{18} \times \frac{0.08}{0.40} \times 100 = 2.22\%$$



% of C =
$$\frac{12}{44} \times \frac{0.39}{0.40} \times 100 = 27.30\%$$

$$\%$$
 of $Q = 100 - (2.22 + 27.30) = 71.48\%$

By usual method, empirical formula of acid $C = CHO_2$

Eq. wt. of acid
$$C = \left(\frac{1.0}{0.71} \times 108\right) - 107 = 45$$

Mol. wt. of acid $C = 45 \times 2 = 90$

:. Mol. formula of $C = C_2H_2O_4$

Since it is dicarboxylic acid, it must have two -COOH

Going back, compound C must be produced from sodium oxalate which in turn is produced from sodium formate. Hence A is formic acid and B is CO_2 . Thus the complete series of reactions can be written as below.

$$2NaOH(aq.) \xrightarrow{2CO_2(B)} HCOONa + HCOONa (A)$$

$$\xrightarrow{\text{NaOH}} \begin{array}{c} \text{COONa} \\ \text{heat} \end{array} \xrightarrow{\begin{array}{c} \text{COONa} \\ \text{COONa} \end{array}} \xrightarrow{\begin{array}{c} \text{H}_2\text{SO}_4 \\ \text{COOH} \end{array}} \xrightarrow{\text{COOH}}$$

73. (i)
$$CH_3COOH \xrightarrow{PCl_5} CH_3COCl$$

Ethanoic acid

$$\xrightarrow{C_6H_5MgBr} C_6H_5COCH_3$$

$$\begin{array}{c}
C_6H_5 \\
 \hline
 \begin{array}{c}
C_6H_5 \\
 \hline
 \end{array}
 \begin{array}{c}
C_6H_5
\end{array}$$

$$\begin{array}{c}
C_6H_5
\end{array}$$

$$\begin{array}{c}
C_6H_5
\end{array}$$

$$\begin{array}{c}
C_6H_5
\end{array}$$

$$\xrightarrow{\text{HOH}} (C_6H_5)_2 \overset{\text{CCH}_3}{\underset{\text{OH}}{|}} \xrightarrow{\text{heat}}$$

$$(C_6H_5)_2C = CH_2$$

(ii)
$$CH_3.CHO \xrightarrow{\text{HCHO/NaOH}} CH_2CH_2CHO$$

Ethanal (cross aldol condens) CH_2CH_2CHO

$$\xrightarrow{\text{Dehydration} \atop \text{(heat)}} \text{CH}_2 = \text{CHCHO}$$

$$\xrightarrow{\text{propenal}}$$

$$\xrightarrow{\text{hydrolysis}} \text{CH}_2 = \text{CH} - \text{CH} - \text{COOH}$$

$$\xrightarrow{\text{OH}} \text{OH}$$
2-Hydroxy-3-butenoic acid

74. P/Cl,, NH, CH, COONH

75. A
$$\xrightarrow{\text{mild}}$$
 C $\xrightarrow{\text{(i) 50% KOH}}$ A + D
$$\downarrow \text{CH}_3\text{COOH}, \text{H}_2\text{SO}_4 \qquad \qquad \text{(i) PCl}_5 \\ \text{(ii) NH}_3 \qquad \qquad \qquad \text{Ester, B} \qquad \qquad \text{HCN} \rightleftharpoons^{\text{(-H}_2\text{O})} \text{E}$$

The above reactions lead to following conclusions.

- (i) Reaction of (A) with CH₃COOH in presence of H₂SO₄ to form ester (B) indicates that (A) is an alcohol.
- (ii) Reaction of (C) with 50% KOH followed by acidification to give alcohol (A) and the compound (D) seems to be the Cannizzaro reaction. Hence, (C) must be an aldehyde and (D) must be an acid. The nature of (C) as aldehyde is again in consistent with the fact that it is obtained by the mild oxidation of (A) which has been established as an alcohol.
- (iii) Structure of acid (D) is established by its given facts.

$$\begin{array}{c}
-\text{COOH} \xrightarrow{\text{PCl}_5} -\text{COCI} \xrightarrow{\text{NH}_3} -\text{CONH}_2 \\
\text{(D)} & \text{(E)} \\
\xrightarrow{-\text{H}_2\text{O}} \text{HCN}
\end{array}$$

Formation of HCN by the dehydration of (E) establishes that (E) is HCOOH, and hence (D) is HCOOH.



(iv) Thus the alcohol (A) produced along with HCOOH during Cannizzaro reaciton of (C) must be CH₃OH and hence, (C) must be HCHO.

Thus, the various compounds are as below:

77. (X) is hydrolysed to give a carboxylic acid (Y) and an alcohol (Z) and thus (X) is an ester; R — C — OR'.

$$\begin{array}{c} R - C - OR' \xrightarrow{HOH} RCOOH + R'OH \\ O \end{array}$$

Oxidation of alcohol (Z) gives acid (Y).

$$R'OH \xrightarrow{Oxidation} RCOOH$$

or $RCH_2OH \longrightarrow RCOOH$ (: R' is $R-CH_2$) Hence (X), (Y) and (Z) are

CH3CH2CH2OH

78. The weaker a base better is its leavability.

This is an example of nucleophilic substitution where the group X (Cl, NH₂, OC₂H₅, OCOCH₃) is replaced by OH. The decreasing basic character of the four concerned groups is:

Hence, Cl- (the weakest base) will be lost most easily, while

NH₂ (the strongest base) will be lost with most difficulty.

Thus, the order of hydrolysis becomes:

79.
$$CH_3CH_2CHO + [O] \xrightarrow{AgNO_3/NH_4OH} CH_3CH_2COOH + 2Ag$$

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{COOH} \\ + \\ \text{CH}_3\text{CH}_2\text{COOH} \end{array} \xrightarrow{P_2\text{O}_5} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CO} \\ \text{CH}_3\text{CH}_2\text{CO} \end{array} O + \text{H}_2\text{O} \\ \\ \text{Propionic anhydride} \end{array}$$

80. (i)
$$C_2H_2 \xrightarrow{H_2SO_4(dil.)} CH_3CHO \xrightarrow{H_2/cat.} CH_3CH_2OH$$

(ii)
$$CH_3I + KCN (alc) \xrightarrow{-KI} CH_3CN$$

$$\xrightarrow{H^+/H_2O} CH_3COOH$$

Acetic acid

81. Ozonolysis of (A) to acetone and an aldehyde indicates the following part structure of alkene (A):

$$CH_3$$
 $C = CHR$
 O_3
 CH_3
 $C = O + OHC.R$
Alkene (A)
Acetone

As per problem:

RCHO
$$\xrightarrow{[O]}$$
 RCOOH[B] $\xrightarrow{P/Br_2}$

Bromo compound $[C] \xrightarrow{\text{H}_2\text{O}} \text{Hydroxy acid } [D]$ Structure of (D) is determined by the reaction:

$$CH_3$$
 CH_3
 CH_3

The compound (D) is obtained by hydrolysis of (C) with aqueous alkali. Since (C) is a bromo compound, therefore it has a bromo group whereas the compound (D) has a hydroxyl group. Therefore, structure of C is

$$CH_3$$
 C $COOH$



The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is

The compound (B) is formed by oxidation of an aldehyde therefore, the structure of the aldehyde is

The aldehyde and acetone are formed by ozonolysis of alkene. Therefore, the double bond in alkene should be between the carbon atoms of the two carbonyl compounds (the aldehyde and acetone). Therefore, the compounds and the reactions are identified as

$$CH_{3}$$

$$C$$

82.
$$CH_3COCI + AICI_3 \rightarrow CH_3C^+ = O + AICI_4$$

$$\begin{array}{c}
CH_3C = O \\
\end{array}$$

$$\begin{array}{c}
CH_3C = O
\end{array}$$

$$\begin{array}{c}
COCH
\end{array}$$

83. First step is Claisen condensation.

$$CH_3 - C + O - C_2H_5 + H + CH_2 - C - O - C_2H_5$$

$$\begin{array}{c}
C_2H_5ONa \\
C_2H_5OH
\end{array}
\xrightarrow{C} CH_3 - C - CH_2 - C - O - C_2H_5 + C_2H_5OH \\
O O O HOH$$

$$H^+$$

$$H^+$$

$$\begin{array}{c} CH_3-C-CH_2-C-OH+C_2H_5OH\\ O\\O\\ (\beta\text{-keto acid}) \end{array}$$