

Chapter

Aldehydes Ketones and

Carboxylic Acids

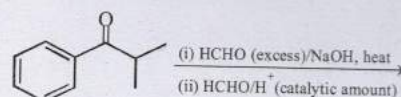


Topic-1: Preparation and Properties of Carbonyl Compounds



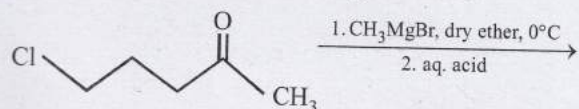
1 MCQs with One Correct Answer

1. The major product of the following reaction sequence is [Adv. 2016]



- (a)
- (b)
- (c)
- (d)

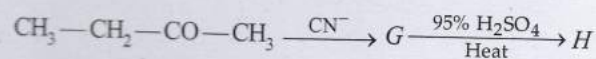
2. The major product in the following reaction is



[Adv. 2014]

- (a)
- (b)
- (c)
- (d)

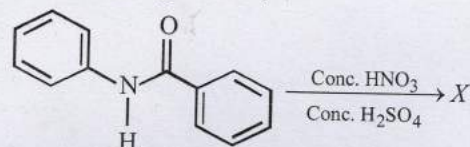
3. The major product *H* of the given reaction sequence is



[2012 - II]

- (a) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
- (b) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CN}$
- (c) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{COOH}$
- (d) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}_2$

4. In the following reaction,

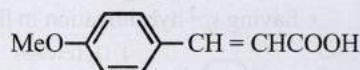
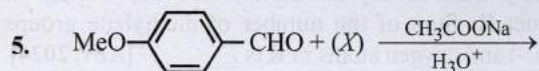
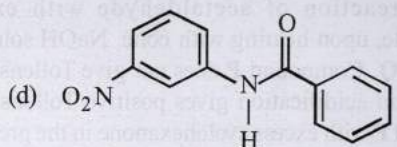
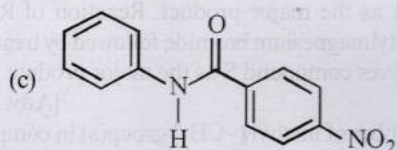


the structure of the major product 'X' is

[2007]

- (a)
- (b)

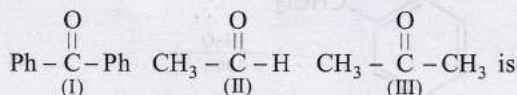




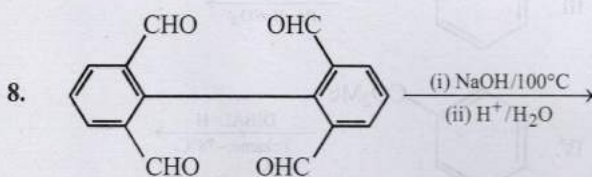
The compound (X) is

[2005S]

- (a) CH_3COOH (b) $\text{BrCH}_2\text{-COOH}$
 (c) $(\text{CH}_3\text{CO})_2\text{O}$ (d) CHO-COOH
6. How will you convert butan-2-one to propanoic acid?
 [2005S]
- (a) Tollen's reagent (b) Fehling's solution
 (c) $\text{NaOH/I}_2/\text{H}^+$ (d) NaOH/NaI/H^+
7. The correct order of reactivity of PhMgBr with [2004S]

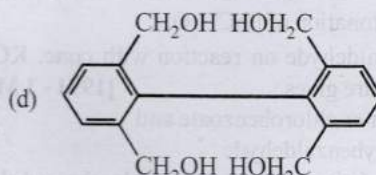
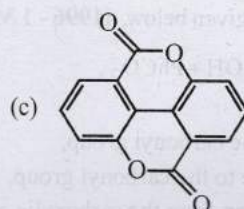
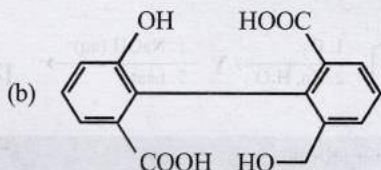
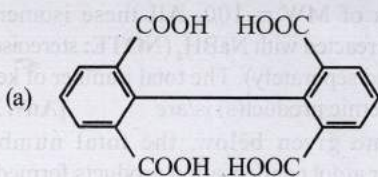


- (a) (I) > (II) > (III) (b) (III) > (II) > (I)
 (c) (II) > (III) > (I) (d) (I) > (III) > (II)

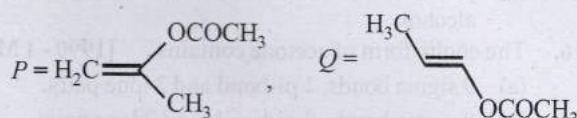


Major product is :

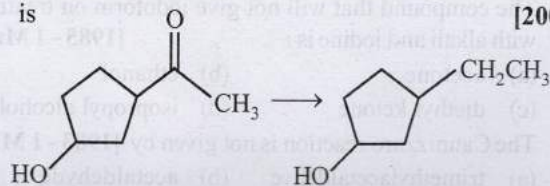
[2003S]



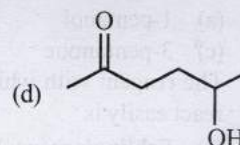
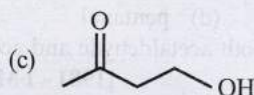
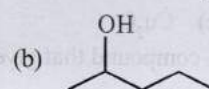
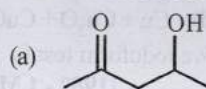
9. The product of acid hydrolysis of P and Q can be distinguished by [2003S]



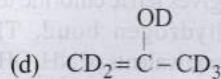
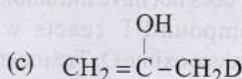
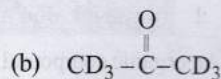
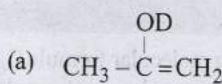
- (a) Lucas Reagent (b) 2,4-DNP
 (c) Fehling's Solution (d) NaHSO_3
10. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives [2001S]
- (a) benzyl alcohol and sodium formate
 (b) sodium benzoate and methyl alcohol
 (c) sodium benzoate and sodium formate
 (d) benzyl alcohol and methyl alcohol
11. The appropriate reagent for the following transformation is [2000S]



- (a) Zn(Hg), HCl (b) $\text{NH}_2\text{NH}_2/\text{OH}^-$
 (c) H_2/Ni (d) NaBH_4
12. Which one of the following will most readily be dehydrated in acidic condition? [2000S]



13. The enol form of acetone, after treatment with D_2O , gives. [1999 - 2 Marks]



14. In the Cannizzaro reaction given below, [1996 - 1 Mark]
 $2\text{PhCHO} \xrightarrow{\text{OH}^-} \text{PhCH}_2\text{OH} + \text{PhCO}_2^-$,
 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_2OH .
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
17. Polarisation of electrons in acrolein may be written as [1988 - 1 Mark]
 (a) $\overset{\delta^-}{\text{CH}_2} = \overset{\delta^+}{\text{CH}} - \overset{\delta^+}{\text{C}} = \overset{\delta^-}{\text{O}}$ (b) $\overset{\delta^-}{\text{CH}_2} = \overset{\delta^-}{\text{CH}} - \overset{\delta^+}{\text{C}} = \overset{\delta^+}{\text{O}}$
 (c) $\overset{\delta^-}{\text{CH}_2} = \overset{\delta^+}{\text{CH}} - \overset{\delta^+}{\text{C}} = \overset{\delta^-}{\text{O}}$ (d) $\overset{\delta^+}{\text{CH}_2} = \overset{\delta^-}{\text{CH}} - \overset{\delta^-}{\text{C}} = \overset{\delta^+}{\text{O}}$
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) trimethylacetaldehyde (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) Cu_2O (d) $\text{Cu} + \text{Cu}_2\text{O} + \text{CuO}$
21. A compound that gives a positive iodoform test is [1982 - 1 Mark]
 (a) 1-pentanol (b) 2-pentanone
 (c) 3-pentanone (d) pentanal
22. 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

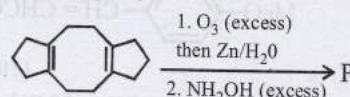
23. An organic compound P having molecular formula $\text{C}_6\text{H}_6\text{O}_3$ gives ferric chloride test and does not have intramolecular hydrogen bond. The compound P reacts with 3 equivalents of NH_2OH to produce oxime Q. Treatment of P with excess methyl iodide in the presence of KOH produces

compound R as the major product. Reaction of R with excess iso-butylmagnesium bromide followed by treatment with H_3O^+ gives compound S as the major product.

[Adv. 2024]

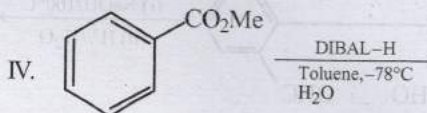
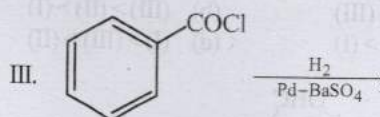
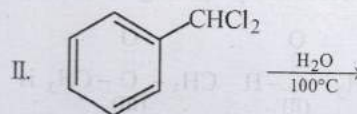
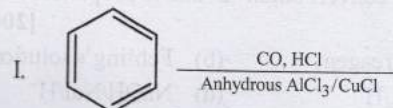
The total number of methyl ($-\text{CH}_3$) group(s) in compound S is _____.

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 ($-\text{CH}_2-$) and oxygen atoms in R is _____. [Adv. 2024]
25. In the reaction given below, the total number of atoms having sp^2 hybridization in the major product P is _____

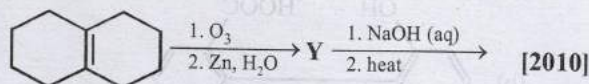


[Adv. 2021]

26. 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 NaBH_4 (NOTE: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are [Adv. 2014]
28. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



[2010]



4 Fill in the Blanks

29. The structure of the enol form of $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$ with intramolecular hydrogen bonding is [1993 - 1 Mark]

30. The structure of the intermediate product, formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is

[1992 - 1 Mark]

31. Fehling's solution 'A' consists of an aqueous solution of copper sulphate, while Fehling's solution 'B' consists of an alkaline solution of

[1990 - 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 × 10 = 10 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

33. 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]

35. Benzaldehyde undergoes aldol condensation in an alkaline medium.

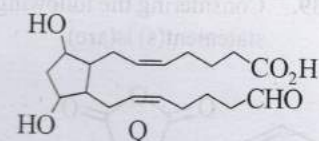
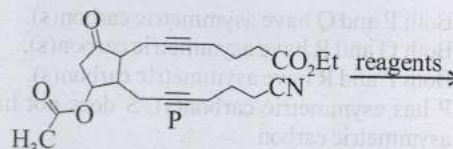
[1982 - 1 Mark]



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):

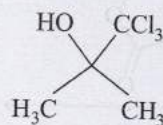
[Adv. 2024]



- (a) (i) Lindlar's catalyst, H_2 ; (ii) SnCl_2/HCl ; (iii) NaBH_4 ; (iv) H_3O^+
- (b) (i) Lindlar's catalyst, H_2 ; (ii) H_3O^+ ; (iii) SnCl_2/HCl ; (iv) NaBH_4
- (c) (i) NaBH_4 ; (ii) SnCl_2/HCl ; (iii) H_3O^+ ; (iv) Lindlar's catalyst, H_2
- (d) (i) Lindlar's catalyst, H_2 ; (ii) NaBH_4 ; (iii) SnCl_2/HCl ; (iv) H_3O^+
37. Reaction of *iso*-propylbenzene with O_2 followed by the treatment with H_3O^+ forms phenol and a by-product P. Reaction of P with 3 equivalents of Cl_2 gives compound Q. Treatment of Q with $\text{Ca}(\text{OH})_2$ produces compound R and calcium salt S. The correct statement(s) regarding P, Q, R and S is(are)

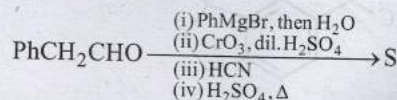
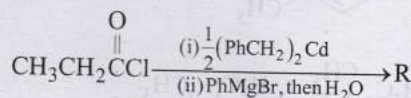
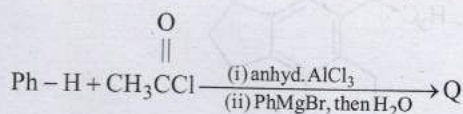
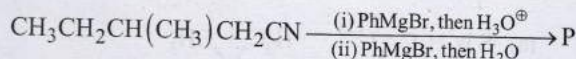
[Adv. 2024]

- (a) Reaction of P with R in the presence of KOH followed by acidification gives



- (b) Reaction of R with O_2 in the presence of light gives phosgene gas
- (c) Q reacts with aqueous NaOH to produce $\text{Cl}_3\text{CCH}_2\text{OH}$ and Cl_3CCOONa
- (d) S on heating gives P
38. In the following reactions, P, Q, R and S are the major products.

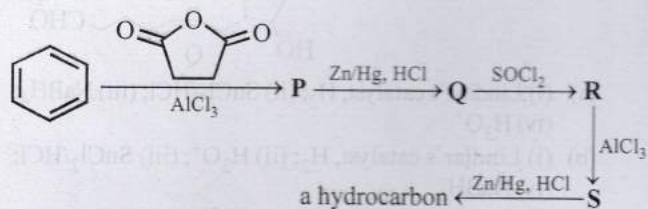
[Adv. 2023]



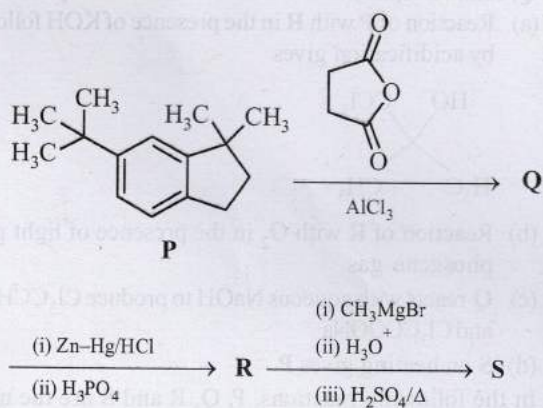
The correct statement(s) about P, Q, R and S is(are)

- (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.

39. Considering the following reaction sequence, the correct statement(s) is(are) [Adv. 2022]

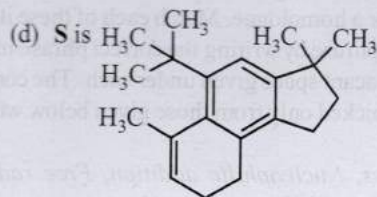
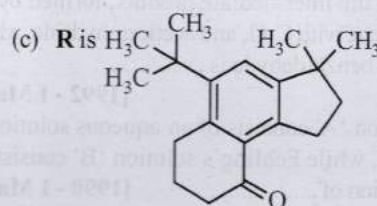


- (a) Compounds P and Q are carboxylic acids.
 (b) Compound S decolorizes bromine water.
 (c) Compounds P and S react with hydroxylamine to give the corresponding oximes.
 (d) Compound R reacts with dialkylcadmium to give the corresponding tertiary alcohol.
40. In the reaction scheme shown below, Q,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

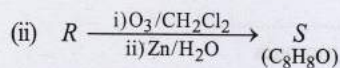
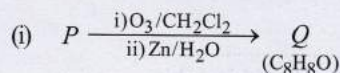


The correct structure of

- (a) S is
- (b) Q is



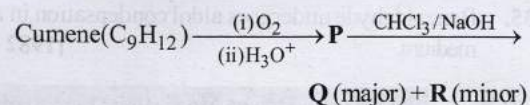
41. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O . Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction



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

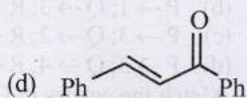
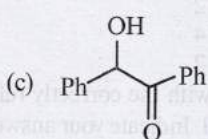
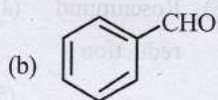
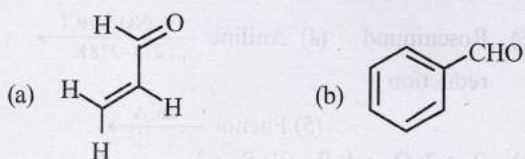
- (a) and
- (b) and
- (c) and
- (d) and

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

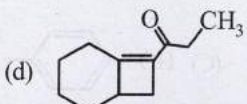
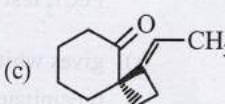
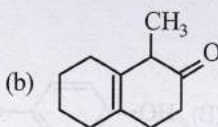
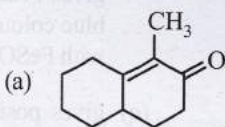
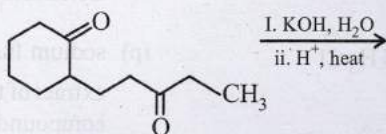


- (a) R is steam volatile
 (b) Q gives dark violet coloration with 1% aqueous FeCl_3 solution
 (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
 (d) S gives dark violet coloration with 1% aqueous FeCl_3 solution

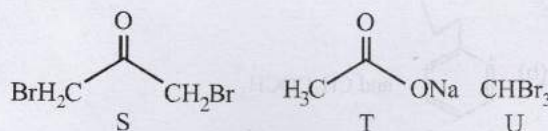
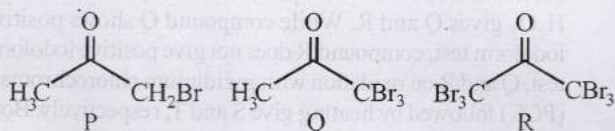
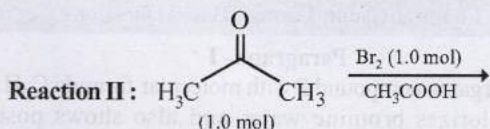
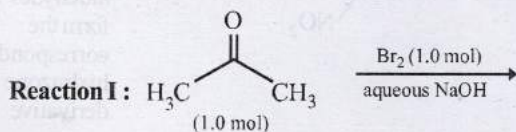
43. Positive Tollen's test is observed for [Adv. 2016]



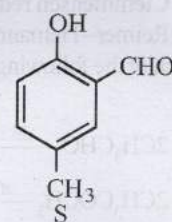
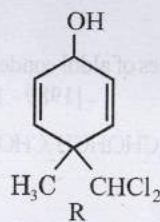
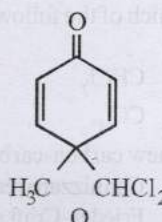
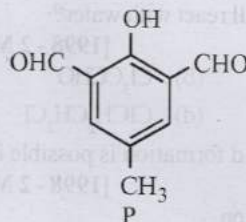
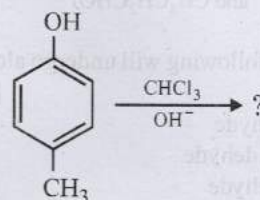
44. The major product of the following reaction is [Adv. 2015]



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



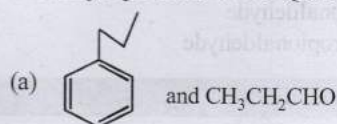
- (a) Reaction I : P and Reaction II : P
 (b) Reaction I : U, acetone and Reaction II : Q, acetone
 (c) Reaction I : T, U, acetone and Reaction II : P
 (d) Reaction I : R, acetone and Reaction II : S, acetone
46. In the following reaction, the product(s) formed is (are) [Adv. 2013]

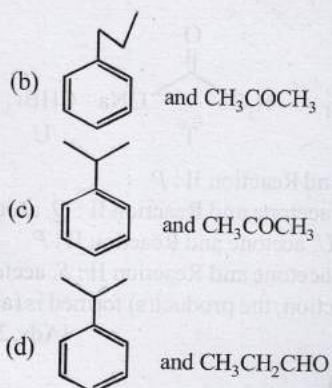


- (a) P (major) (b) Q (minor)
 (c) R (minor) (d) S (major)
47. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime [2006 - 5M, -1]
- (a) Two different oximes are formed
 (b) Three different oximes are formed
 (c) Two oximes formed are optically active
 (d) All oximes formed are optically active

48.

The major products P and Q are [2006 - 5M, -1]





49. Which of the following will undergo aldol condensation? [1998 - 2 Marks]

- (a) acetaldehyde
 (b) propanaldehyde
 (c) benzaldehyde
 (d) trideuteroacetaldehyde

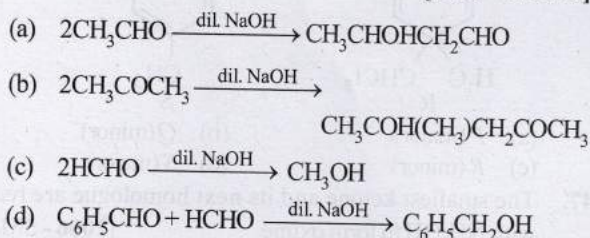
50. Which of the following will react with water? [1998 - 2 Marks]

- (a) CHCl_3 (b) Cl_3CCHO
 (c) CCl_4 (d) $\text{ClCH}_2\text{CH}_2\text{Cl}$

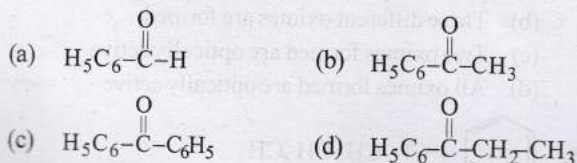
51. A new carbon-carbon bond formation is possible in [1998 - 2 Marks]

- (a) Cannizzaro reaction
 (b) Friedel-Craft alkylation
 (c) Clemmensen reduction
 (d) Reimer-Tiemann reaction

52. Which of the following are examples of aldol condensation? [1989 - 1 Mark]



53. Keto-enol tautomerism is observed in [1988 - 1 Mark]



54. Base catalysed aldol condensation occurs with :

- (a) propionaldehyde [1984 - 1 Mark]
 (b) benzaldehyde
 (c) 2-methylpropionaldehyde
 (d) 2,2-dimethylpropionaldehyde



7 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-I

- (P) Etard reaction
 (Q) Gattermann reaction
 (R) Gattermann-Koch reaction
 (S) Rosenmund reduction

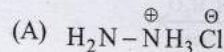
List-II

- (1) Acetophenone $\xrightarrow{\text{Zn-Hg, HCl}}$
 (2) Toluene $\xrightarrow[\text{(ii) SOCl}_2]{\text{(i) KMnO}_4, \text{KOH}, \Delta}$
 (3) Benzene $\xrightarrow[\text{anhyd. AlCl}_3]{\text{CH}_3\text{Cl}}$
 (4) Aniline $\xrightarrow[273-278\text{K}]{\text{NaNO}_2/\text{HCl}}$
 (5) Phenol $\xrightarrow{\text{Zn}, \Delta}$

- (a) $\text{P} \rightarrow 2; \text{Q} \rightarrow 4; \text{R} \rightarrow 1; \text{S} \rightarrow 3$
 (b) $\text{P} \rightarrow 1; \text{Q} \rightarrow 3; \text{R} \rightarrow 5; \text{S} \rightarrow 2$
 (c) $\text{P} \rightarrow 3; \text{Q} \rightarrow 2; \text{R} \rightarrow 1; \text{S} \rightarrow 4$
 (d) $\text{P} \rightarrow 3; \text{Q} \rightarrow 4; \text{R} \rightarrow 5; \text{S} \rightarrow 2$

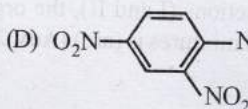
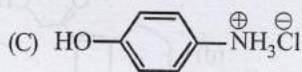
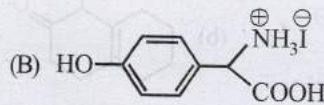
56. Match the entries in Column I with the correctly related quantum number(s) in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS [2008]

Column I



Column II

- (p) sodium fusion extract of the compound gives Prussian blue colour with FeSO_4
 (q) gives positive FeCl_3 test
 (r) gives white precipitate with AgNO_3
 (s) reacts with aldehydes to form the corresponding hydrazone derivative



8 Comprehension/Passage Based Questions

Paragraph - I

An organic compound P with molecular formula $\text{C}_9\text{H}_{18}\text{O}_2$ 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: $\text{H}=1, \text{C}=12, \text{O}=16$]

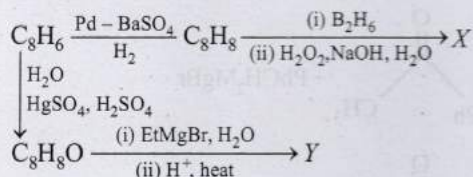


57. Sum of number of oxygen atoms in S and T is _____. [Adv. 2024]
 58. The molecular weight of U is _____. [Adv. 2024]

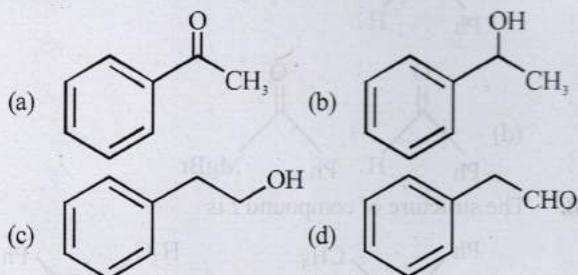
Passage-I

In the following reactions

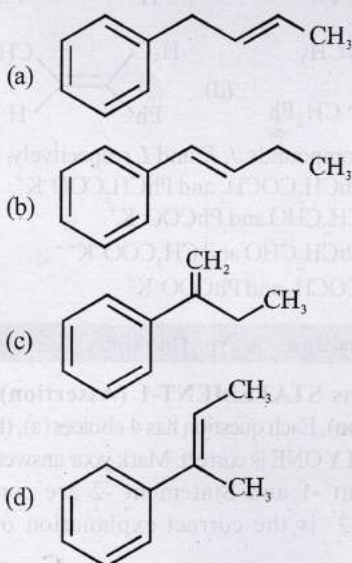
[Adv. 2015]



59. Compound X is

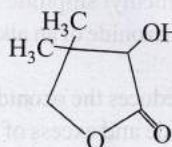


60. The major compound Y is

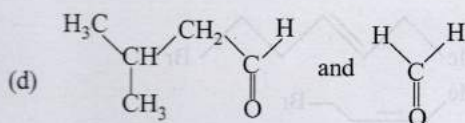
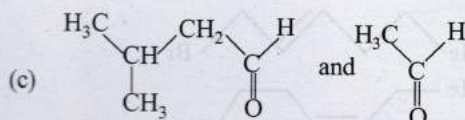
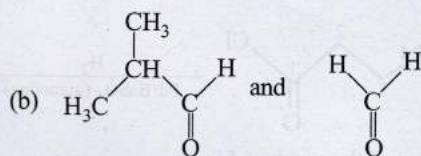
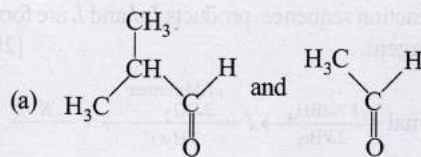


Passage-II

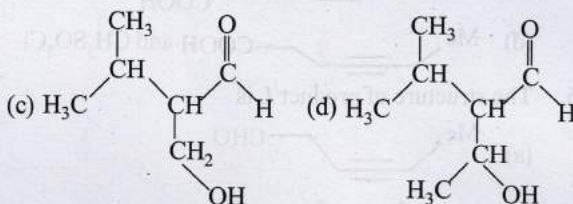
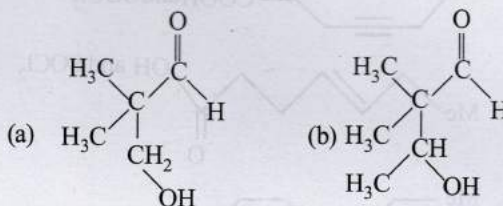
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below. [2010]



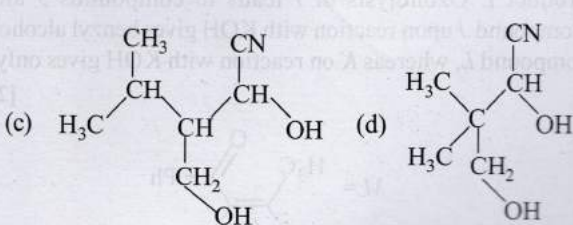
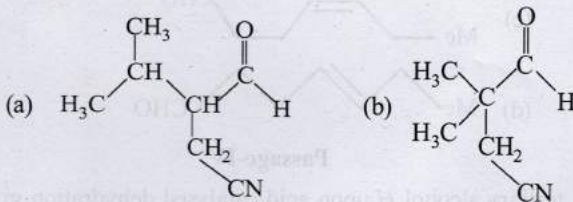
61. The compounds P and Q respectively are :



62. The compound R is :

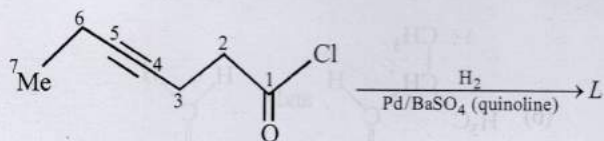
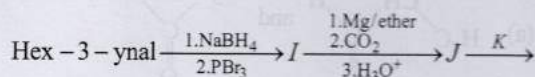


63. The compound S is :



Passage-III

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



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

- (a)
- (b)
- (c)
- (d)

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

- (a)
- (b)
- (c)
- (d)

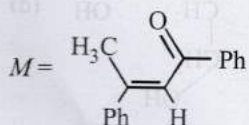
66. The structure of product *L* is

- (a)
- (b)
- (c)
- (d)

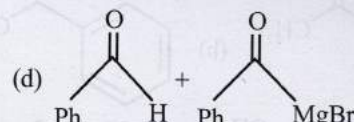
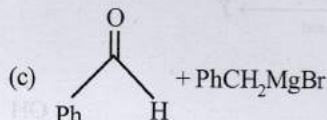
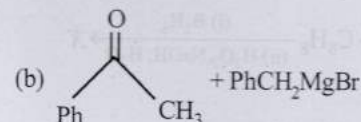
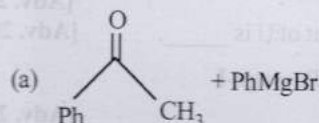
Passage-IV

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*.

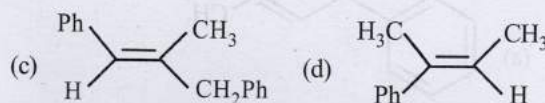
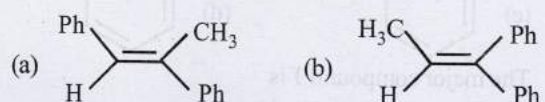
[2008]



67. Compound *H* is formed by the reaction of



68. The structure of compound *I* is



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

- (a) PhCOCH₃, PhCH₂COCH₃ and PhCH₂COO⁻K⁺
- (b) PhCHO, PhCH₂CHO 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

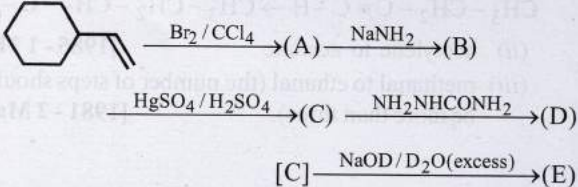
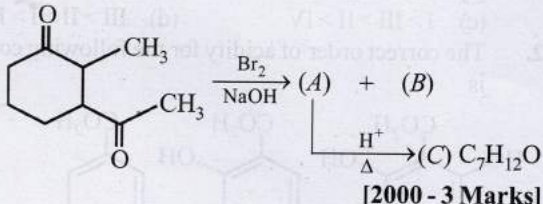
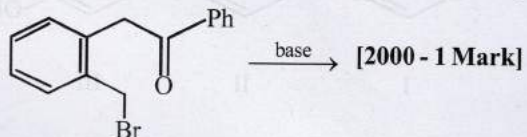
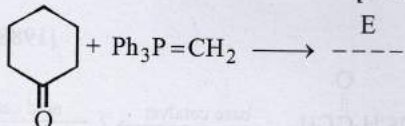
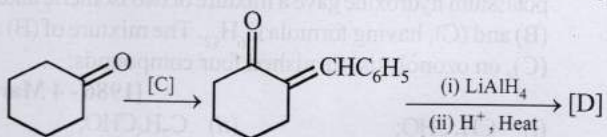
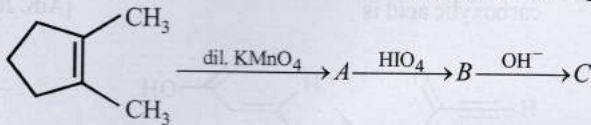
- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is 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.

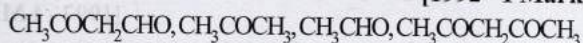
Statement-2 : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. [2001S]



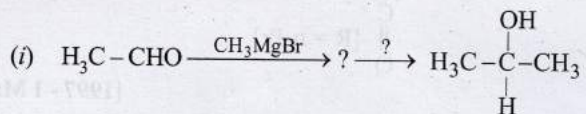
10 Subjective Problems

71. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO . Write the structure of monomer and write all - 'cis' configuration of polymer chain. [2005 - 2 Marks]
72. $A(\text{C}_6\text{H}_{12}) \xrightarrow{\text{HCl}} B + C$ [2003 - 4 Marks]
 $(\text{C}_6\text{H}_{13}\text{Cl})$
 $B \xrightarrow{\text{alc. KOH}} D$ (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).
 $F + G \xrightarrow{\text{conc. NaOH}} \text{HCOONa} + A$ primary alcohol.
 Identify from A to G .
73. Compound 'A' of molecular formula $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$ exists in keto form and predominantly in enolic form 'B'. On oxidation with KMnO_4 , '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]
- 
75. An organic compound A, $\text{C}_6\text{H}_{10}\text{O}$ on reaction with CH_3MgBr 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.
-  [2000 - 3 Marks]
- (ii)  [2000 - 1 Mark]
- (iii) $\text{H}_3\text{CCOCOC}_6\text{H}_5 + \text{NaOH} / \text{H}_3\text{O}^{\oplus} \longrightarrow \text{---}$ [1997 - 1 Mark]
- (iv) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COPh} + \text{KOH} + \text{MeOH} \longrightarrow \text{---}$ [1997 - 1 Mark]
- (v) $\text{R}-\text{C}=\text{C}-\text{R} + \text{HClO}_4 \longrightarrow \text{---}$ [1997 - 1 Mark]
 $\text{C} \parallel \text{O}$ [R = n-Pr]
- (vi)  [1997 - 1 Mark]
- (vii) Complete the following reaction with appropriate structure. [1996 - 1 Mark]
- $\text{CH}_3\text{CH}_2-\text{C}(=\text{O})-\text{H} \xrightarrow[2. \text{LiAlH}_4]{1. \text{KCN} / \text{H}_2\text{SO}_4} \text{D}$
- (viii) $\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CHO} + \text{HCHO} \xrightarrow{\text{KOH}}$ [1992 - 1 Mark]
- (ix) propanal $\xrightarrow[\text{heat}]{\text{NaOH}}$ [1985 - 1 Mark]
- (x) methanal reacts with ammonia [1981 - 1/2 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. [1998 - 2 Marks]
- $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{C}\equiv\text{CH} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$
79. An aldehyde A ($\text{C}_{11}\text{H}_{18}\text{O}$), 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]
- 
81. An organic compound A, C_8H_6 , 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]

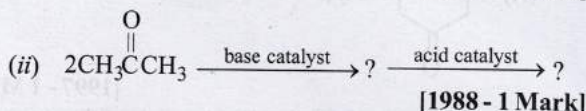
82. Arrange the following in increasing order of expected enol content
[1992 - 1 Mark]



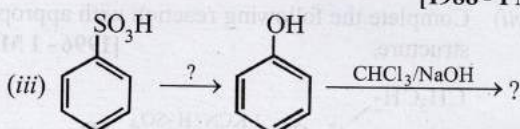
83. Complete the following reactions :



[1988 - 1 Mark]



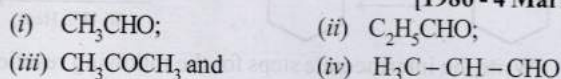
[1988 - 1 Mark]



[1988 - 1 Mark]

84. 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]

85. A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula $\text{C}_6\text{H}_{13}\text{Cl}$. 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:



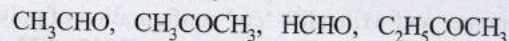
[1986 - 4 Marks]

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

86. 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]



88. Give reasons for the following :

(i) Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid. [1999 - 2 Marks]

(ii) In acylium ion, the structure $\text{R}-\text{C} \equiv \text{O}^+$ is more stable than $\text{R}-\text{C}^+=\text{O}$. [1994 - 1 Mark]

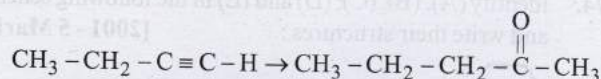
(iii) Iodoform is obtained by the reaction of acetone with hypiodite but not with iodide ion. [1991 - 1 Mark]

(iv) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. [1986 - 1 Mark]

(v) 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

(i) Carry out the following transformation in not more than three steps. [1999 - 3 Marks]



(ii) acetylene to acetone [1985 - 1 Mark]

(iii) methanal to ethanal (the number of steps should not be more than three). [1981 - 2 Marks]

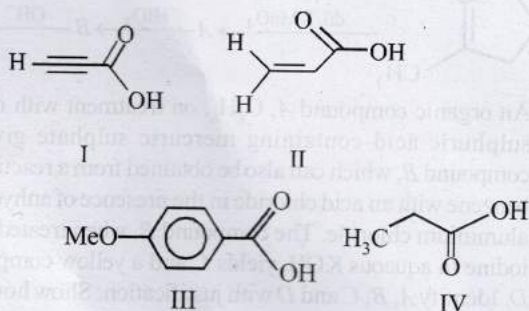


Topic-2: Preparation and Properties of Carboxylic Acids and its Derivatives

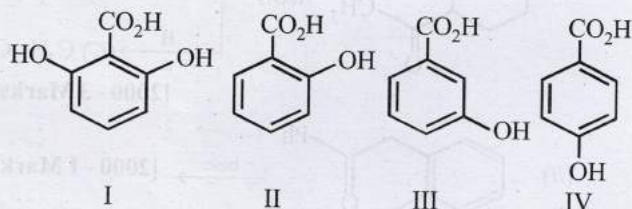


I MCQs with One Correct Answer

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



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



[Adv. 2016]

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

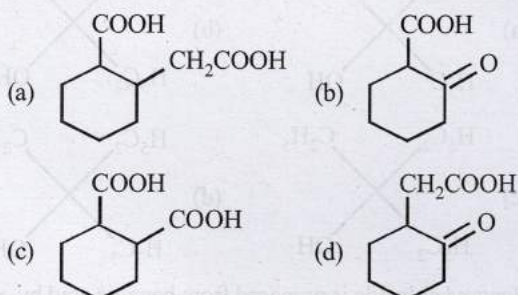
3. The compound that does **NOT** liberate CO_2 , on treatment with aqueous sodium bicarbonate solution, is

[Adv. 2013]

- (a) Benzoic acid (b) Benzenesulphonic acid
(c) Salicylic acid (d) Carbolic acid (Phenol)

4. The compound that undergoes decarboxylation most readily under mild condition is

[2012]



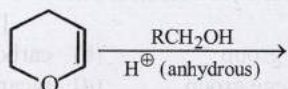
5. The carboxyl functional group ($-\text{COOH}$) is present in

[2012]

- (a) picric acid (b) barbituric acid
(c) ascorbic acid (d) aspirin

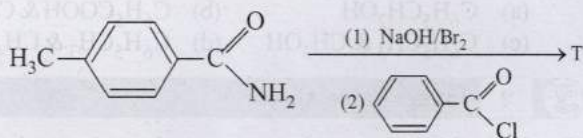
6. The major product of the following reaction is

[2011]



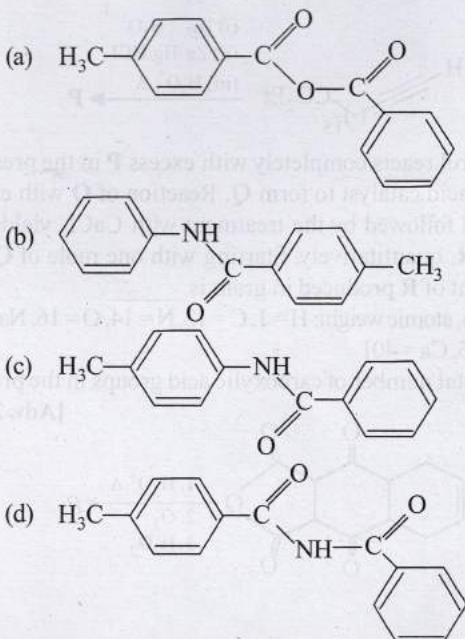
- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester

7. In the reaction

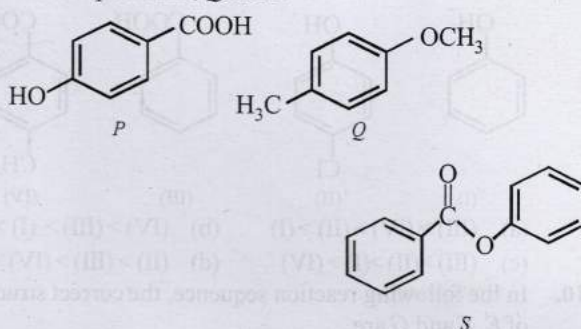


the structure of the product T is :

[2010]

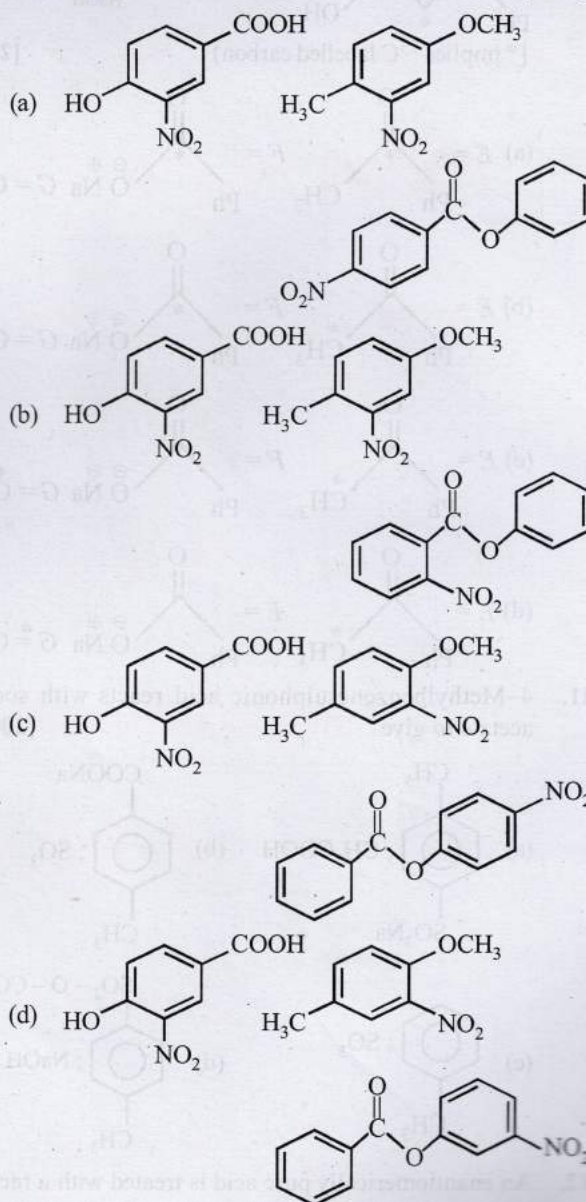


8. The compounds *P*, *Q* and *S*

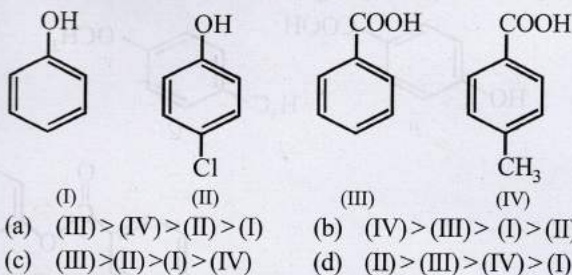


were separately subjected to nitration using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively, is :

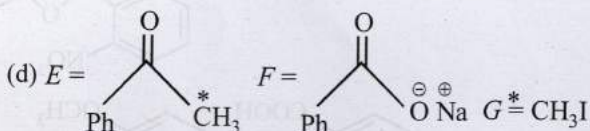
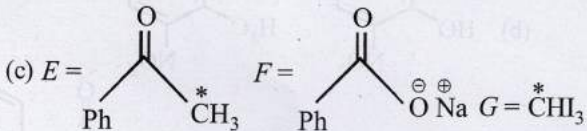
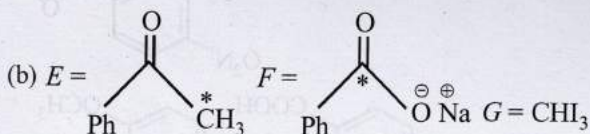
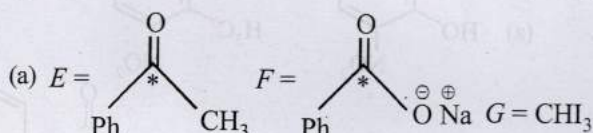
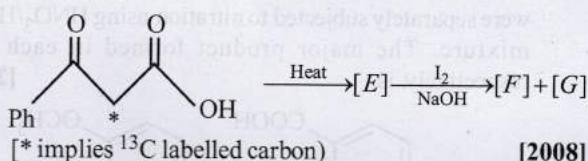
[2010]



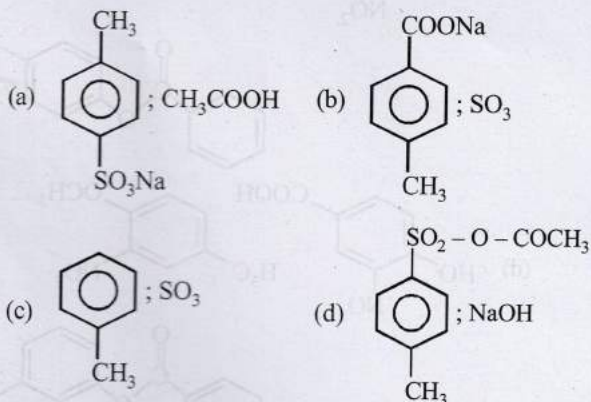
9. The correct acidity order of the following is [2009S]



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



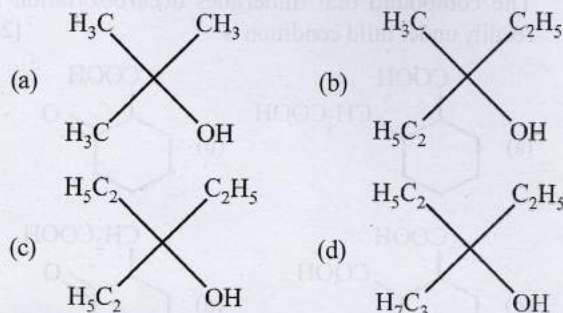
11. 4-Methylbenzenesulphonic acid reacts with sodium acetate to give [2005S]



12. 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
 (c) Meso compound (d) Racemic mixture

13. Ethyl ester $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P will be [2003S]



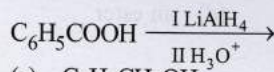
14. Benzoyl chloride is prepared from benzoic acid by [2000S]

- (a) Cl₂, hν (b) SO₂Cl₂
 (c) SOCl₂ (d) Cl₂, H₂O

15. 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

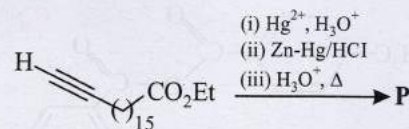
16. The organic product formed in the reaction [1995S]



- (a) C₆H₅CH₂OH (b) C₆H₅COOH & CH₄
 (c) C₆H₅CH₃ & CH₃OH (d) C₆H₅CH₃ & CH₄

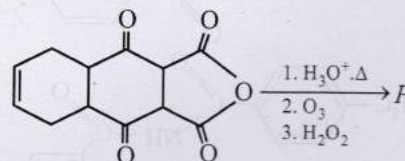
2 Integer Value Answer

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

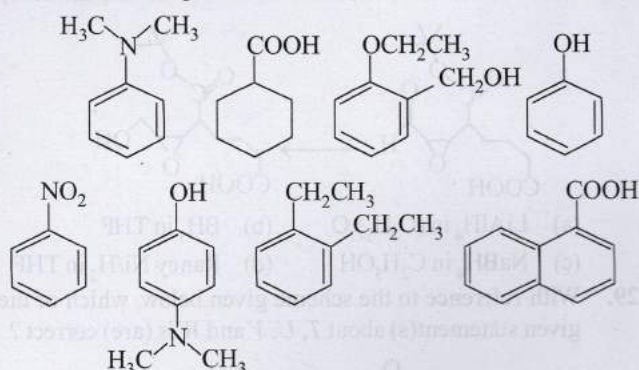


Glycerol reacts completely with excess P in the presence of an acid catalyst to form Q. Reaction of Q with excess NaOH followed by the treatment with CaCl₂ yields Ca-soap R, quantitatively. Starting with one mole of Q, the amount of R produced in gram is _____. [Given, atomic weight: H = 1, C = 12, N = 14, O = 16, Na = 23, Cl = 35, Ca = 40]

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

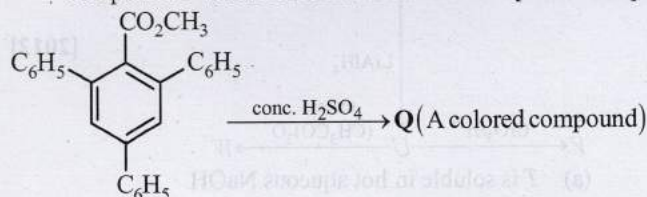


19. Amongst the following, the total number of compounds soluble in aqueous NaOH is [2010]



3 Numeric / New Stem Based Questions

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



P
What is the degree of unsaturation of Q?

4 Fill in the Blanks

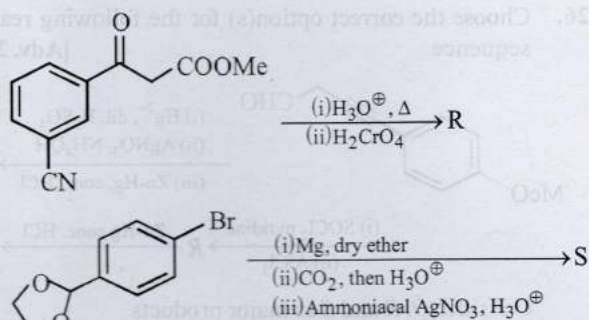
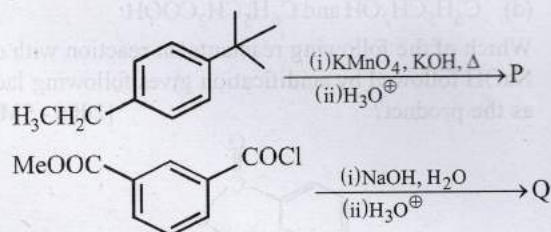
21. Formic acid when heated with conc. H_2SO_4 produces [1983 - 1 Mark]

5 True / False

22. The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. [1991 - 1 Mark]
23. Hydrolysis of an ester in presence of a dilute acid is known as saponification. [1983 - 1 Mark]

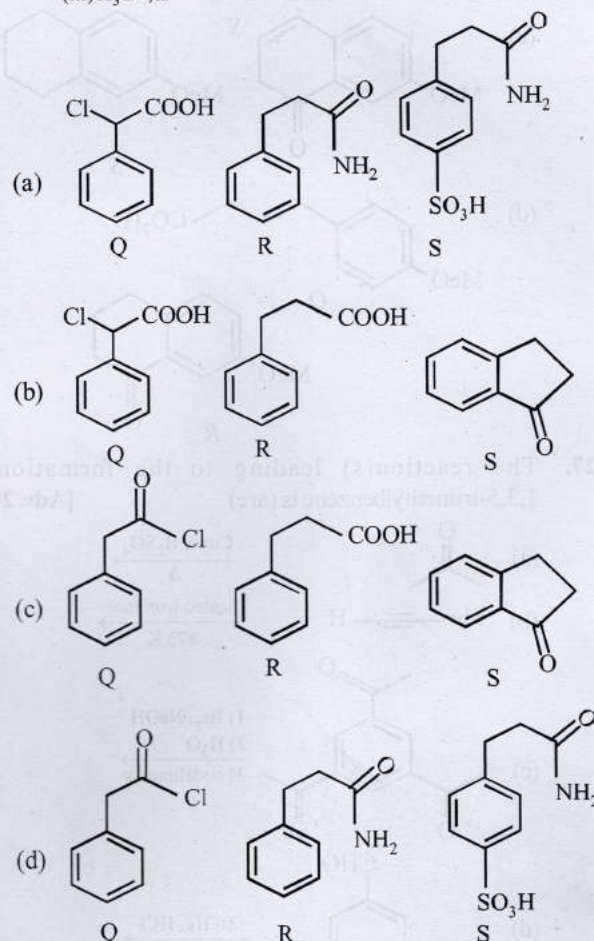
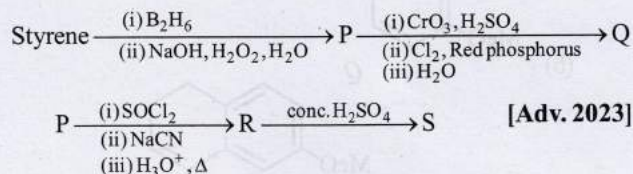
6 MCQs with One or More than One Correct Answer

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

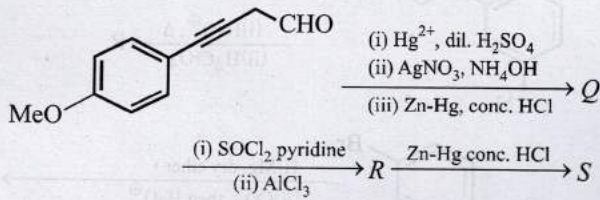


The correct statement(s) about P, Q, R, and S is(are)

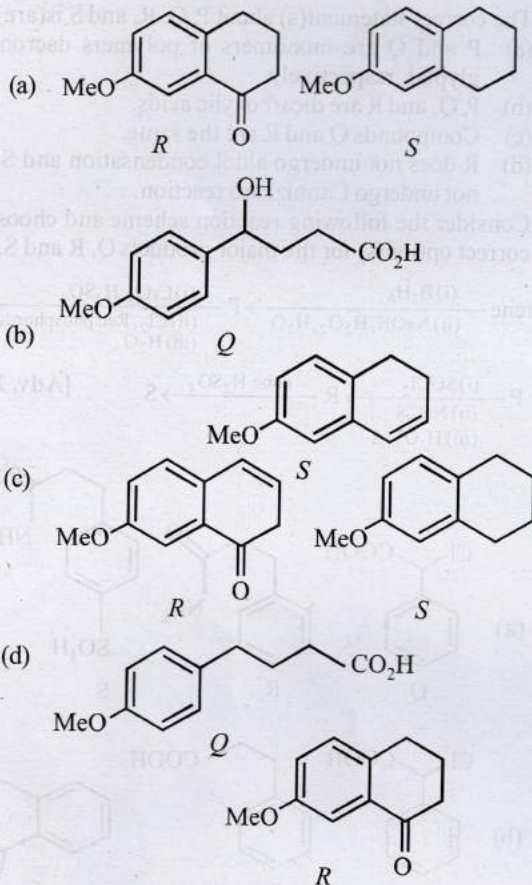
- (a) P and Q are monomers of polymers dacron and glyptal, respectively.
 (b) P, Q, and R are dicarboxylic acids.
 (c) Compounds Q and R are the same.
 (d) R does not undergo aldol condensation and S does not undergo Cannizzaro reaction.
25. Consider the following reaction scheme and choose the correct option(s) for the major products Q, R and S.



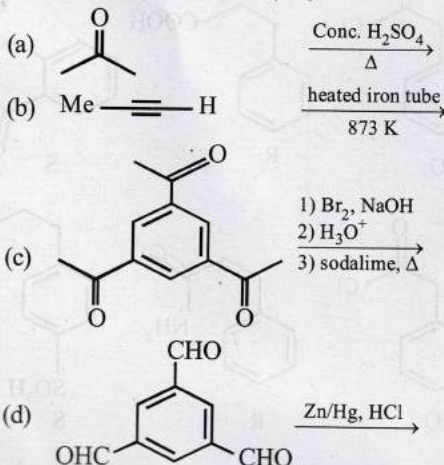
26. Choose the correct option(s) for the following reaction sequence [Adv. 2019]



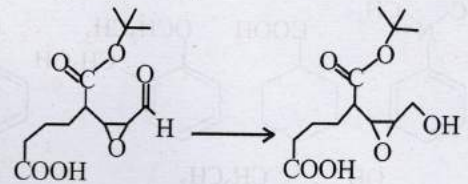
Consider *Q*, *R* and *S* as major products.



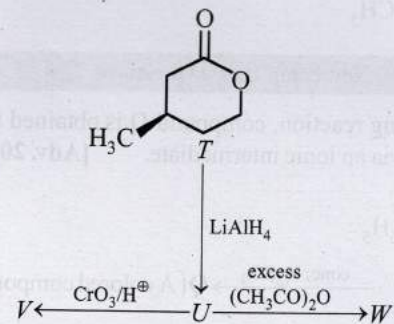
27. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) [Adv. 2018]



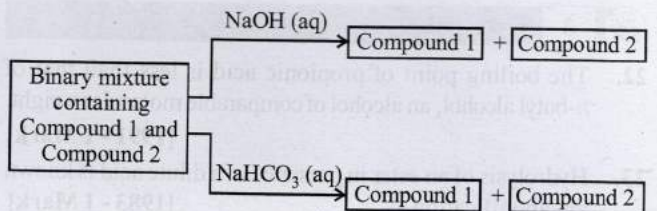
28. Reagent(s) which can be used to bring about the following transformation is (are) [Adv. 2016]



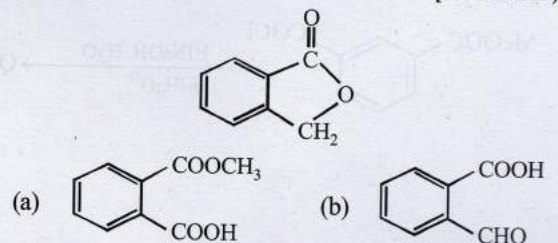
- (a) LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$ (b) BH_3 in THF
 (c) NaBH_4 in $\text{C}_2\text{H}_5\text{OH}$ (d) Raney Ni/ H_2 in THF
29. With reference to the scheme given below, which of the given statement(s) about *T*, *U*, *V* and *W* is (are) correct? [2012]

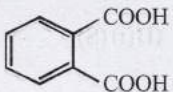
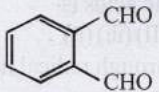


- (a) *T* is soluble in hot aqueous NaOH
 (b) *U* is optically active
 (c) Molecular formula of *W* is $\text{C}_{10}\text{H}_{18}\text{O}_4$
 (d) *V* gives effervescences on treatment with aqueous NaHCO_3 .
30. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction as shown in the given scheme. [2012]



- (a) $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{COOH}$
 (b) $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{OH}$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
31. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? [2006 - 5M, -1]



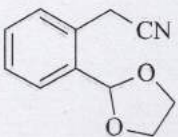
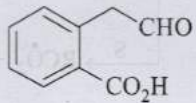
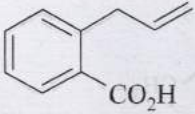
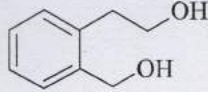
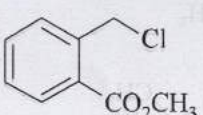
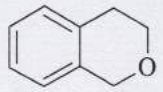
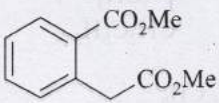
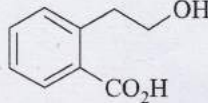
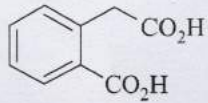
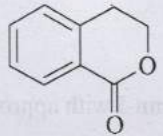
- (c)  (d) 
32. Which of the following compounds will react with ethanolic KCN? [1984 - 1 Mark]

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



7 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. [Adv. 2019]

List-I		List-II
(I) 	(i) DIBAL-H (ii) dil. HCl (iii) NaBH ₄ (iv) conc. H ₂ SO ₄	(P) 
(II) 	(i) O ₃ (ii) Zn, H ₂ O (iii) NaBH ₄ (iv) conc. H ₂ SO ₄	(Q) 
(III) 	(i) KCN (ii) H ₃ O ⁺ , Δ (iii) LiAlH ₄ (iv) conc. H ₂ SO ₄	(R) 
(IV) 	(i) LiAlH ₄ (ii) conc. H ₂ SO ₄	(S) 
		(T) 
		(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) (d) (II), (P), (S), (T)
35. Which of the following options has correct combination considering List-I and List-II?
- (a) (IV), (Q), (R) (b) (IV), (Q), (U) (c) (III), (S), (R) (d) (III), (T), (U)

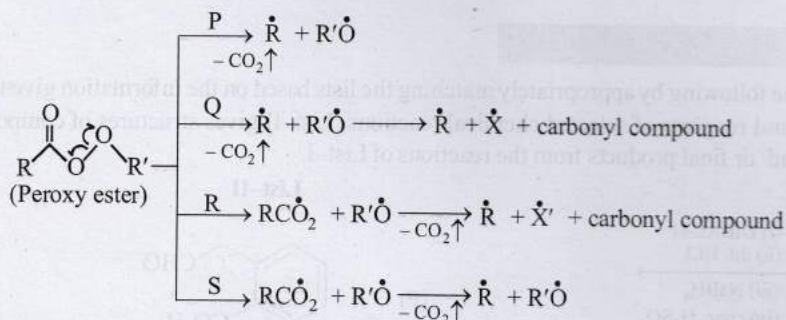
Directions [Qs. 36-38] : By appropriately matching the information given in the three columns of the following table. Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. [Adv. 2017]

Column 1	Column 2	Column 3
(I) Toluene	(i) NaOH/Br ₂	(P) Condensation
(II) Acetophenone	(ii) Br ₂ /hν	(Q) Carboxylation
(III) Benzaldehyde	(iii) (CH ₃ CO) ₂ O/CH ₃ COOK	(R) Substitution
(IV) Phenol	(iv) NaOH/CO ₂	(S) Haloform

36. 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]



List-I

P. Pathway P

Q. Pathway Q

R. Pathway R

S. Pathway S

Code :

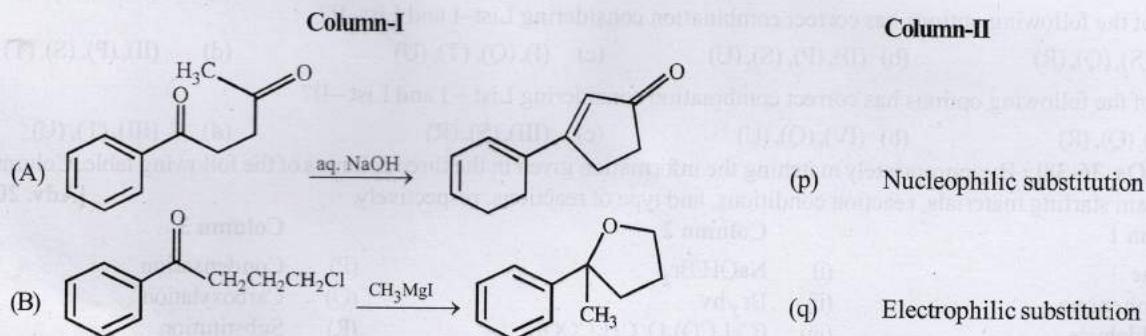
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1

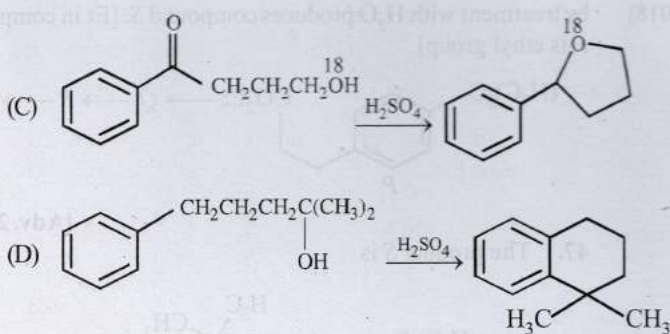
List-II

-
-
-
-

	P	Q	R	S
(c)	4	1	2	3
(d)	3	2	1	4

40. Match the reactions in Column-I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column-II. [2011]





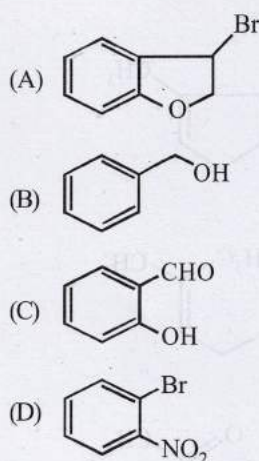
(r) Dehydration

(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

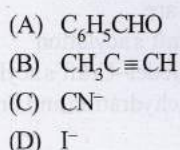
(r) Nucleophilic addition

(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**Column-II**

(p) gives precipitate with 2, 4-dinitrophenylhydrazine

(q) gives precipitate with $AgNO_3$

(r) is a nucleophile

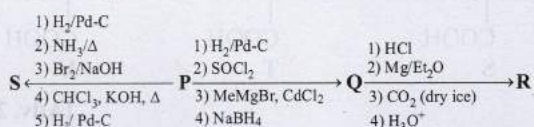
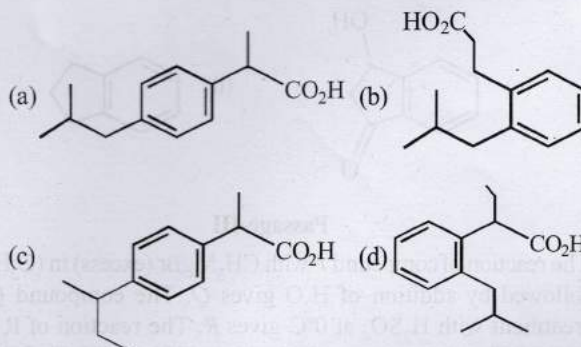
(s) is involved in cyanohydrin formation



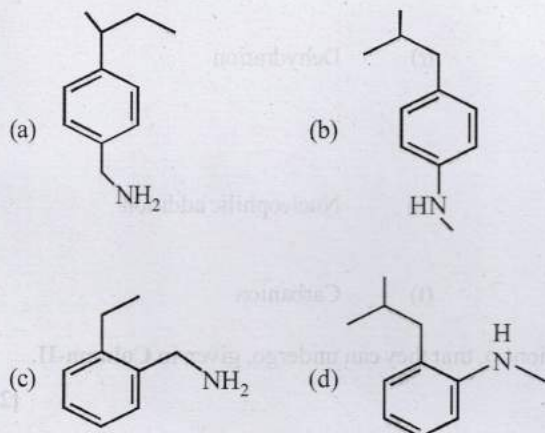
8 Comprehension Passage Based Questions

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]

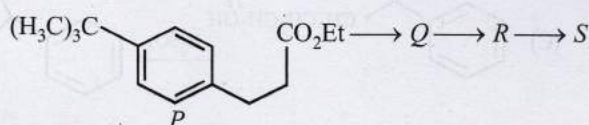
43. The compound **R** is

44. The compound S is



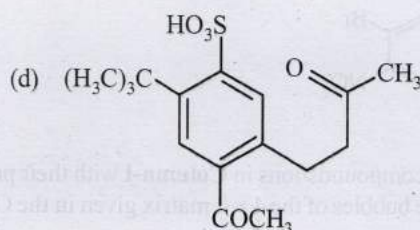
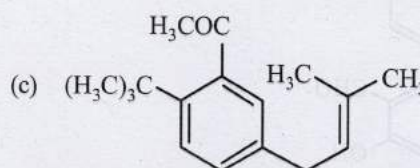
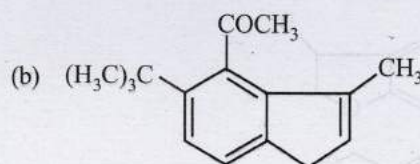
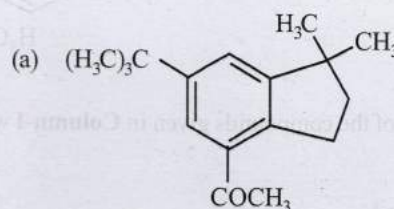
[Adv. 2018]

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



[Adv. 2017]

47. The product S is

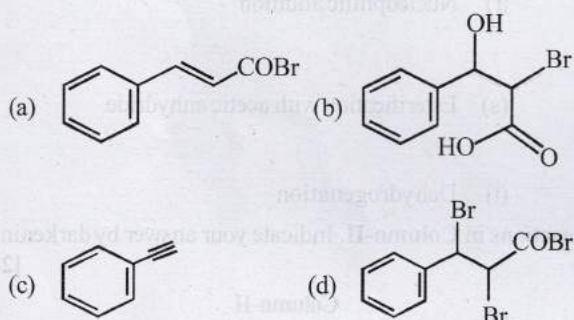


Passage-II

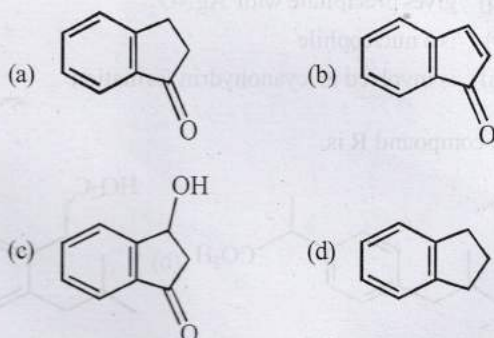
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3/CuCl$ followed by reaction with $Ac_2O/NaOAc$ gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3 , followed by heating at 473 K with alc. KOH furnishes Y as the major product. Reaction of X with $H_2/Pd-C$, followed by H_3PO_4 treatment gives Z as the major product.

[Adv. 2018]

45. The compound Y is



46. The compound Z is



Passage-III

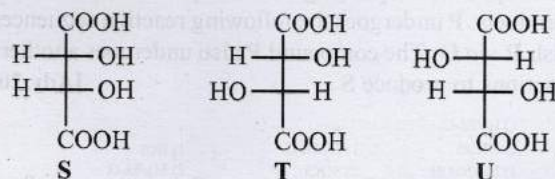
The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives Q. The compound Q on treatment with H_2SO_4 at $0^\circ C$ gives R. The reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed

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

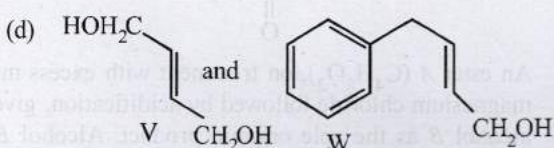
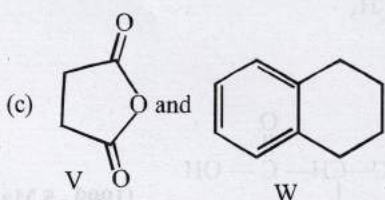
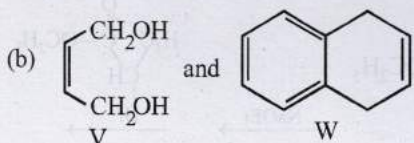
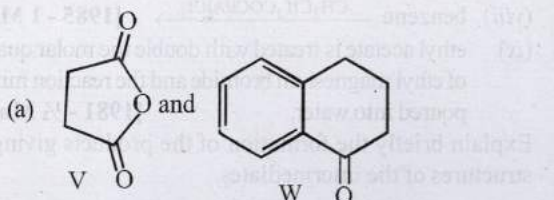
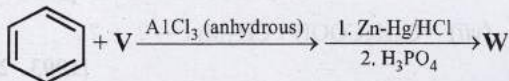
Passage-IV

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.



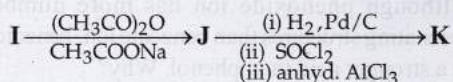
[Adv. 2013]

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



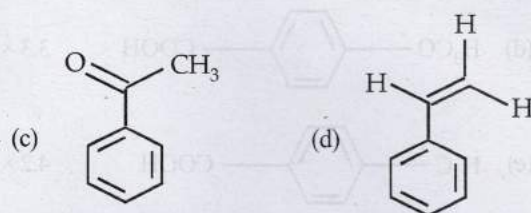
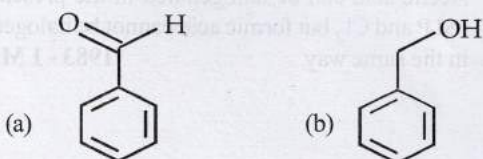
Passage-V

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

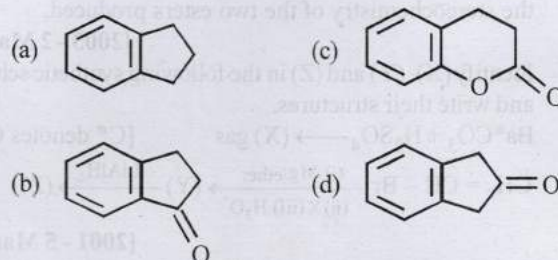


J ($C_9H_8O_2$) gives effervescences on treatment with $NaHCO_3$ and also give positive Baeyer's test. [2012]

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

- If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- If Statement -1 is correct but Statement -2 is incorrect.
- 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]

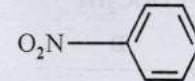
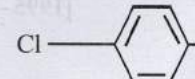
54. **Statement-1** : Acetic acid does not undergo haloform reaction. **Statement-2** : Acetic acid has no alpha hydrogens. [1998 - 2 Marks]

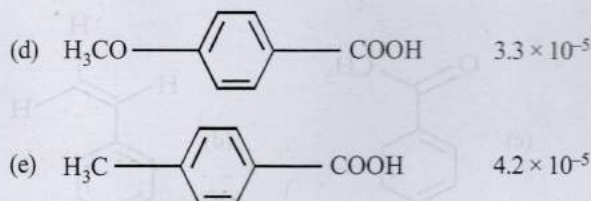
55. **Statement-1** : Acetate ion is more basic than the methoxide ion. **Statement-2** : The acetate ion is resonance stabilized. [1994 - 2 Marks]



10 Subjective Problems

56. Match the K_a values [2003]

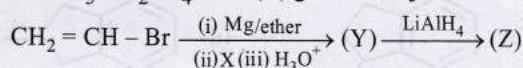
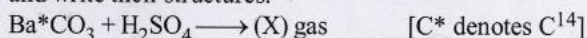
	K_a
(a) Benzoic acid	6.4×10^{-5}
(b) 	30.6×10^{-5}
(c) 	10.2×10^{-5}



57. A racemic mixture of (\pm) 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.



[2001 - 5 Marks]

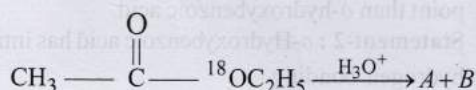
Explain the formation of labelled formaldehyde ($\text{H}_2\text{C}^*\text{O}$) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C^* carbon in the entire scheme.

59. An organic compound A, $\text{C}_8\text{H}_4\text{O}_3$, in dry benzene in the presence of anhydrous AlCl_3 gives compound B. The compound B on treatment with PCl_5 , followed by reaction with H_2/Pd (BaSO_4) gives compound C, which on reaction with hydrazine gives a cyclic compound D ($\text{C}_{14}\text{H}_{10}\text{N}_2$). 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 :

(i) Write the structures of the products A and B.



[2000 - 2 Marks]

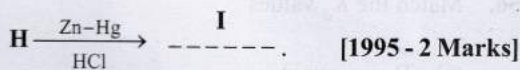
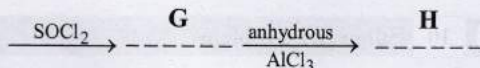
(ii) $(\text{COOH})_2 + (\text{CH}_2\text{OH})_2 + \text{Conc. H}_2\text{SO}_4$

F

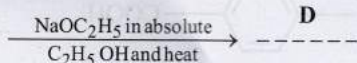


[1997 - 1 Mark]

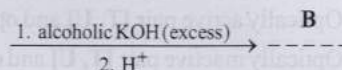
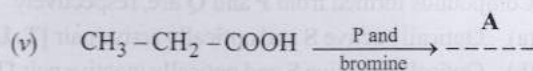
(iii) $o\text{-HOOC-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_5$



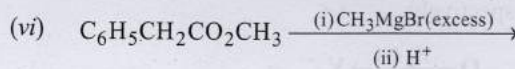
(iv) $\text{C}_6\text{H}_5\text{-CHO} + \text{CH}_3\text{-COOC}_2\text{H}_5$



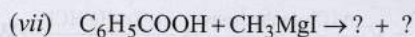
[1995 - 1 Mark]



[1995 - 2 Marks]



[1994 - 1 Mark]

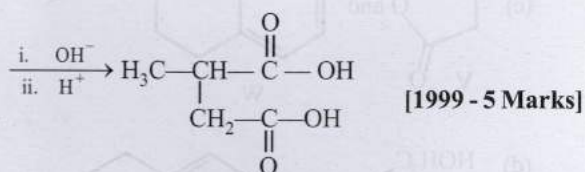
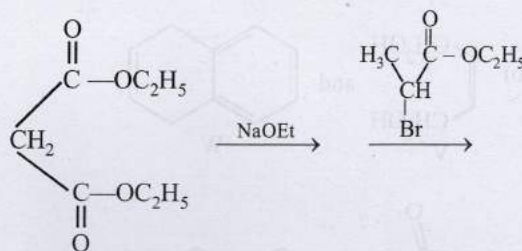


[1993 - 2 Marks]



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

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



[1999 - 5 Marks]

62. An ester A ($\text{C}_4\text{H}_8\text{O}_2$), 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]

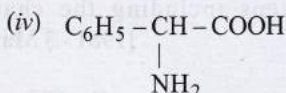
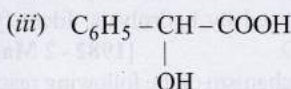
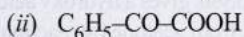
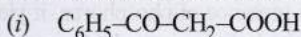
63. Give reasons for the following :

(i) 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]

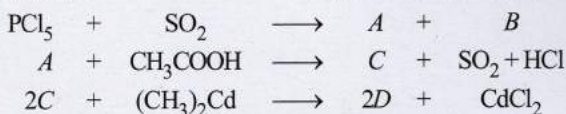
(iii) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. [1983 - 1 Mark]

64. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly. [1995 - 2 Marks]



65. An organic compound *A*, C_8H_6 , 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 $KMnO_4$ also gives 'B'. 'B' on heating with $Ca(OH)_2$ gives 'E' (molecular formula, C_3H_6O). 'E' does not give Tollen's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenylhydrazone. Identify 'A', 'B', 'C', 'D' and 'E'. [1992 - 3 Marks]

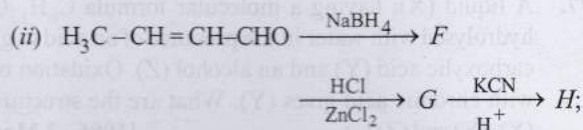
68. Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO_2 to give ethanol. Suggest structures for 'X', 'Y' and 'Z'. [1992 - 1 Mark]

69. Arrange the following in :

Increasing order of acid strength : [1991]

- (I) $ClCH_2COOH$, (II) CH_3CH_2COOH ,
(III) $ClCH_2CH_2COOH$, (IV) $(CH_3)_2CHCOOH$,
(V) CH_3COOH

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]



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

71. Compound *A* ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ 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]

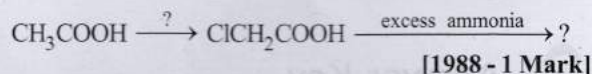
73. Outline the reaction sequence for the conversion of

(i) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. [1990 - 2 Marks]

(ii) Ethanal to 2-hydroxy-3-butenic acid. [1990 - 2 Marks]

(iii) acetic acid to tertiary-butyl alcohol. [1989 - 1½ Marks]

74. Complete the following reactions :



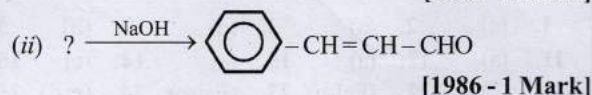
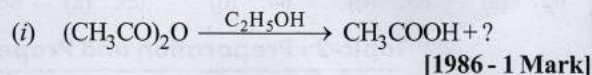
[1988 - 1 Mark]

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.

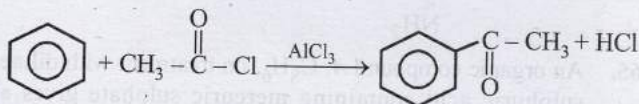
Identify the compounds *A*, *B*, *C*, *D* and *E*.

[1987 - 5 Marks]

76. Complete the following with appropriate structures :



77. A liquid (X), having a molecular formula $C_6H_{12}O_2$ 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 $CH_3COOC_2H_5$, CH_3COCl , $(CH_3CO)_2O$, CH_3CONH_2 . [1986 - 1 Mark]
79. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis: Propionic anhydride from propionaldehyde $[AgNO_3/NH_4OH, P_2O_5]$. [1984 - 2 Marks]
80. State the conditions under which the following preparations are carried out. Give the necessary equations which need not be balanced.
- Ethanol from acetylene [1983 - 1 Mark]
 - 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]



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

Topic-1 : Preparation and Properties of Carbonyl Compounds

- | | | | | | | | | | |
|---|---------------------|--------------|-------------|----------------------------------|-------------|------------|-------------|-----------|---------|
| 1. (a) | 2. (d) | 3. (a) | 4. (b) | 5. (c) | 6. (c) | 7. (c) | 8. (b) | 9. (c) | 10. (a) |
| 11. (b) | 12. (a) | 13. (b) | 14. (b) | 15. (d) | 16. (a) | 17. (d) | 18. (c) | 19. (b) | 20. (c) |
| 21. (b) | 22. (b) | 23. (12) | 24. (18) | 25. (12) | 26. (4) | 27. (5) | 28. (1) | | |
| 30. $C_6H_5CH(OCOCH_3)_2$ | benzylidene acetate | | | 31. (sodium potassium tartarate) | 33. (False) | 34. (True) | 35. (False) | | |
| 36. (a,c,d) | 37. (a,b,d) | 38. (c,d) | 39. (a,c) | 40. (b,d) | 41. (a,b) | 42. (b,c) | 43. (a,b,c) | 44. (a) | 45. (c) |
| 46. (b,d) | 47. (b,c) | 48. (c) | 49. (a,b,d) | 50. (b) | 51. (b,d) | 52. (a,b) | 53. (b,d) | 54. (a,c) | 55. (d) |
| 56. (A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s | 57. (2) | 58. (102018) | 59. (c) | 60. (d) | 61. (b) | | | | |
| 62. (a) | 63. (d) | 64. (d) | 65. (a) | 66. (c) | 67. (b) | 68. (a) | 69. (d) | 70. (a) | |

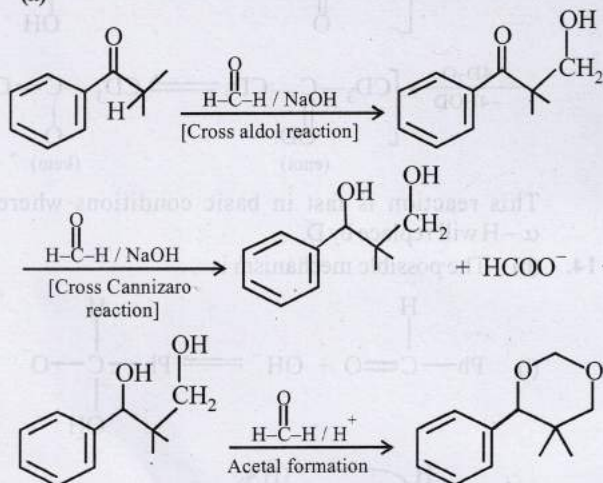
Topic-2 : Preparation and Properties of Carboxylic Acids and its Derivatives

- | | | | | | | | | | |
|---|---|-------------|-----------|---------|---|-------------|-----------|-------------|-------------|
| 1. (a) | 2. (a) | 3. (d) | 4. (b) | 5. (d) | 6. (b) | 7. (c) | 8. (c) | 9. (a) | 10. (c) |
| 11. (a) | 12. (a) | 13. (a) | 14. (c) | 15. (d) | 16. (a) | 17. (909) | 18. (2) | 19. (4) | 20. (18.00) |
| 21. (CO) | 22. (False) | 23. (False) | 24. (c,d) | 25. (b) | 26. (a,d) | 27. (a,b,d) | 28. (c,d) | 29. (a,c,d) | |
| 30. (b,d) | 31. (d) | 32. (a,b,d) | 33. (a,b) | 34. (b) | 35. (a) | 36. (a) | 37. (c) | 38. (d) | |
| 39. (a) | 40. A - r, s, t; B - p, s; C - r, s; D - q, r | | | | 41. (A) - p, q, t; (B) - p, s, t; (C) - r, s; (D) - p | | | | |
| 42. (A) - p, q, s; (B) - q; (C) - q, r, s; (D) - q, r | 43. (a) | 44. (b) | 45. (c) | 46. (a) | 47. (a) | 48. (a) | | | |
| 49. (b) | 50. (a) | 51. (a) | 52. (b) | 53. (d) | 54. (c) | 55. (d) | | | |

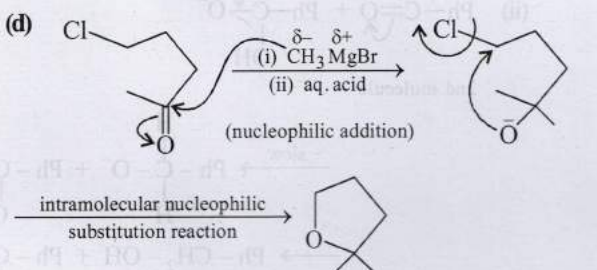
Hints & Solutions

Topic-1: Preparation and Properties of Carbonyl Compounds

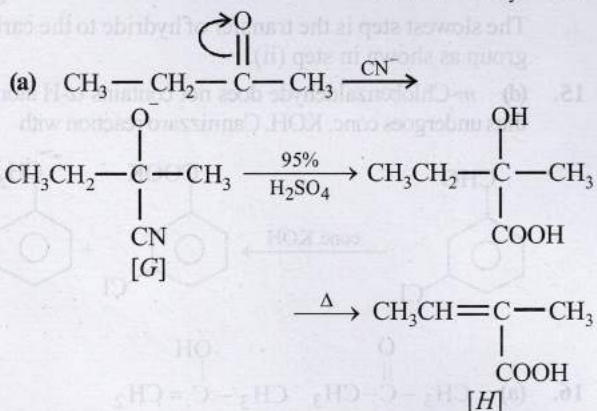
1. (a)



2. (d)

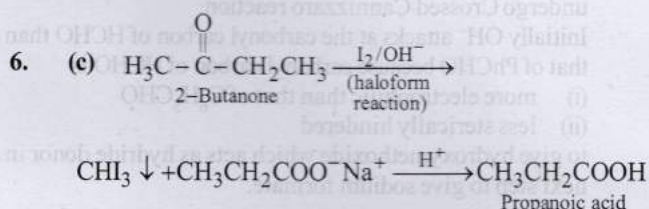


3. (a)

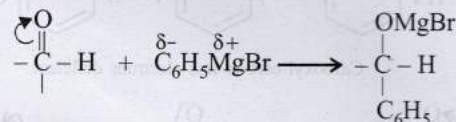


4. (b) The ring to which $-\text{NH}$ group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which $-\text{C}=\text{O}$ is attached is deactivated. Hence, the electrophile NO_2^+ would go to the *para*-position of the activated ring.

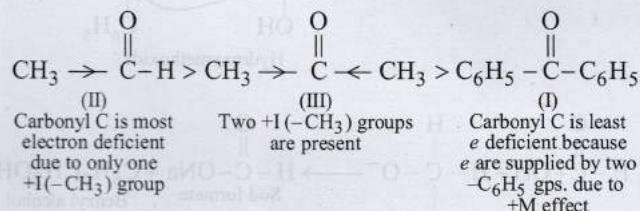
5. (c) This reaction is an example of "Perkin reaction". The compound X should be $(\text{CH}_3\text{CO})_2\text{O}$. In this step the carbanion is obtained by removal of an α -H atom from a molecule of an acid anhydride, the anion of the corresponding acid acting as a necessary base.



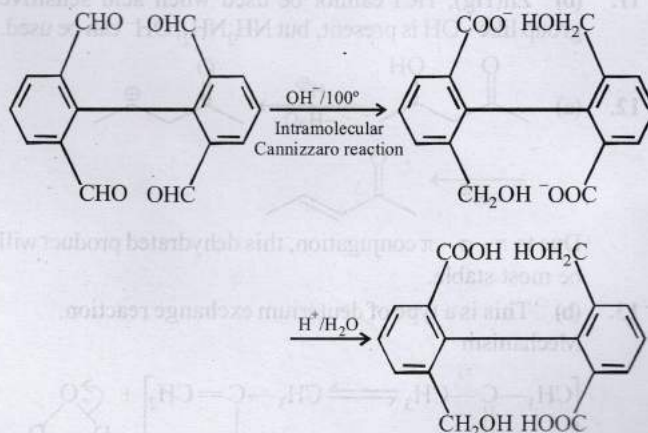
7. (c) Reaction of PhMgBr with carbonyl compounds is an example of nucleophilic addition on carbonyl group which increases with the increase in electron-deficiency of carbonyl carbon.



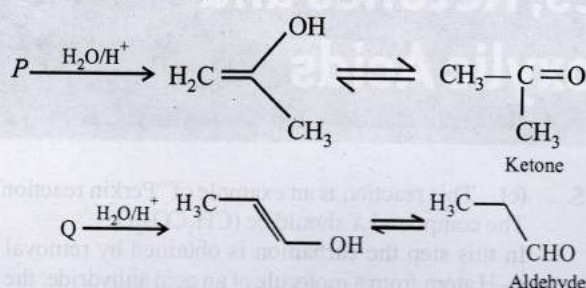
Thus the decreasing order should be



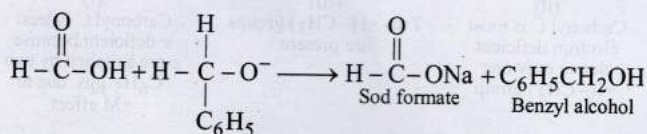
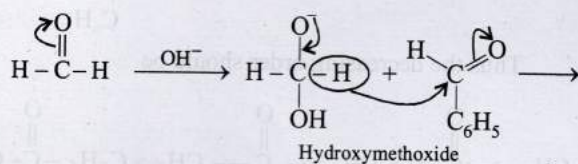
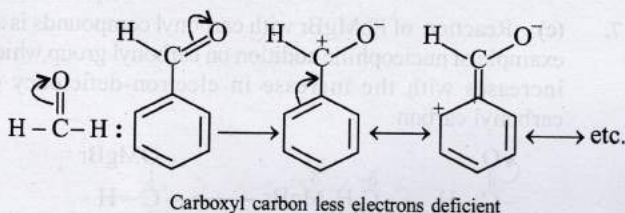
8. (b)



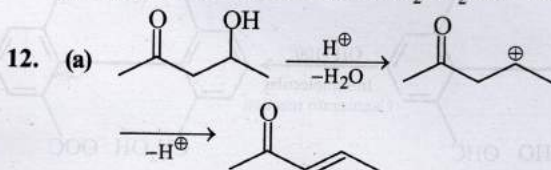
9. (c) Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.



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
- more electrophilic than that of $\text{C}_6\text{H}_5\text{CHO}$
 - less sterically hindered
- to give hydroxymethoxide which acts as hydride donor in next step to give sodium formate.

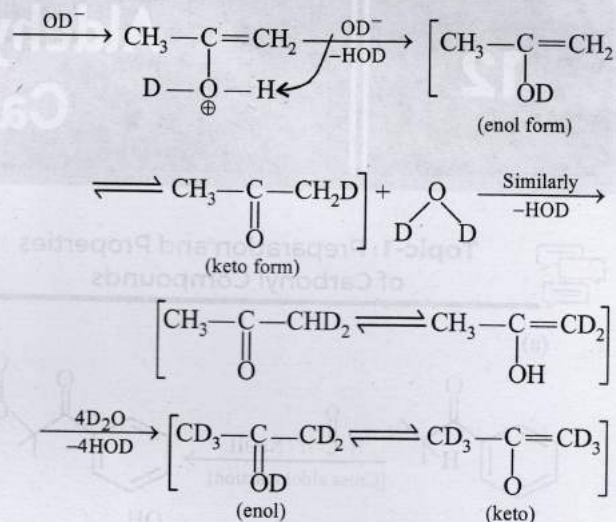
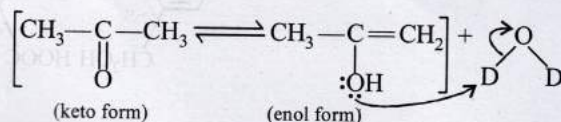


11. (b) $\text{Zn}(\text{Hg})$, HCl cannot be used when acid sensitive group like $-\text{OH}$ is present, but NH_2NH_2 , OH^- can be used.



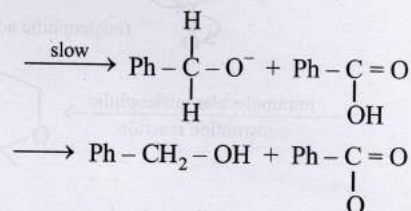
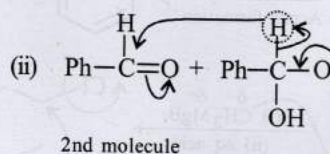
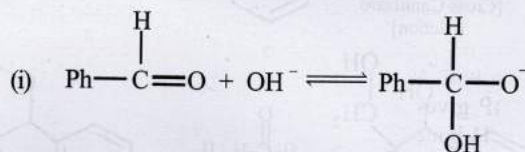
Due to $\pi-\sigma-\pi$ conjugation, this dehydrated product will be most stable.

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



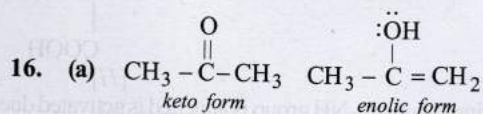
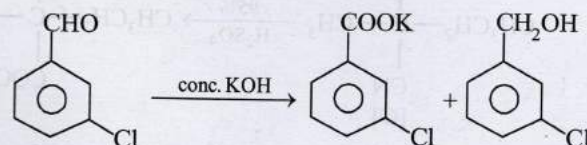
This reaction is fast in basic conditions where all α -H will replace by D.

14. (b) The possible mechanism is



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

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

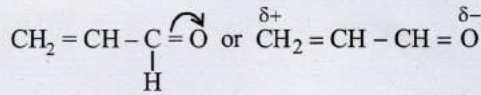


No. of σ bonds in enolic form : $3 + 1 + 1 + 1 + 1 + 2 = 9$

No. of π bonds in enolic form : 1

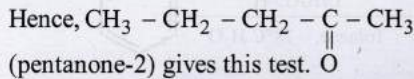
No. of lone pairs of electrons in enolic form = 2

17. (d) $-\text{CHO}$ withdraws electrons from the double bond or from a conjugated system towards itself.

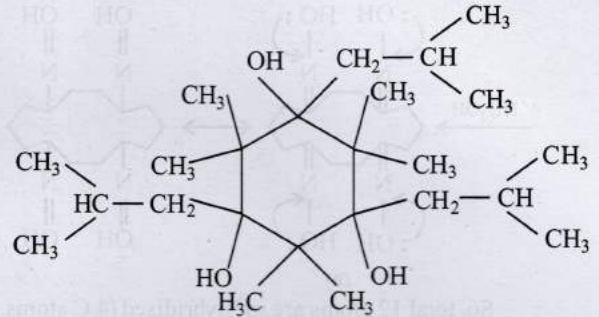
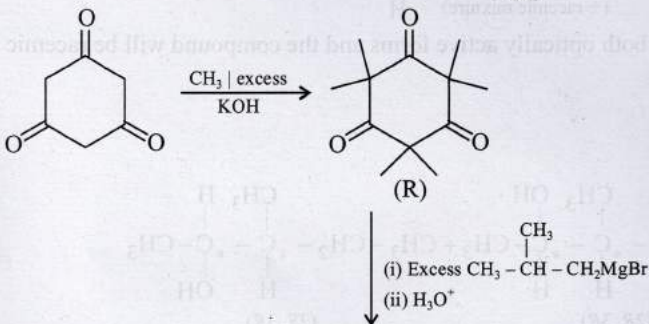
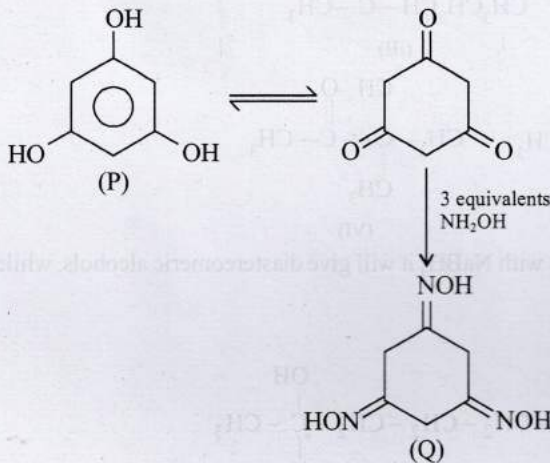


18. (c) Iodoform test is given by compounds having $-\text{COCH}_3$, CHOHCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$. Thus diethyl ketone does not give this test.
19. (b) The compound containing $\alpha\text{-H}$ atom (CH_3CHO) does not undergo Cannizzaro's reaction. The other three reaction $\alpha\text{-hydrogen}$.
20. (c) $\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + \text{OH}^- \rightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O} \downarrow$
 Fehling solution (red)
21. (b) Compounds having $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ groups, show

positive iodoform test.

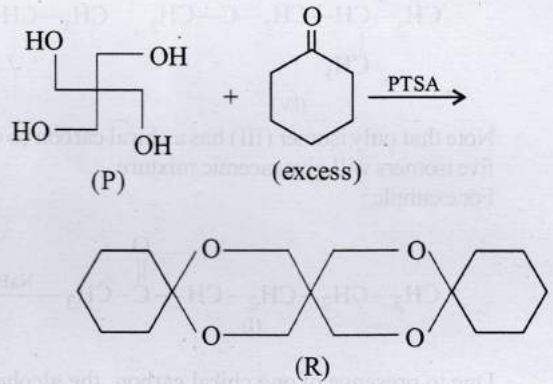
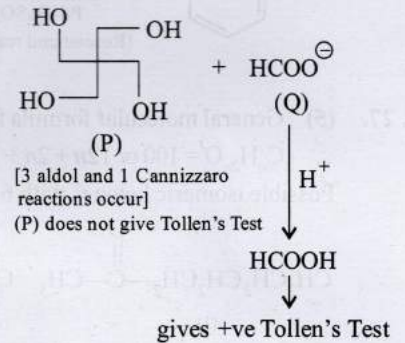
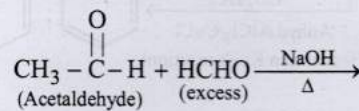


22. (b) Fehling solution, Schiff's reagent & Tollen's reagent react only with aldehydes, but Grignard reagents react both with aldehydes and ketones.
23. (12)P gives FeCl_3 test and there are no intramolecular H-bonds. Thus, P will be a trihydric phenol.



Number of CH_3 groups = 12

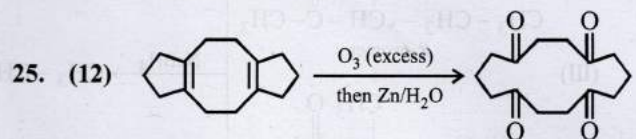
24. (18) Reactions taking place as:

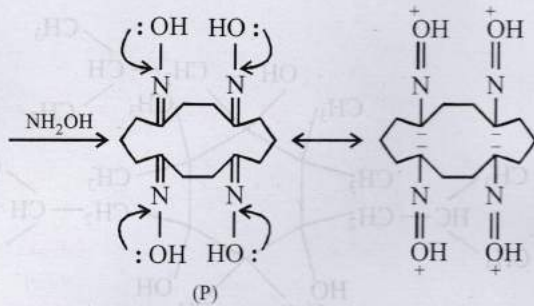


Number of CH_2 groups in R = 14

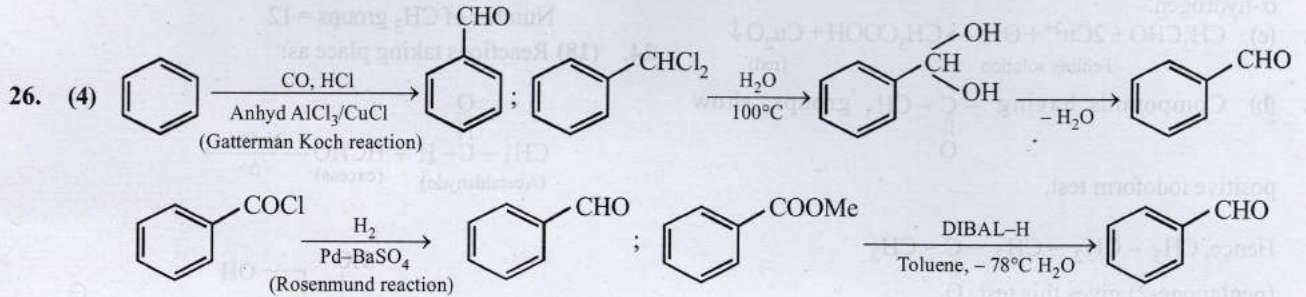
Number of O-atoms = 4

Required Answer = 14 + 4 = 18



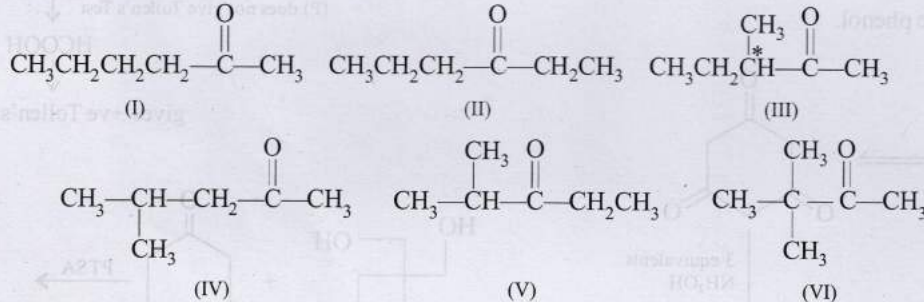


So, total 12 atoms are sp^2 hybridised (4 C atoms, 4 N atoms and 4 O atoms)



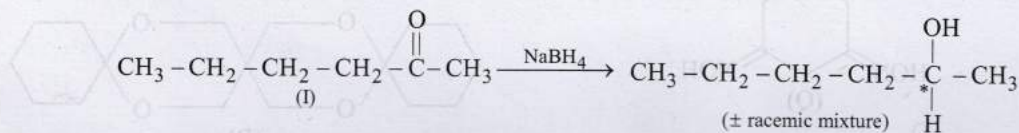
27. (5) General molecular formula for ketones is $C_nH_{2n}O$
 $\therefore C_nH_{2n}O = 100$ or $12n + 2n + 16 = 100, n = 6$

Possible isomeric ketones with 6 carbon atoms are

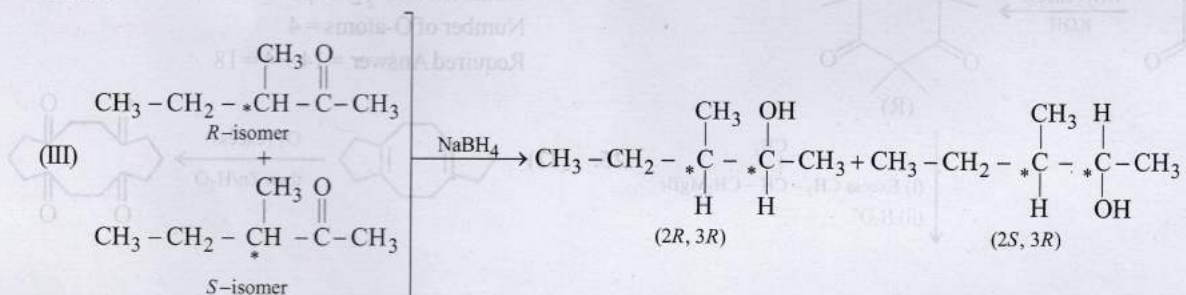


Note that only isomer (III) has a chiral carbon so on reduction with NaBH_4 it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

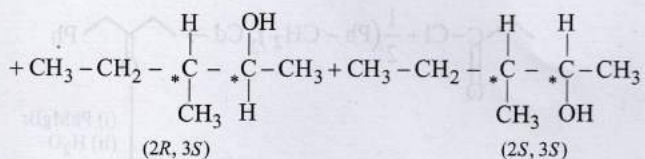
For example :



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



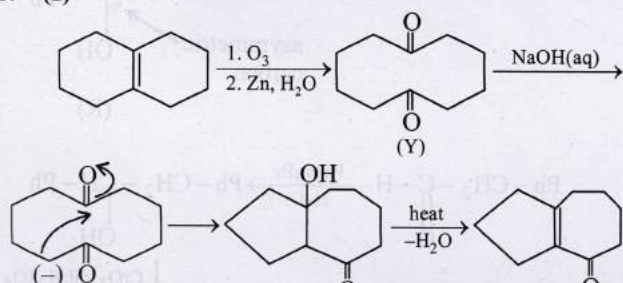
A pair of diastereomers from R-isomer of ketone



A pair of diastereomers from *S*-isomer of ketone

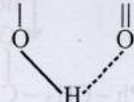
Note : All stereoisomers are reacted separately.

28. (1)

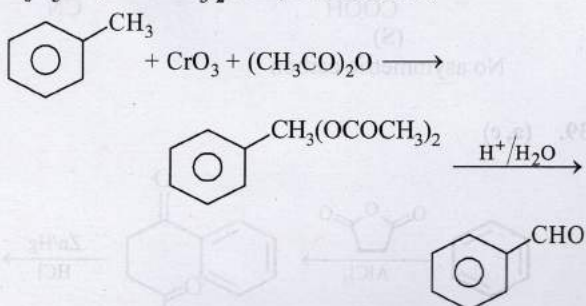


The number of intra molecular aldol condensation products (α, β -unsaturated carbonyl compound formed from Y is 1.

29. $\text{CH}_3 - \text{C} = \text{CH} - \text{C} - \text{CH}_3$



30. $\text{C}_6\text{H}_5\text{CH}(\text{OCOCH}_3)_2$ benzylidene acetate;



31. sodium potassium tartarate.

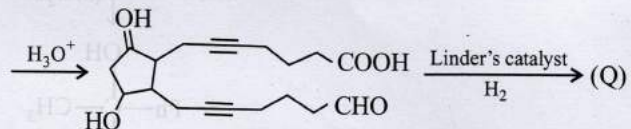
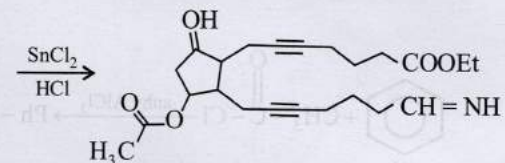
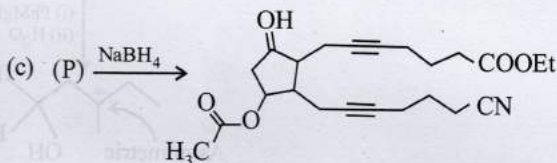
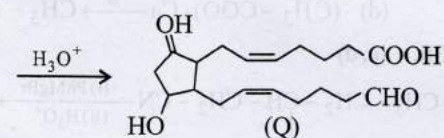
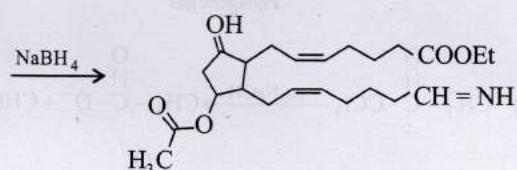
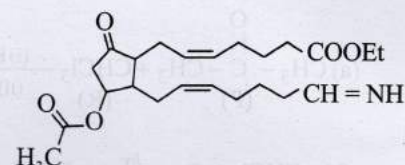
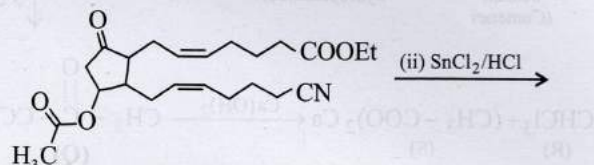
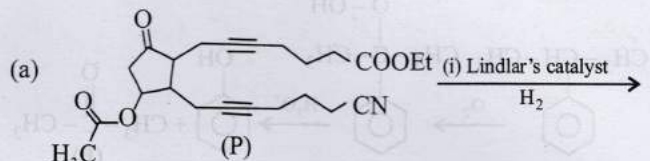
32. (i) Free radical substitution (ii) Thermite process
 (iii) Nucleophilic addition (iv) Cyanamide process;
 (v) Nucleophilic substitution (vi) Bayer's process
 (vii) Homologous pair
 (viii) Electrophilic substitution (ix) Ostwald's process
 (x) Homolytic addition.

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

34. **True :** Aldehydes (from primary alcohols) 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)



(i) Lindlar's catalyst, H_2 ,

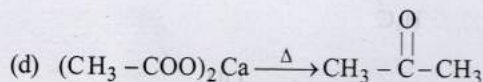
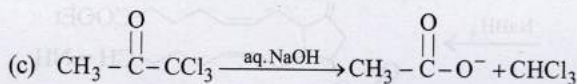
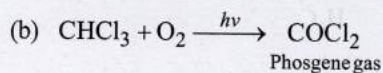
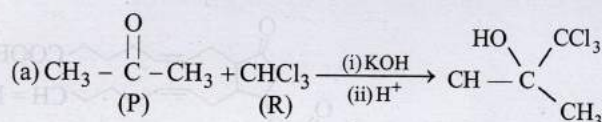
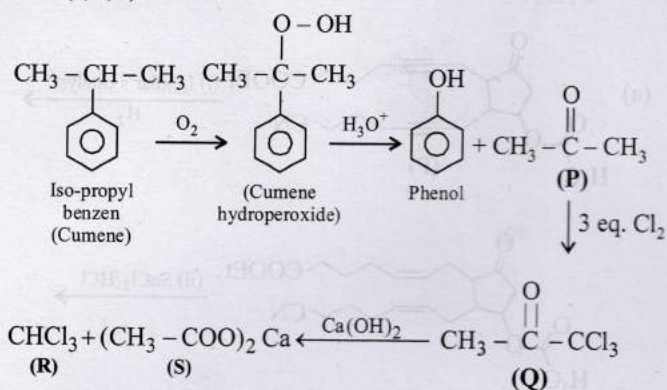
(ii) NaBH_4 ,

(iii) SnCl_2/HCl , (iv) H_3O^+

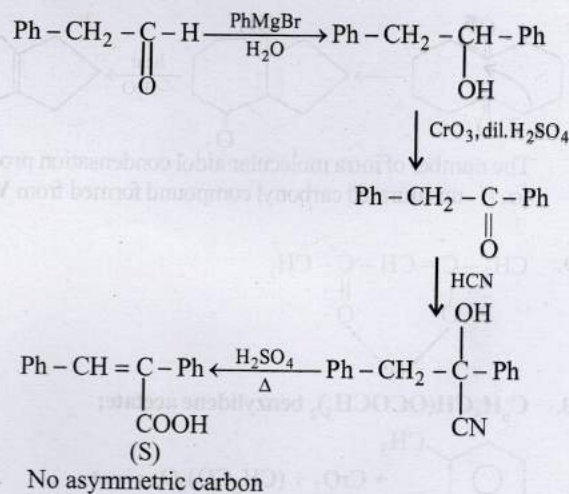
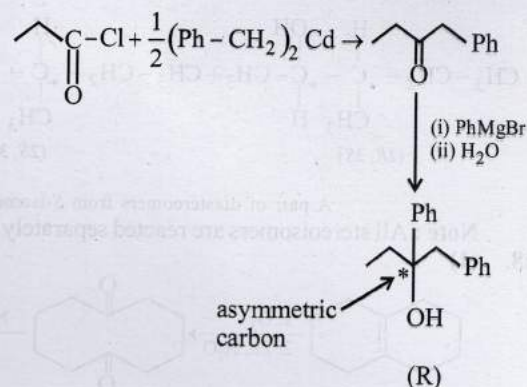
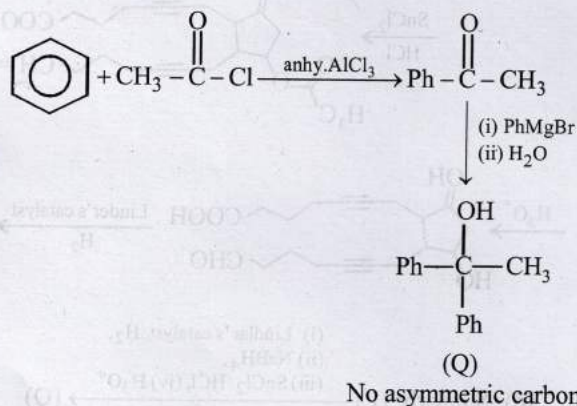
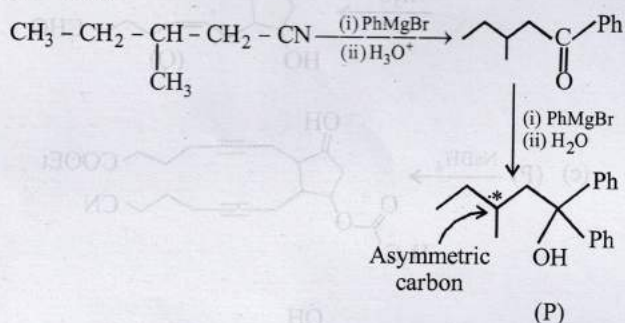
(d) Similarly, (P) $\xrightarrow{\text{(i) Lindlar's catalyst, H}_2, \text{(ii) NaBH}_4, \text{(iii) SnCl}_2/\text{HCl}, \text{(iv) H}_3\text{O}^+}$ (Q)

Hydrolysis of $-\text{CN}$ gives $-\text{COOH}$ and thus option (b) is not correct.

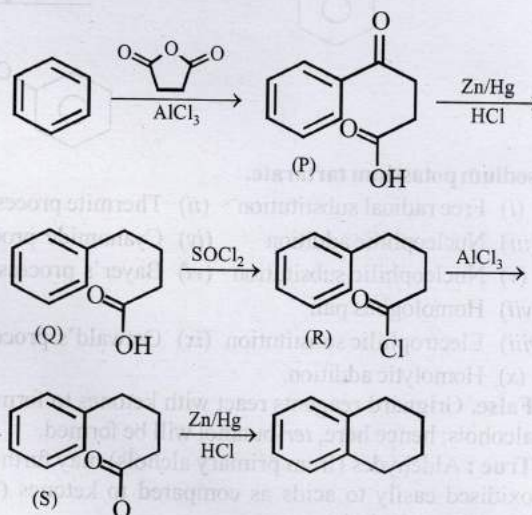
37. (a, b, d)



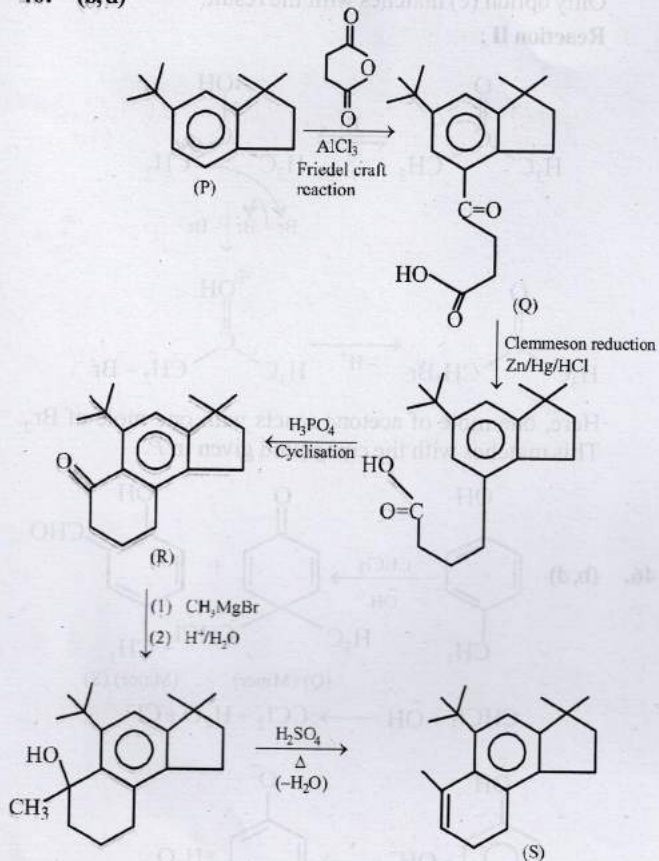
38. (c, d)



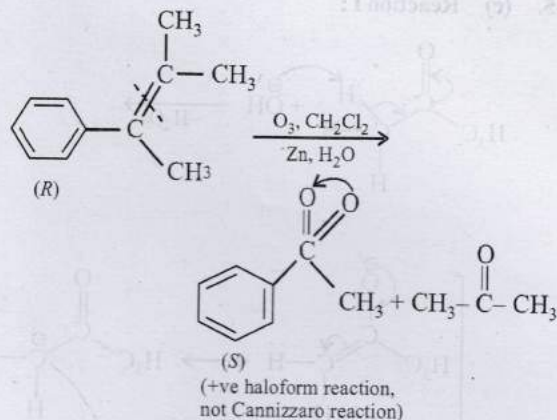
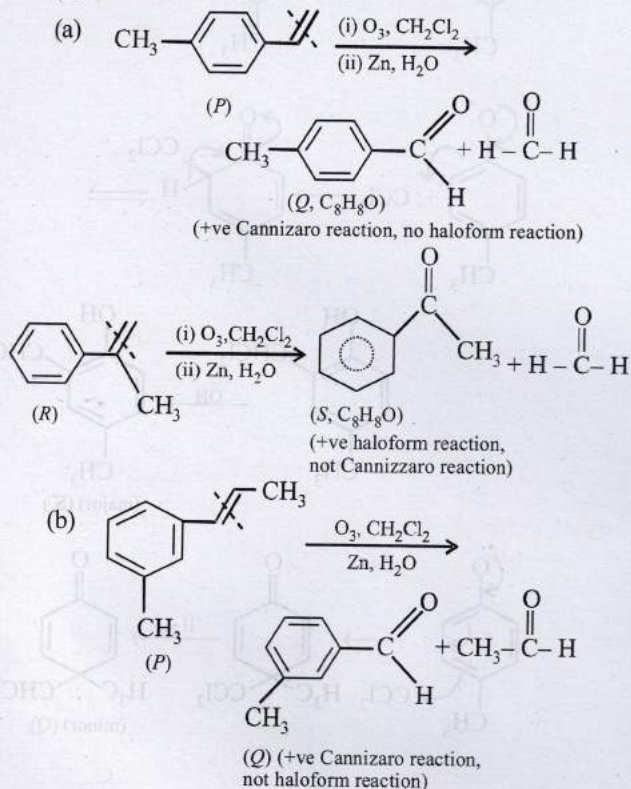
39. (a, c)



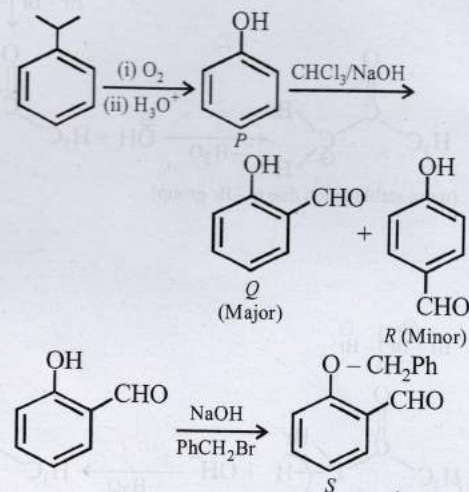
40. (b, d)



41. (a, b)



42. (b, c)



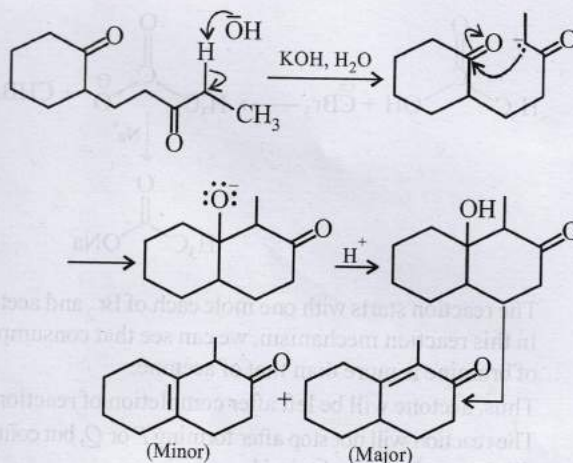
Q is steam volatile, but not R.

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

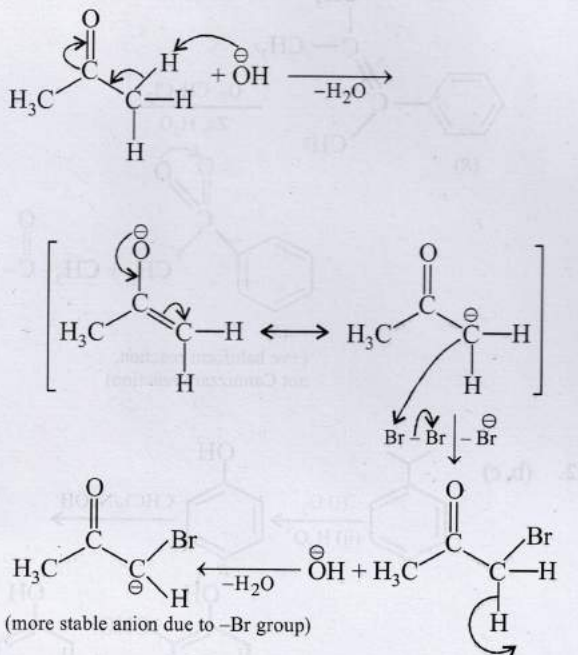
Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

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

44. (a)



45. (c) Reaction I:



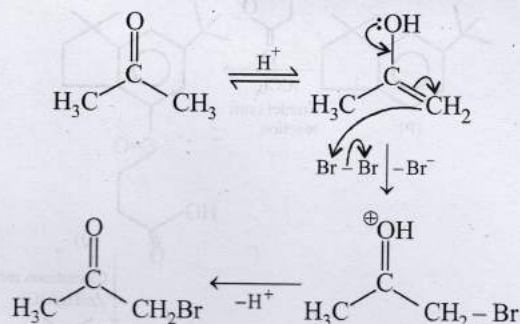
The reaction starts with one mole each of Br_2 and acetone. In this reaction mechanism, we can see that consumption of bromine is more than that of acetone.

Thus, acetone will be left after completion of reaction.

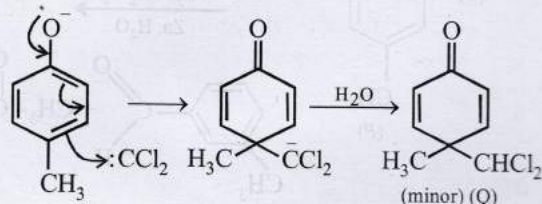
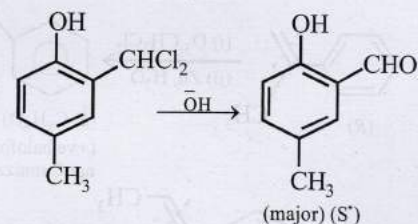
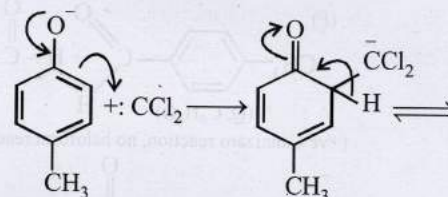
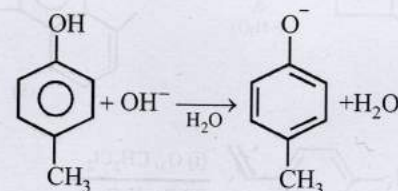
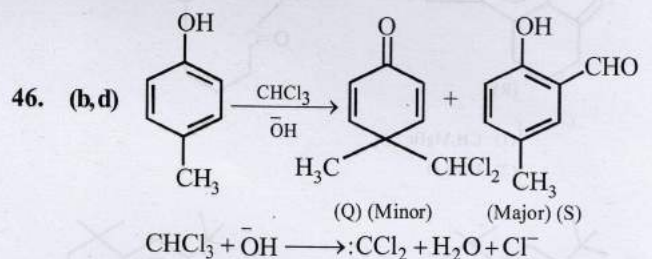
The reaction will not stop after forming *P* or *Q*, but continue till the product *I* is obtained.

Only option (c) matches with the result.

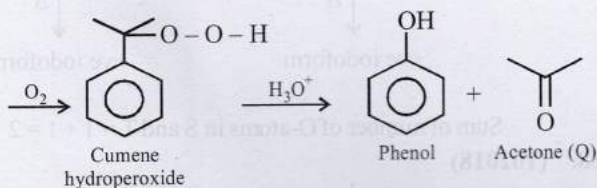
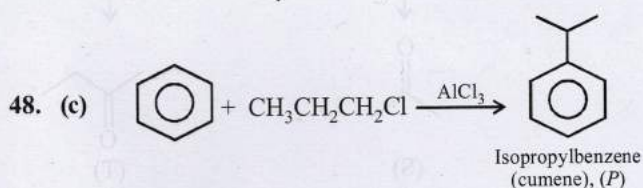
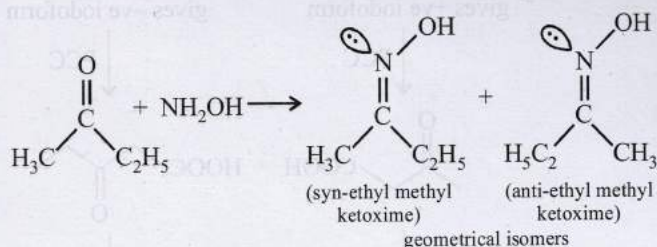
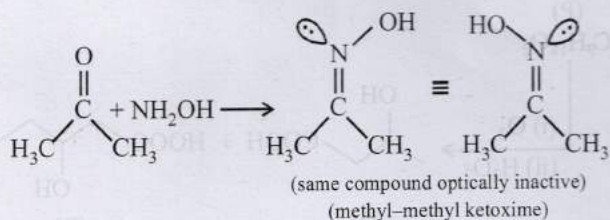
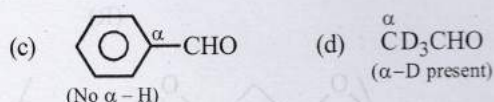
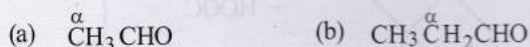
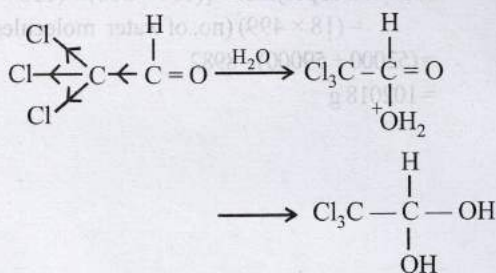
Reaction II:



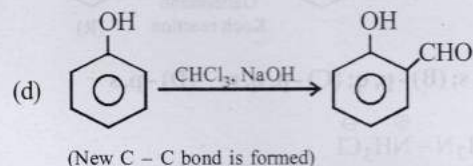
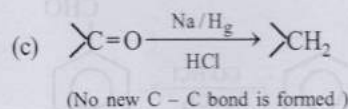
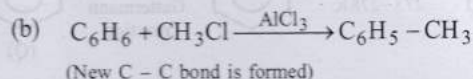
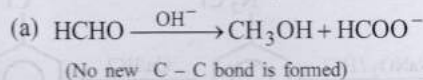
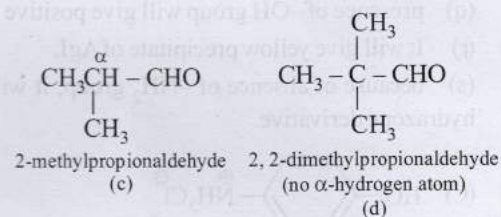
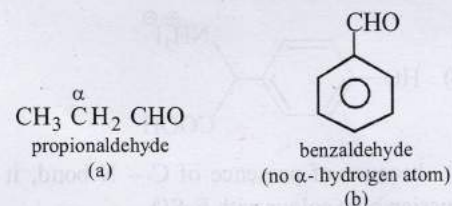
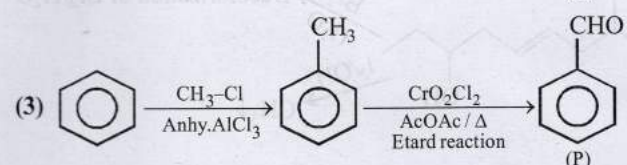
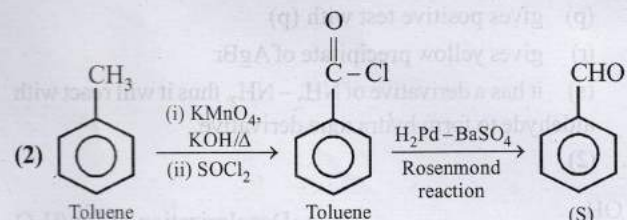
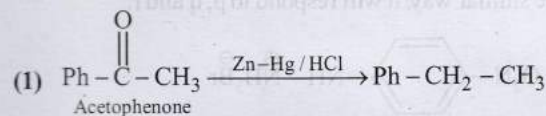
Here, one mole of acetone reacts with one mole of Br_2 . This matches with the compound given in *P*.

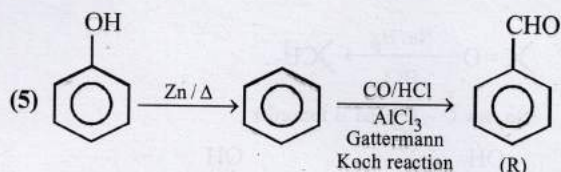
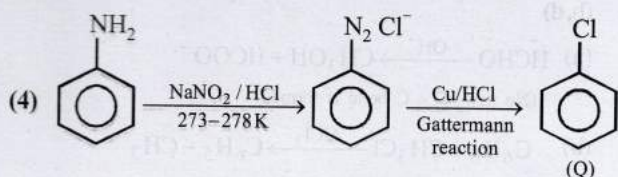


47. (b, c)

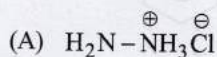
49. (a, b, d) Carbonyl compounds having α -H or α -D undergo aldol condensation.50. (b) Three Cl of chloral makes its carbonyl carbon highly electron deficient, hence H_2O , a nucleophile easily adds on it forming chloral hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$, which is quite stable due to intramolecular H-bonding between two -OH groups.

51. (b, d)

52. (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.54. (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



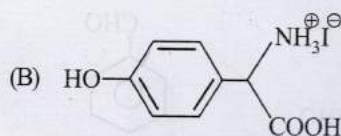
56. (A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s



(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 AgNO_3 .

(s) because of $-\text{NH}_2$ group it will react with aldehydes to form hydrazone derivative.

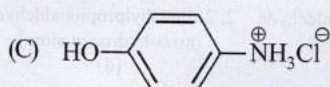


(p) because of presence of C - N bond, it will form prussian blue colour with FeSO_4 .

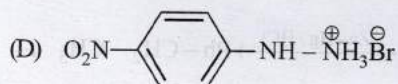
(q) presence of $-\text{OH}$ group will give positive FeCl_3 test.

(r) It will give yellow precipitate of AgI .

(s) because of absence of $-\text{NH}_2$ group, it will not give hydrazone derivative.



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

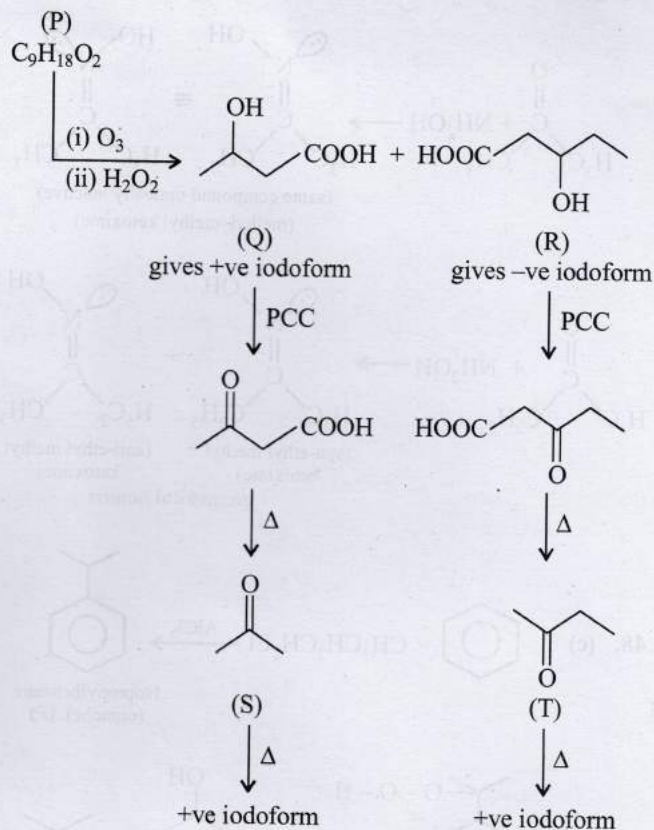
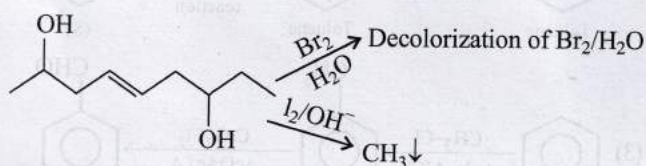


(p) gives positive test with (p)

(r) gives yellow precipitate of AgBr

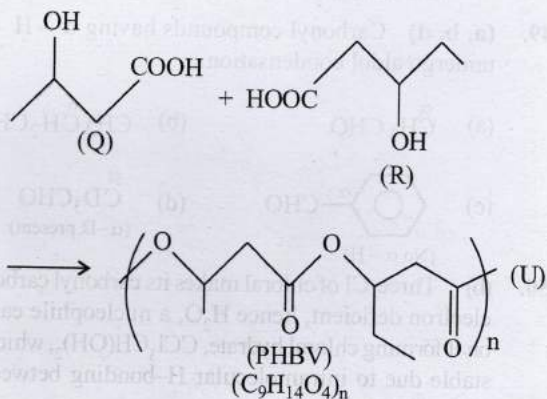
(s) it has a derivative of NH_2-NH_2 , thus it will react with aldehyde to form hydrazone derivative.

57. (2)



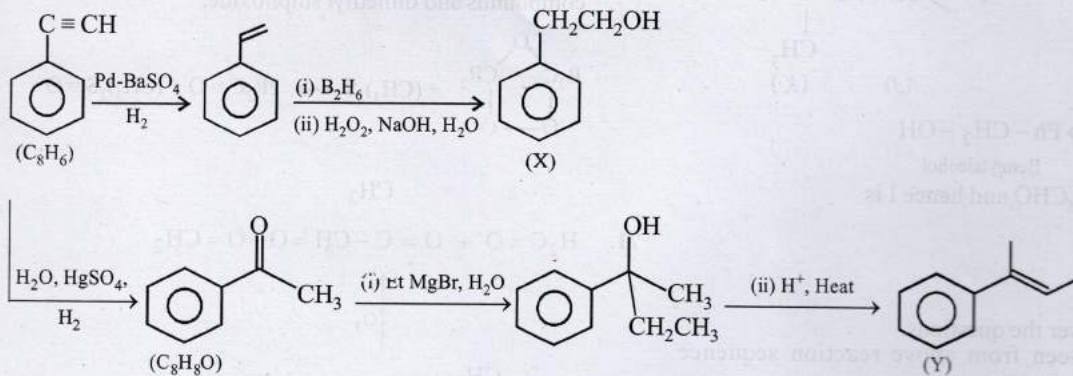
Sum of number of O-atoms in S and T = 1 + 1 = 2

58. (102018)



$$\begin{aligned} \text{Mol. Wt. of polymer} &= [(104 \times 500) + (118 \times 500)] \\ &\quad - (18 \times 499) \text{ (no. of water molecules released)} \\ &= (52000 + 59000) - 8982 \\ &= 102018 \text{ g} \end{aligned}$$

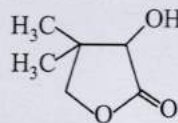
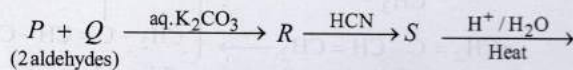
For 59-60. (Passage-I)



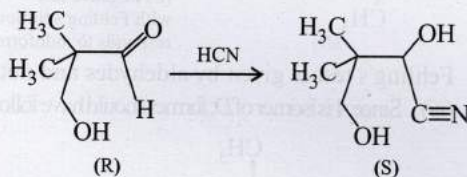
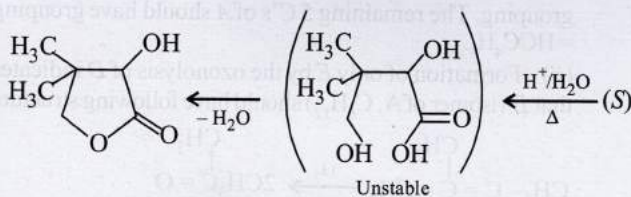
59. (c) 60. (d)

For 61-63. (Passage-II)

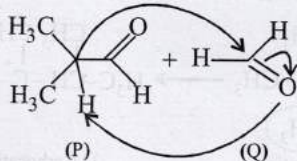
Let us summarize the given facts of the problem.



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



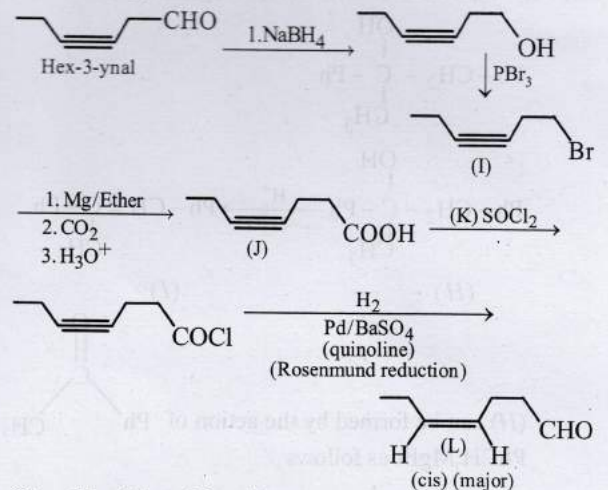
Aldol $\xrightarrow{\text{aq. K}_2\text{CO}_3}$



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)



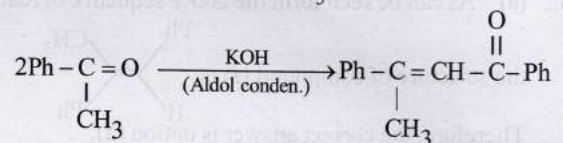
64. (d) 65. (a) 66. (c)

For 67-69. (Passage-IV)

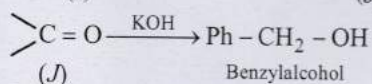
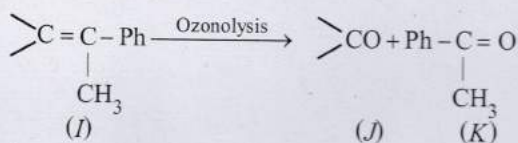
Before answering these question let us complete the sequence of reactions given in data.

The given compound (M) i.e. C=C(C)C(=O)Ph is the only product formed by the action of KOH on compound K.

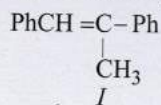
The compound K is Ph-C(=O)CH_3



Compound K (i.e. Ph-C(=O)CH_3) is one of the products of ozonolysis of compound I. Therefore the compound I may be



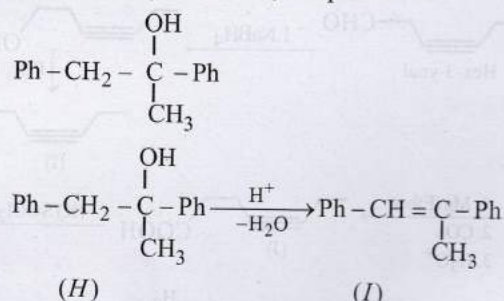
Thus J seems to be C_6H_5CHO and hence I is



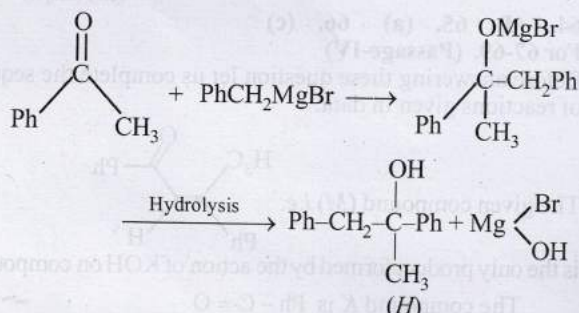
Now we will try to answer the questions.

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

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

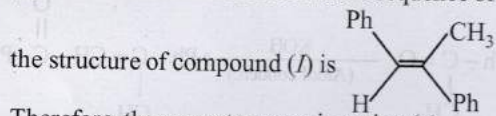


(H) can be formed by the action of $Ph-C(=O)-CH_3$ with $PhCH_2MgBr$ as follows



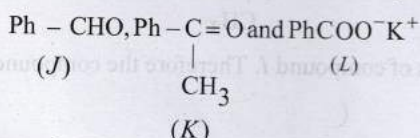
Therefore, the correct answer is option (b)

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



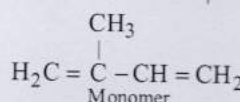
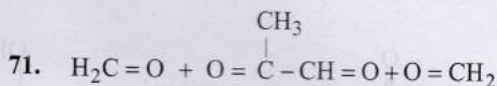
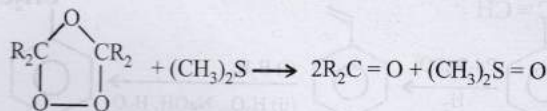
Therefore, the correct answer is option (a).

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

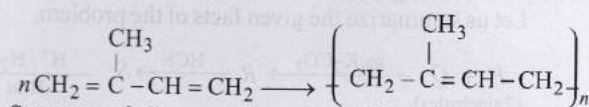


Thus, the correct answer is option (d),

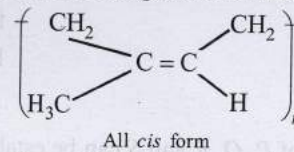
70. (a) Ozonide can be reduced by $(CH_3)_2S$ to give carbonyl compounds and dimethyl sulphoxide.



Thus, the possible polymer should be

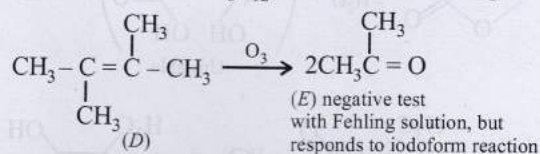


Structure of all cis configuration of the polymer.



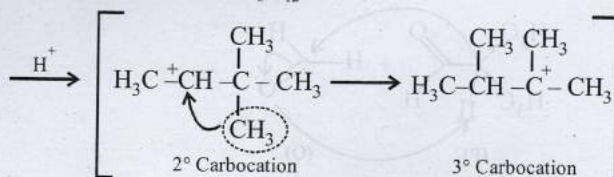
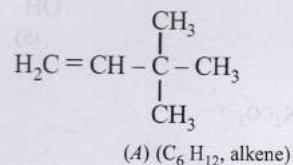
72. (i) Formation of $HCOONa$ and a primary alcohol due to Cannizzaro reaction of F and G indicate that either F or G should be $HCHO$. Thus, the alkene A should have $CH_2 =$ grouping. The remaining 5 C's of A should have grouping $=HCC_4H_9$.

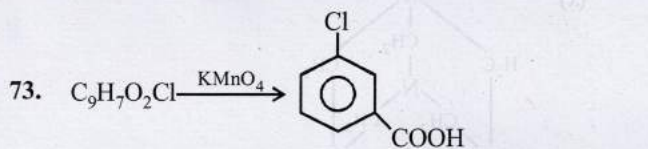
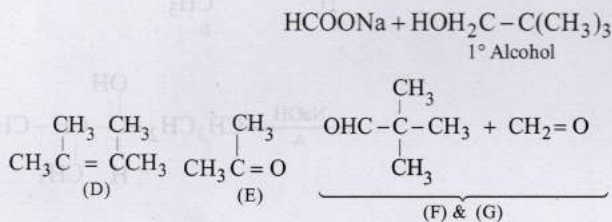
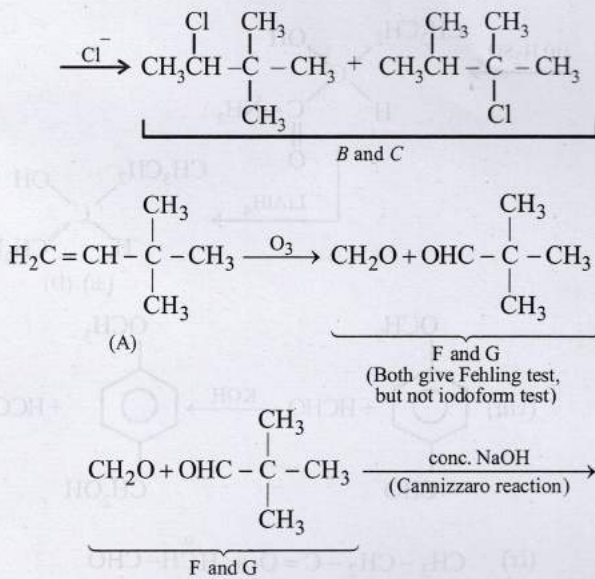
(ii) Formation of only E by the ozonolysis of D indicates that D (isomer of A, C_6H_{12}) should have following structure



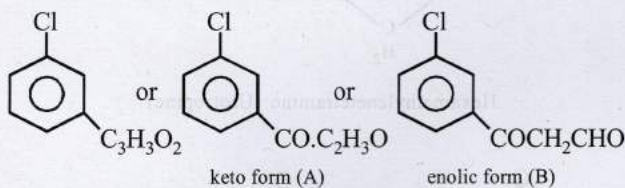
Fehling's test is given by aldehydes and not ketones.

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

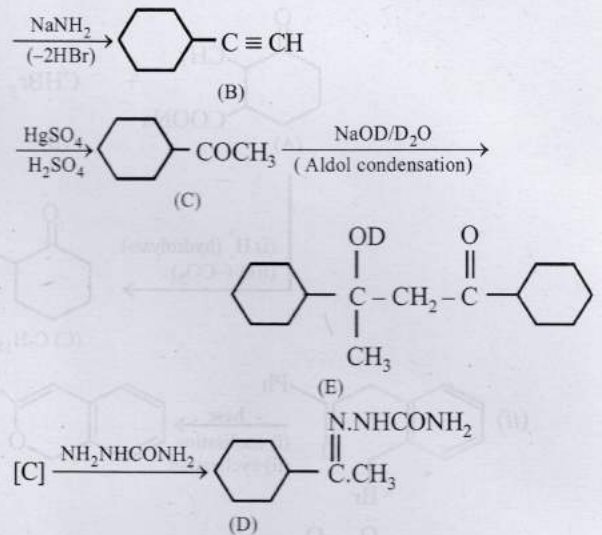
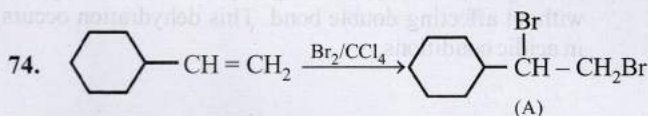
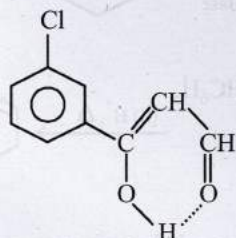




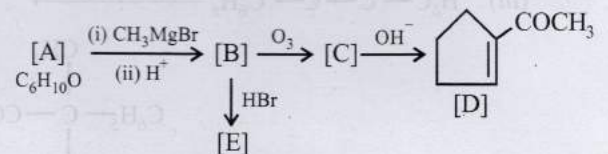
Hence, compound should have following part structure



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

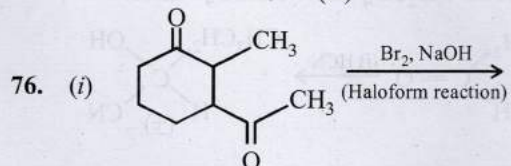
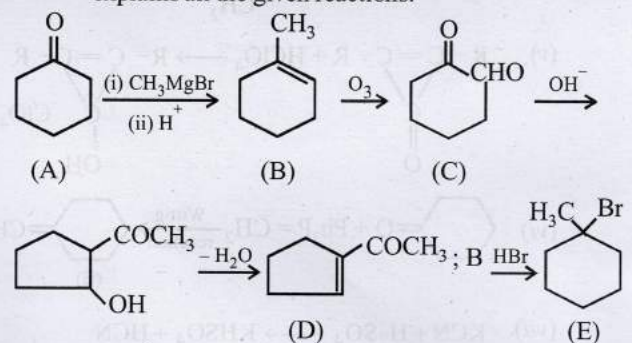


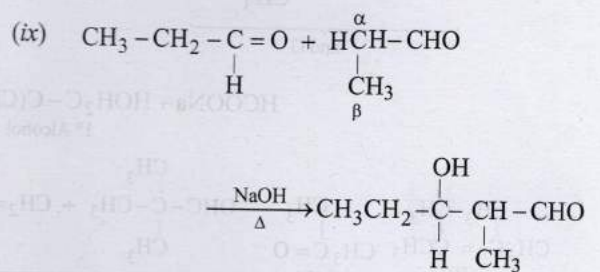
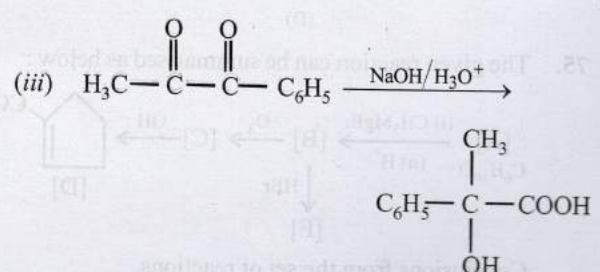
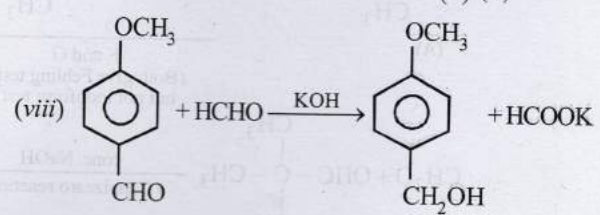
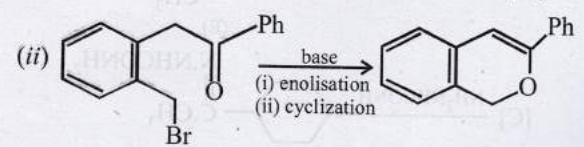
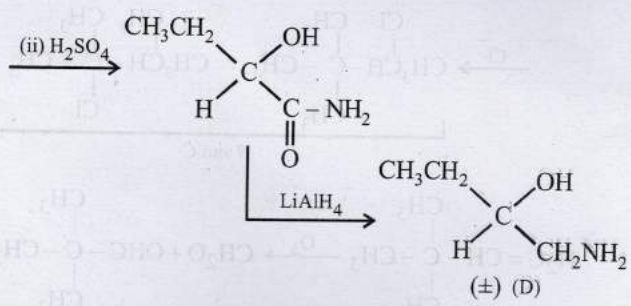
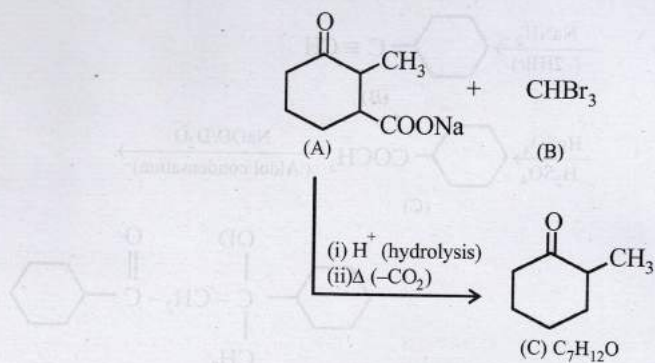
75. The given reaction can be summarised as below :



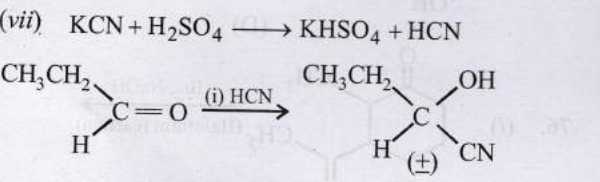
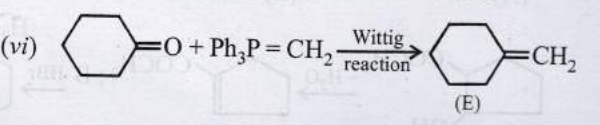
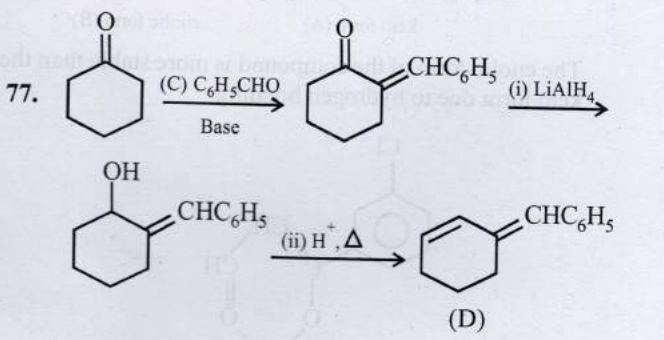
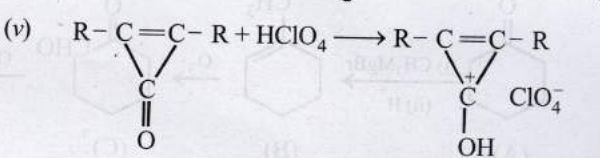
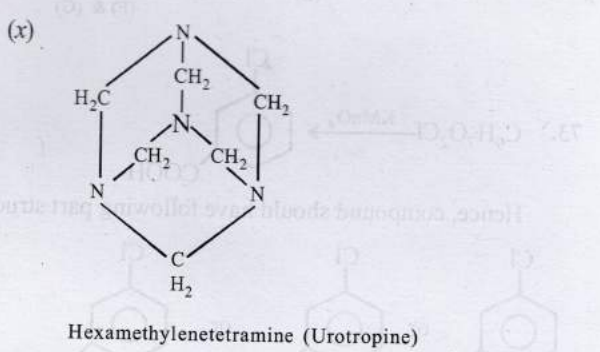
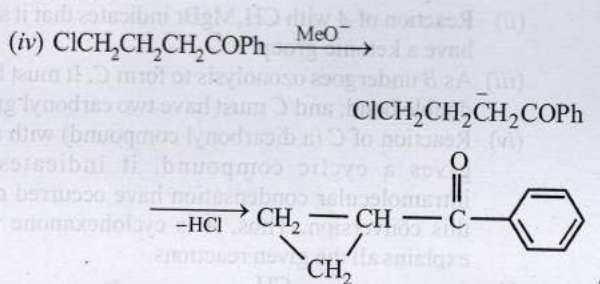
Conclusions from the set of reactions

- (i) Carbon-hydrogen ratio in A indicates that it is a cyclic compound.
- (ii) Reaction of A with CH_3MgBr 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.



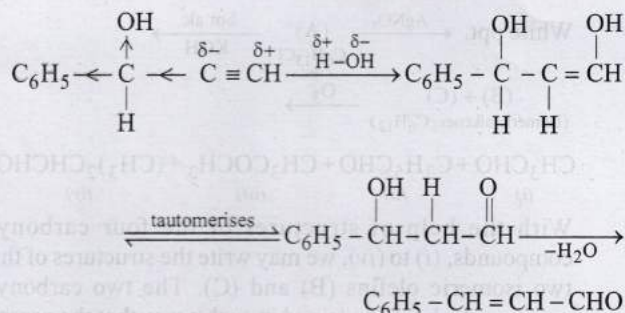


The reaction is an example of benzil-benzilic acid type rearrangement.



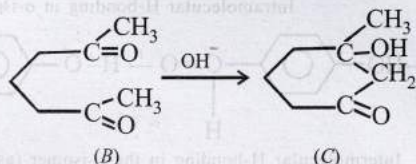
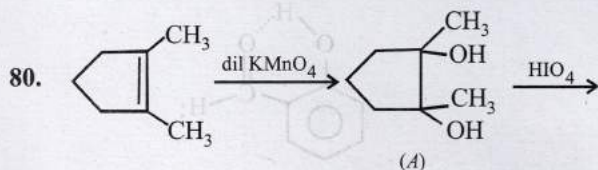
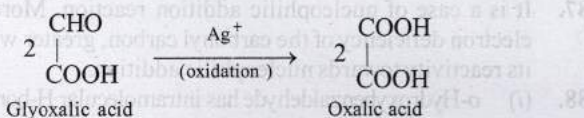
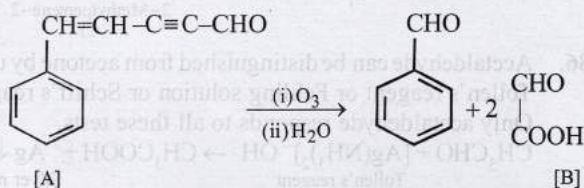
LiAlH_4 reduces only ketonic group to 2° alcoholic group without affecting double bond. This dehydration occurs in acidic conditions.

78.



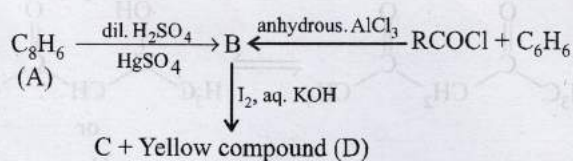
79. Following informations are provided by the problem.

- Since aldehyde *A* ($\text{C}_{11}\text{H}_{18}\text{O}$) gives $\text{C}_6\text{H}_5\text{CHO}$ on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon ($\text{C}_{11}-\text{C}_6=\text{C}_5$), three hydrogen ($\text{H}_8-\text{H}_5=\text{H}_3$) and one oxygen atom, i.e., it should be $\text{C}_5\text{H}_3\text{O}$. Further the compound *A* has an aldehydic group, so the side chain can be written as $\text{C}_4\text{H}_2\text{CHO}$.
- 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.
- Further, since the aldehyde *A* does not undergo aldol condensation, α -hydrogen is absent and hence triple bond should be present between C_2 and C_3 .
- Thus the side chain $\text{C}_4\text{H}_2\text{CHO}$ of *A* can be written as $-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CHO}$.
- Thus compound *A* should possess following structure which explains all the given reactions.



The last step is intramolecular aldol condensation.

81.

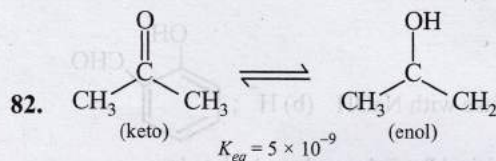
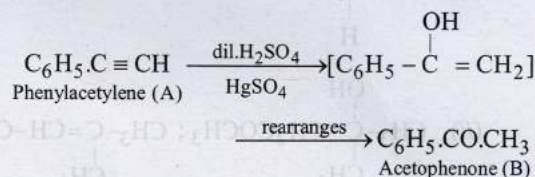


- Formation of (B) from benzene and acid chloride in presence of anhydrous AlCl_3 (Friedel-Craft reaction) indicates that it is a ketone, $\text{C}_6\text{H}_5\text{COR}$.
- Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone (B) is $-\text{CH}_3$. Hence, (B) should be $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$.
- Since ketone (B) is also formed from the hydrocarbon C_8H_6 (A) by reaction with $\text{dil. H}_2\text{SO}_4$ and HgSO_4 , the hydrocarbon (A) must have an acetylenic hydrogen atom, i.e. $\equiv\text{C}-\text{H}$ grouping. Hence, (A) must be $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$.

Thus, compounds (A) to (D) are

$$\begin{array}{cccc}
 \text{C}_6\text{H}_5\cdot\text{C}\equiv\text{CH} & \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3 & \text{C}_6\text{H}_5\text{COOH} & \text{CHI}_3 \\
 \text{(A)} & \text{(B)} & \text{(C)} & \text{(D)}
 \end{array}$$

Formation of (B) from (A)

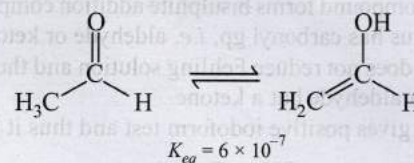


The methyl group stabilizes the $\text{C}=\text{C}$ in the enol form due to hyperconjugation.

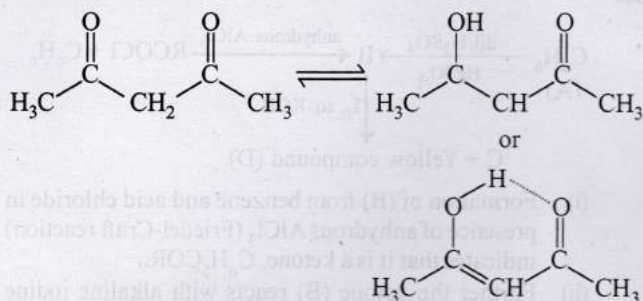
However, the methyl group also stabilizes the carbonyl double bond in the keto form.

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

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

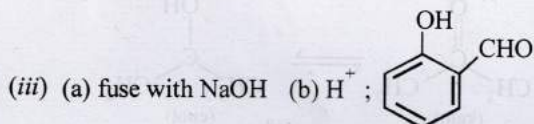
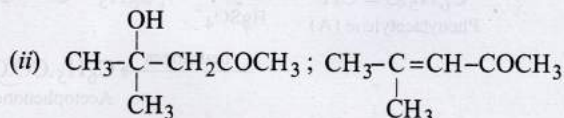
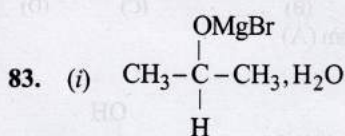
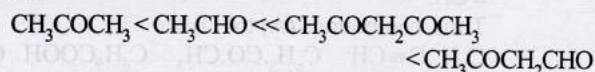


As a result, simple aldehydes generally have a higher enol content than simple ketones.



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:



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
O	18.60	1.16	1

\therefore Empirical formula of compound is $\text{C}_5\text{H}_{10}\text{O}$ and empirical formula wt. = 86.

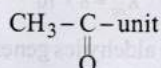
Also molecular wt. = 86.

\therefore Molecular formula of compound is $\text{C}_5\text{H}_{10}\text{O}$.

(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.

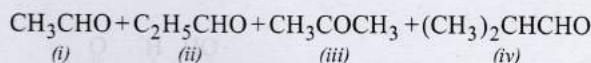
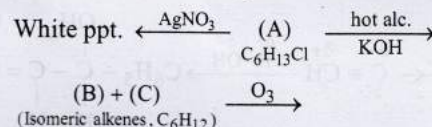
(iv) It gives positive iodoform test and thus it has



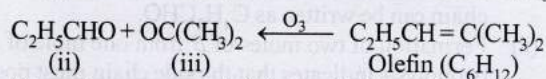
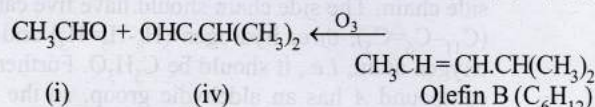
(v) Above facts reveal that the compound is $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ or $(\text{CH}_3)_2\text{CHCOCH}_3$

Pentan-2-one 3-Methylbutan-2-one

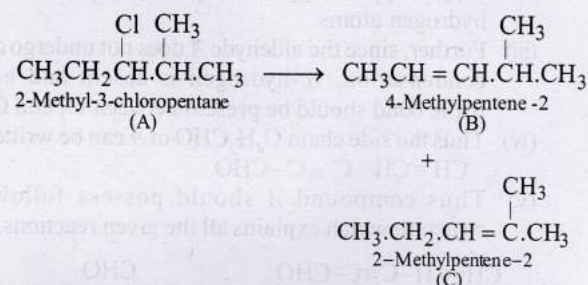
85. Let us summarise the given facts.



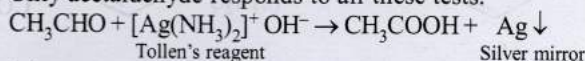
With the help of structures of the four carbonyl compounds, (i) to (iv), we may write the structures of the two isomeric olefins (B) and (C). The two carbonyl compounds should be joined in such a way that the parent olefin has 6 carbon atoms. Two such possibilities are the combination of carbonyl compounds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



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

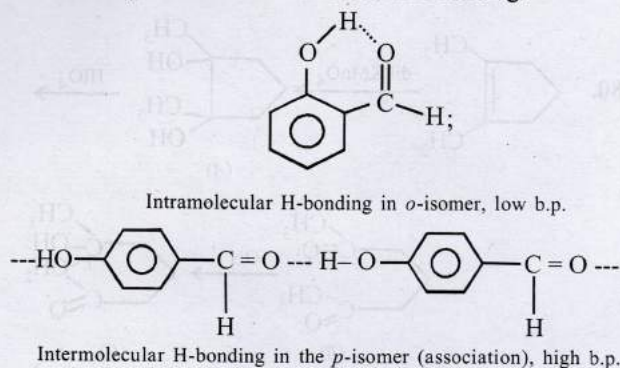


86. Acetaldehyde can be distinguished from acetone by using Tollen's reagent or Fehling solution or Schiff's reagent. Only acetaldehyde responds to all these tests.

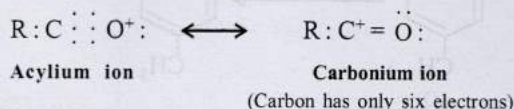


87. It is a case of nucleophilic addition reaction. More the electron deficiency of the carbonyl carbon, greater will be its reactivity towards nucleophilic addition.

88. (i) *o*-Hydroxybenzaldehyde has intramolecular H-bonding while the *p*-isomer has intermolecular H-bonding.

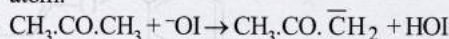


- (ii) In the acylium ion ($R-C \equiv O^+$), each and every element has a complete octet, while in carbonium ion ($R-C^+ = O$), carbon bearing positive charge has incomplete octet which makes it more reactive than the acylium ion.

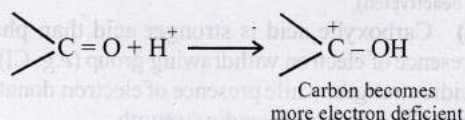


- (iii) Hypiodite (^-OI) is a strong base than iodide ion (I^-). (O is more electronegative thus easily accommodates negative charge than I in I^-).

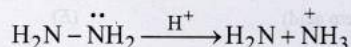
Haloform reaction is base-promoted reaction (the first step involves removal of acidic hydrogen atom of acetone by base). Hypiodite ion being strong base than iodide ion, can easily remove acidic hydrogen atom.



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



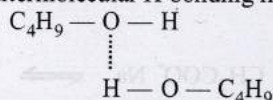
In strongly acidic medium ($pH < 3.5$), the unshared pair of electrons of N of the reagent is protonated, with the result nucleophile (NH_2NH_2) is converted to an electrophile ($NH_2NH_3^+$) which cannot react.



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

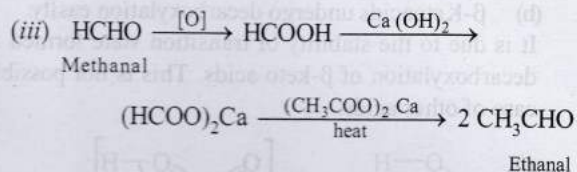
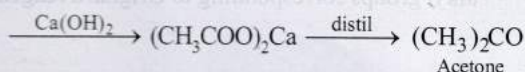
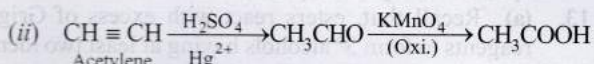
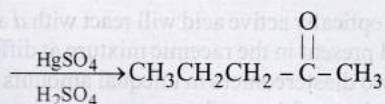
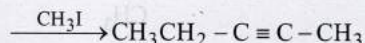
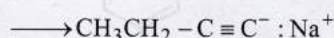
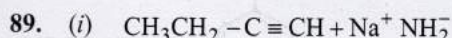
- (v) Alcohols show hydrogen bonding.

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



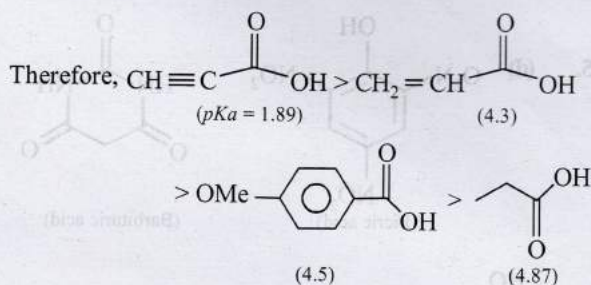
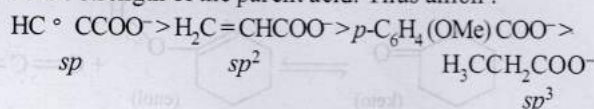
(H-bonding between two butanol molecules)

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

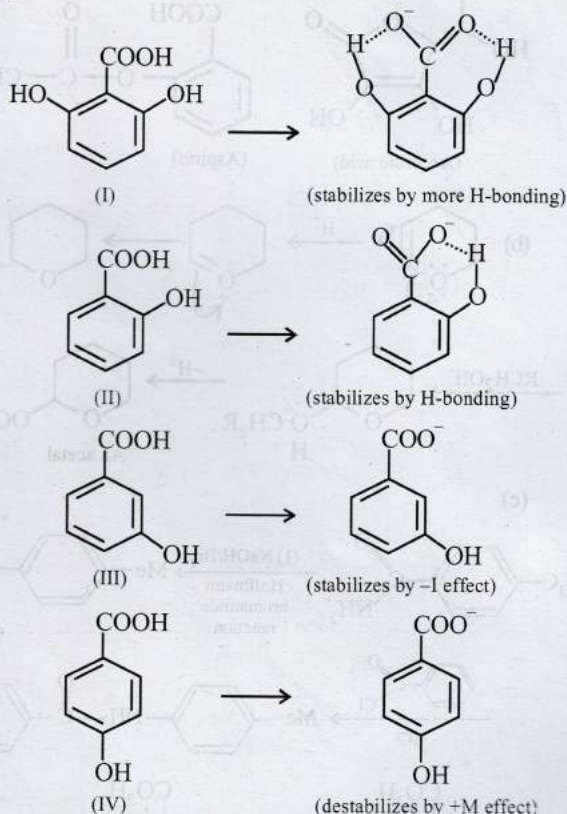


Topic-2: Preparation and Properties of Carboxylic Acids and its Derivatives

1. (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 :



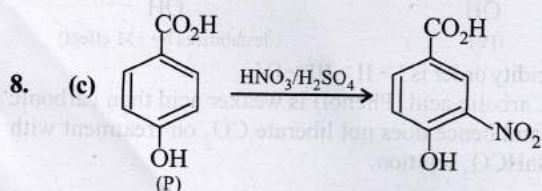
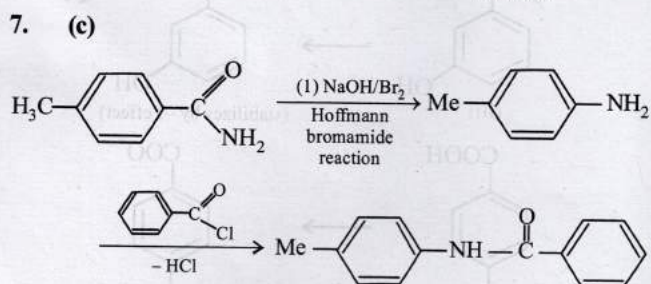
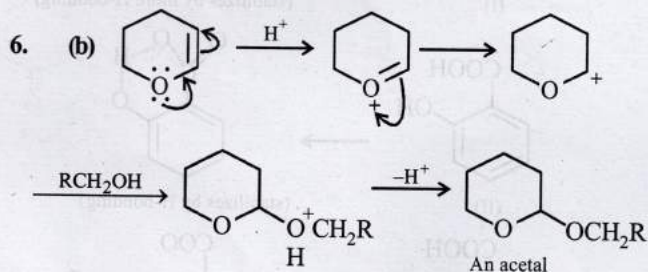
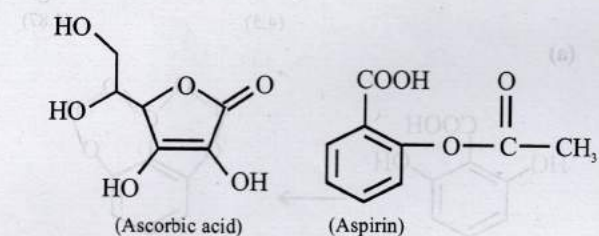
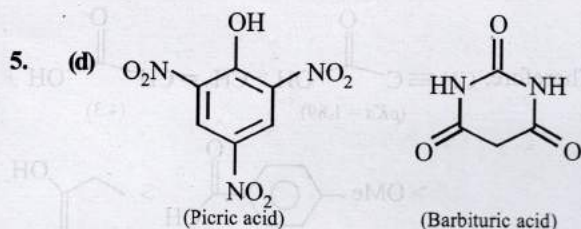
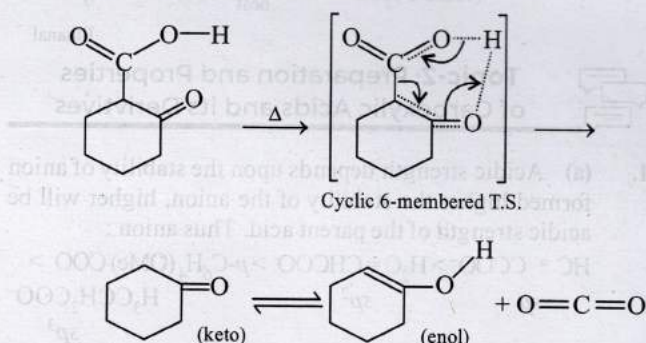
2. (a)



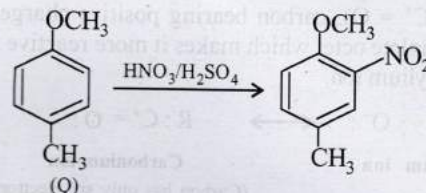
\therefore Acidity order is I > II > III > IV

3. (d) Carboic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO_2 on treatment with aq. $NaHCO_3$ solution.

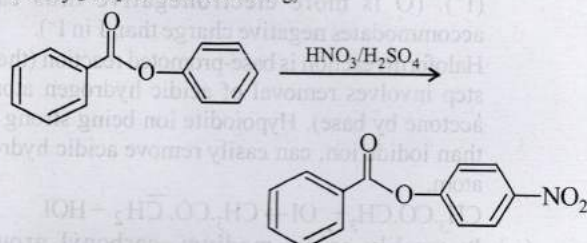
4. (b) β -Ketoacids undergo decarboxylation easily. It is due to the stability of transition state formed after decarboxylation of β -keto acids. This is not possible in case of other acids.



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

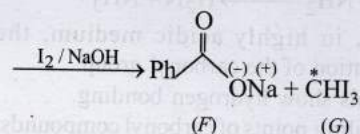
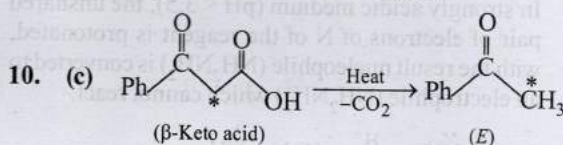


(OCH₃ group is more activating)

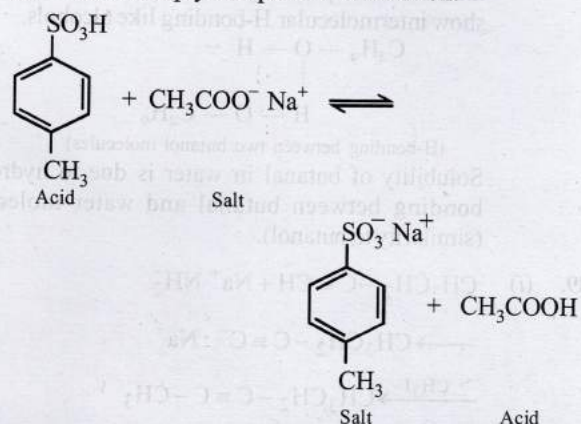


(Benzene ring having -O- is activated, benzene ring having -CO is deactivated)

9. (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.

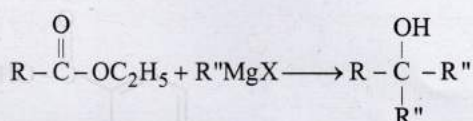


11. (a) This is simply a displacement reaction.



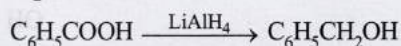
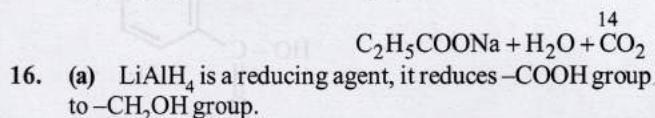
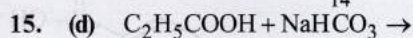
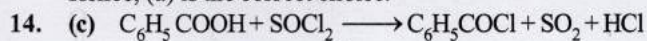
12. (a) The optically active acid will react with *d* and *l* forms of alcohol present in the racemic mixture at different rates to form two diastereomers in unequal amounts leading to optical activity of the product.

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.

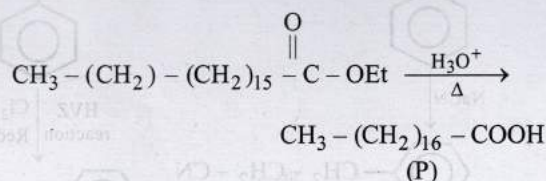
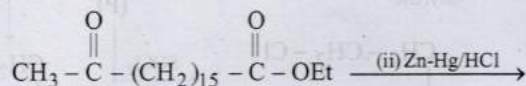
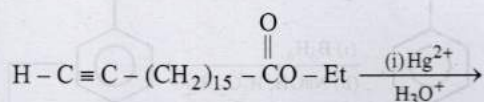


Since, here Grignard reagent is CH_3MgBr , the 3° alcohol should have at least two methyl groups.

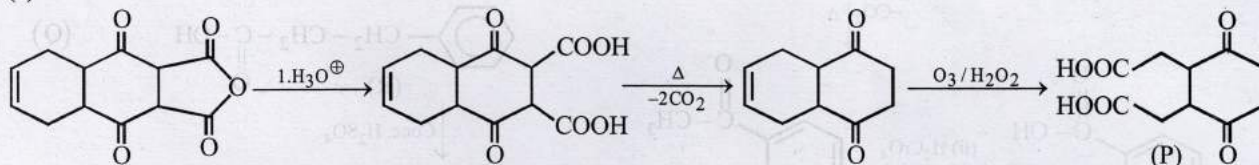
Hence, (a) is the correct choice.



17. (909) Reactions involves are:



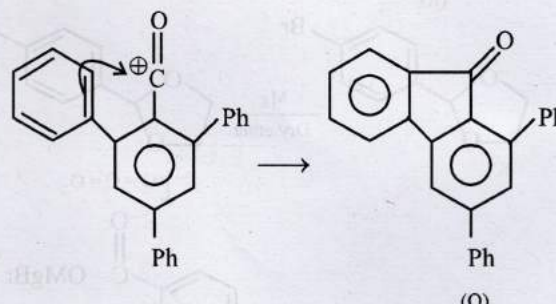
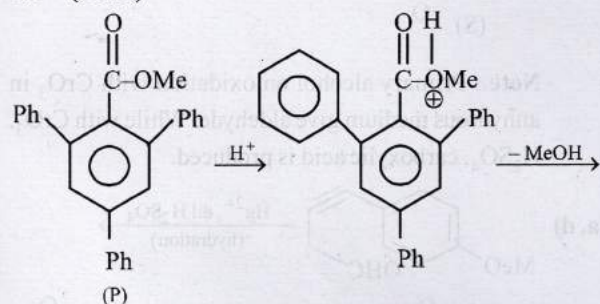
18. (2)



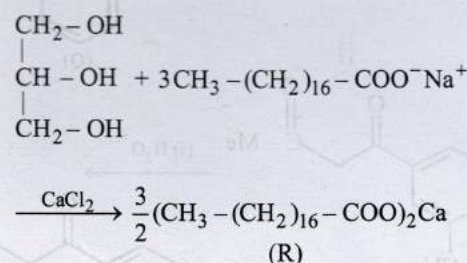
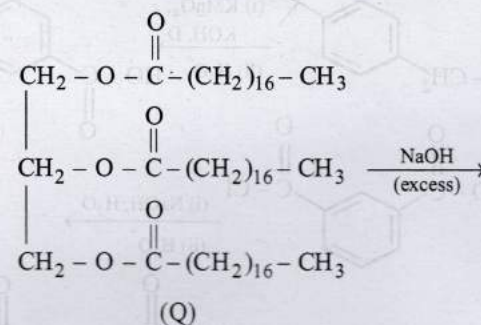
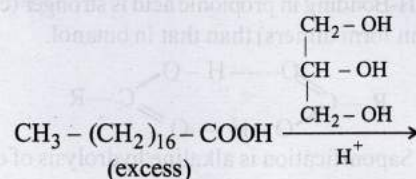
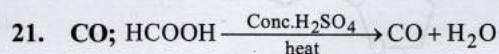
No. of $-COOH$ group is '2'.

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

20. (18.00)



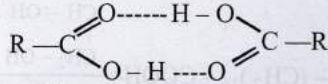
DBE = 18



1 mole of Q will 1.5 mole of R.

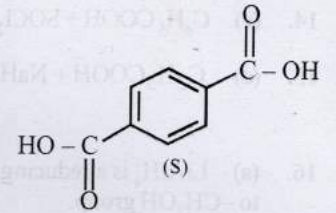
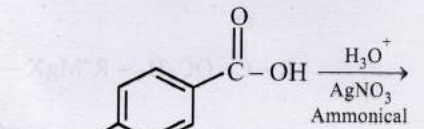
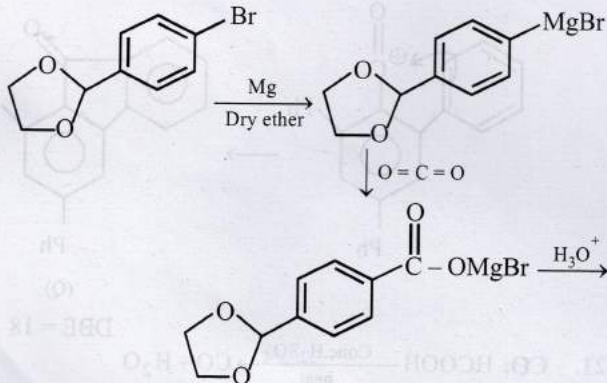
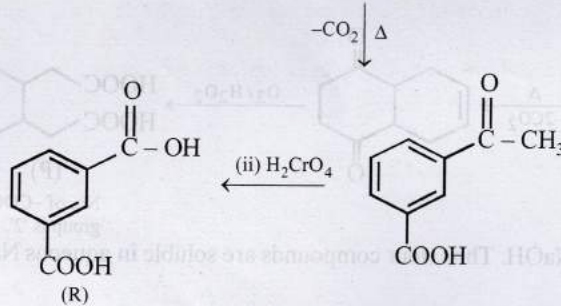
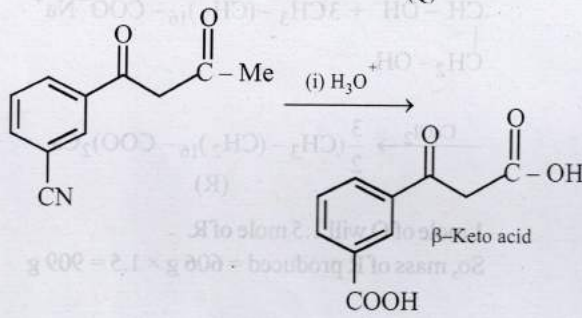
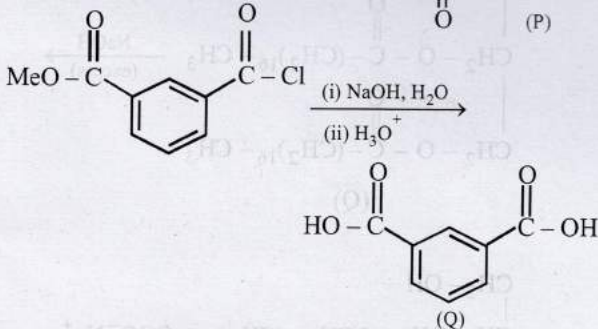
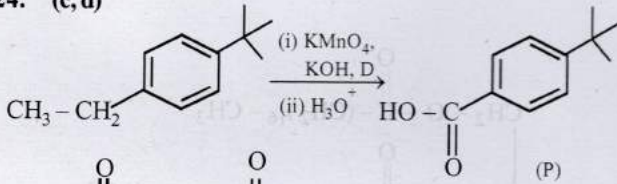
So, mass of R produced = $606 \text{ g} \times 1.5 = 909 \text{ g}$

22. **False** : H-Bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.

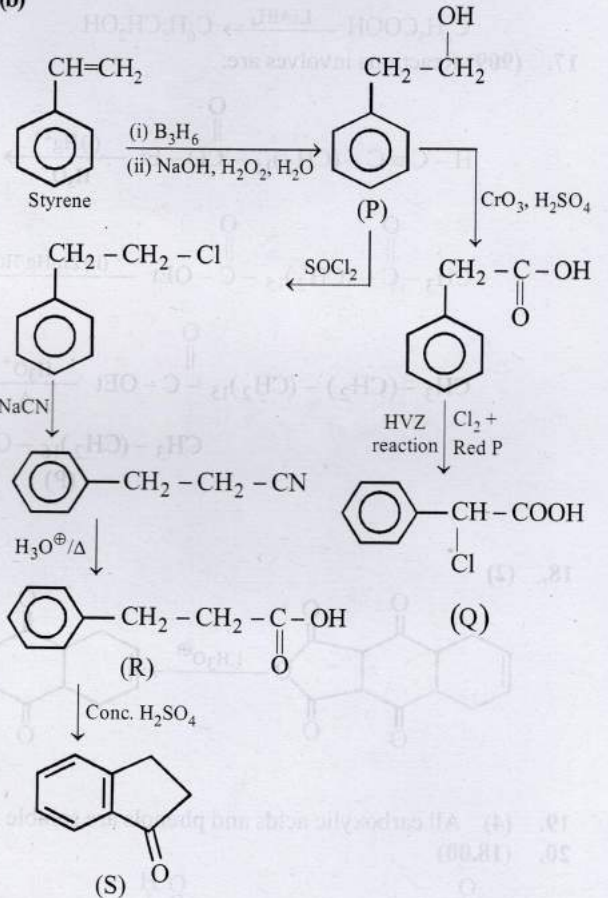


23. **False** : Saponification is alkaline hydrolysis of esters.

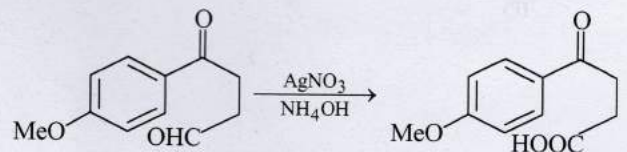
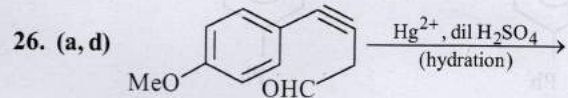
24. (c, d)

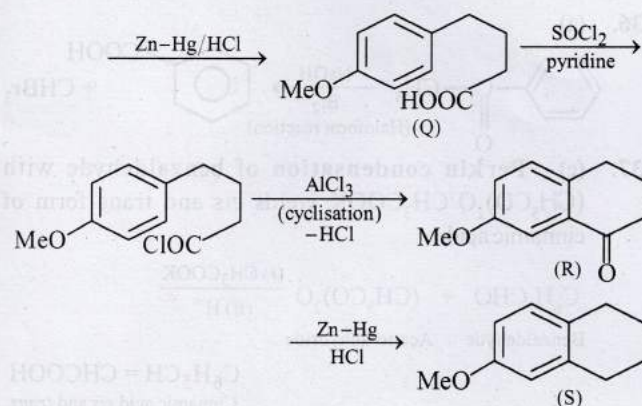


25. (b)

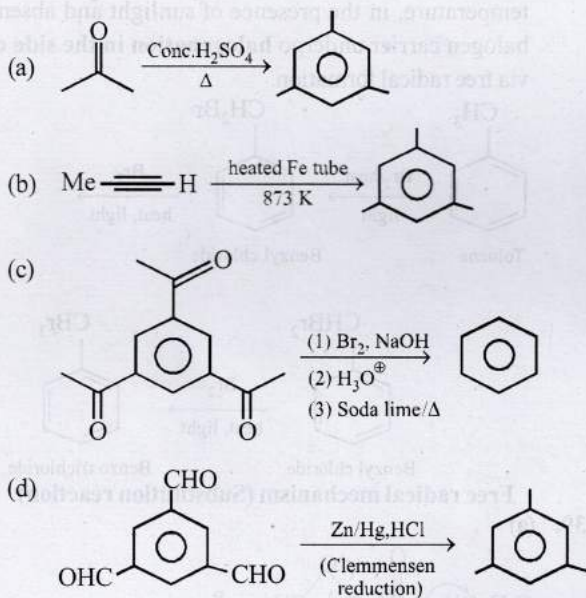


Note : Primary alcohol on oxidation with CrO_3 in anhydrous medium give aldehyde. While with CrO_3 , H_2SO_4 , carboxylic acid is produced.





27. (a, b, d)



28. (c, d)

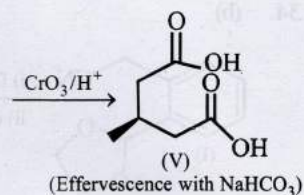
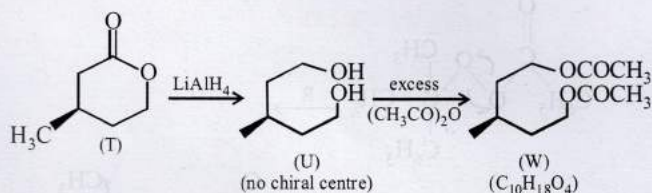
LiAlH₄/(C₂H₅)₂O : Reduces esters, carboxylic acids, epoxides and aldehydes and ketones.

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)

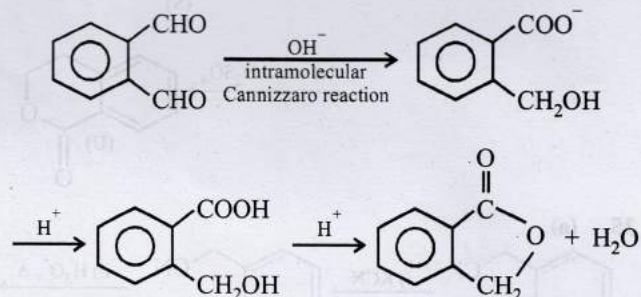
(a) Both are soluble in NaOH. Hence, **inseparable**.

(b) Only benzoic acid (C₆H₅COOH) is soluble in NaOH and NaHCO₃, while benzyl alcohol (C₆H₅CH₂OH) is not. Hence, **separable**.

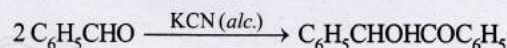
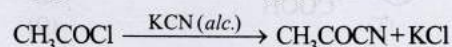
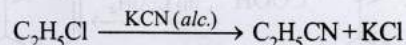
(c) Although NaOH can enable separation between benzyl alcohol (C₆H₅CH₂OH) and phenol (C₆H₅OH) as only the latter is soluble in NaOH. However, in NaHCO₃, both are insoluble. Hence, **inseparable**.

(d) α-Phenylacetic acid (C₆H₅CH₂COOH) is soluble in NaOH and NaHCO₃, while benzyl alcohol (C₆H₅CH₂OH) is not. Hence, **separable**.

31. (d)



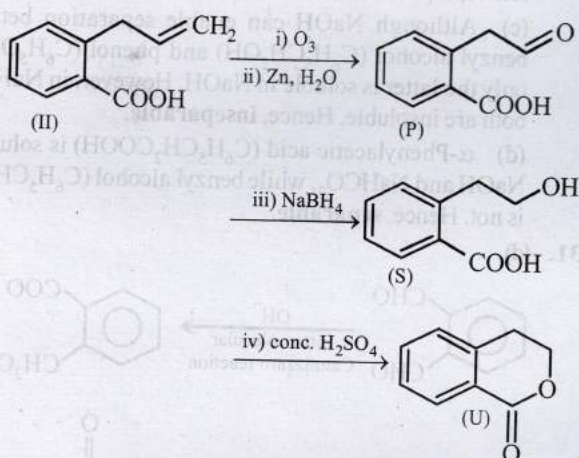
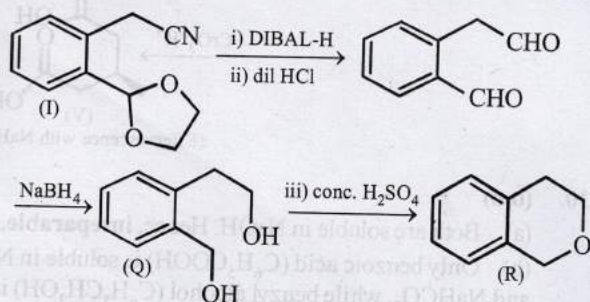
32. (a, b, d) Ethyl chloride and acetyl chloride react with alc. KCN by nucleophilic substitution reaction while benzaldehyde undergoes benzoin condensation :



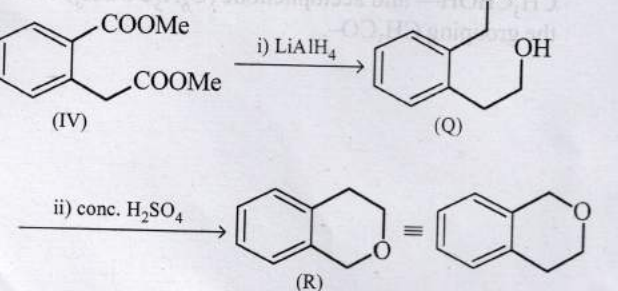
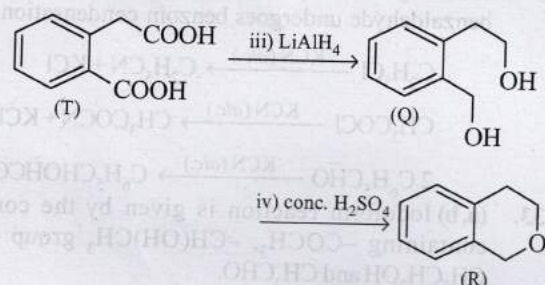
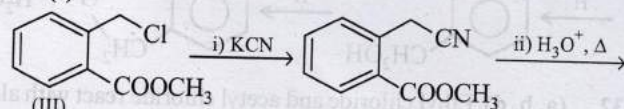
33. (a, b) Iodoform reaction is given by the compounds containing -COCH₃, -CH(OH)CH₃ group and also CH₃CH₂OH and CH₃CHO.

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

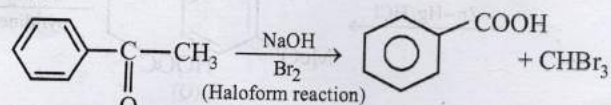
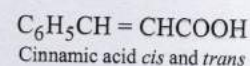
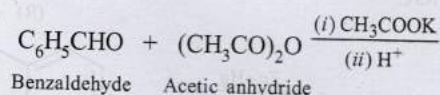
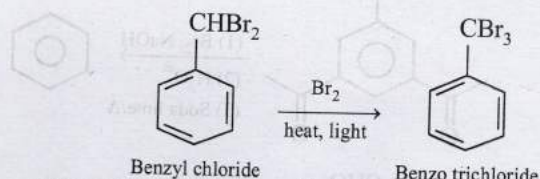
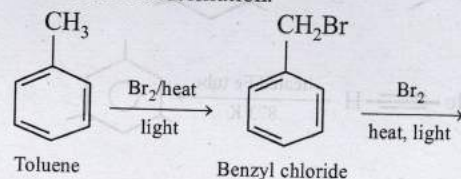
34. (b)



35. (a)

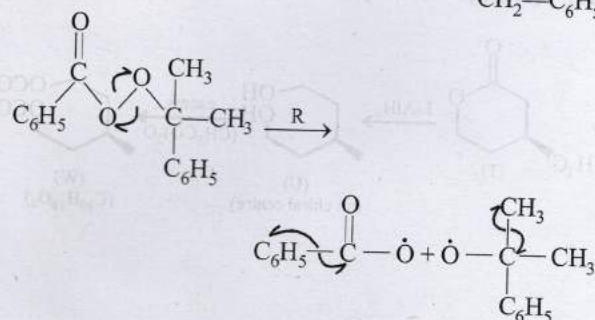
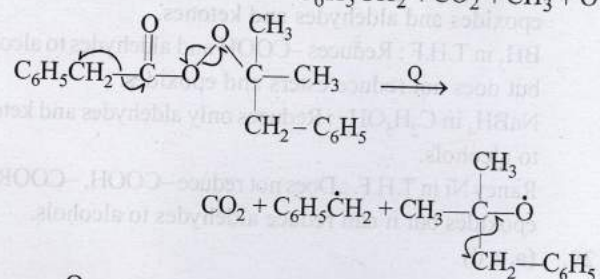
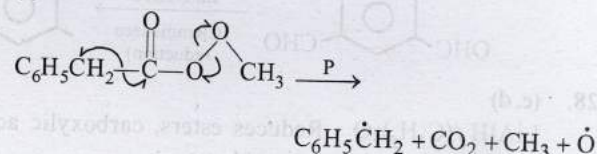


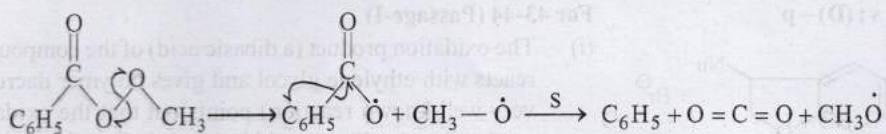
36. (a)

37. (c) Perkin condensation of benzaldehyde with $(\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COOK}$ yields cis and trans form of cinnamic acid.38. (d) Alkylbenzenes when treated with Br_2 at high temperature, in the presence of sunlight and absence of halogen carrier undergo halogenation in the side chain via free radical formation.

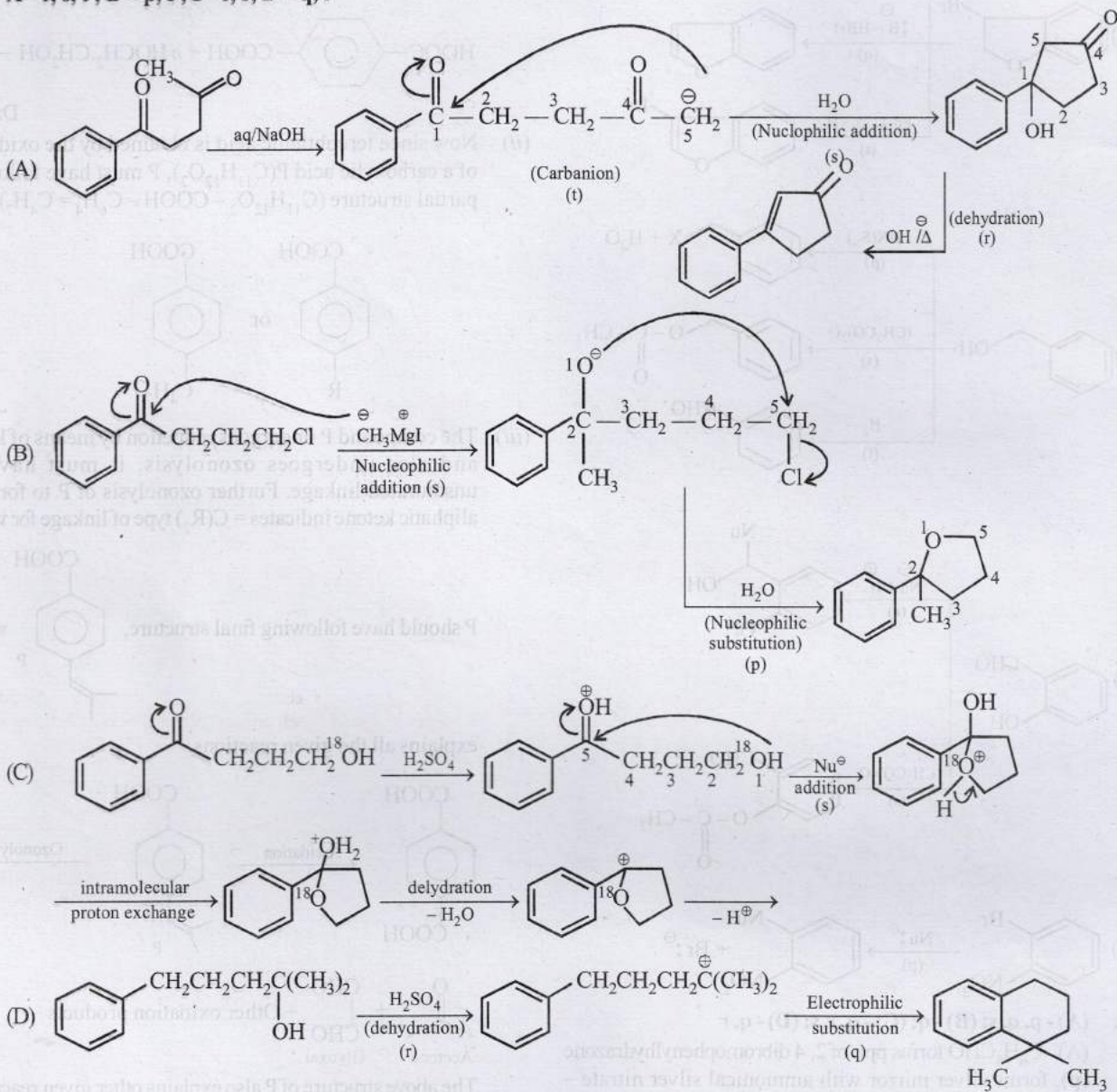
Free radical mechanism (Substitution reaction)

39. (a)

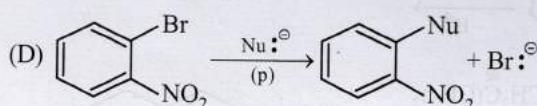
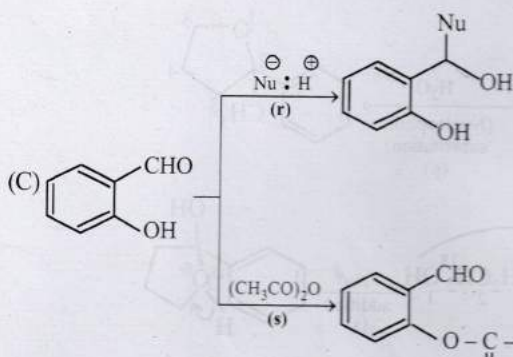
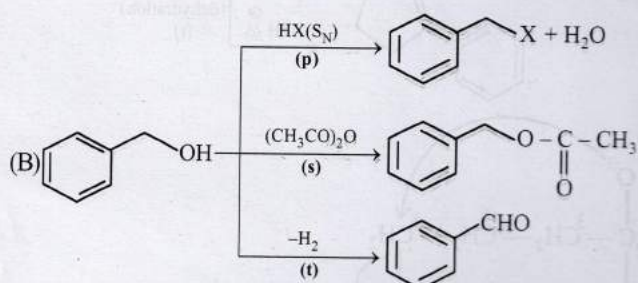
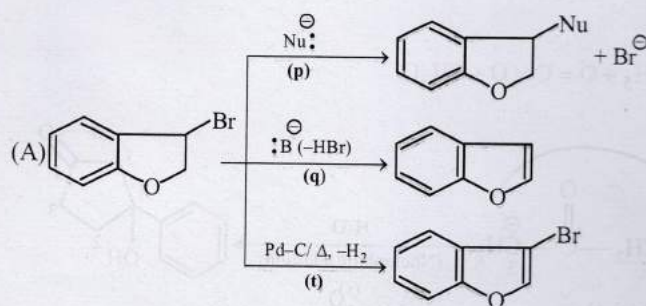




40. A-r, s, t; B-p, s; C-r, s; D-q, r



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



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

(A) C_6H_5CHO forms ppt. of 2, 4 dibromophenylhydrazone (p), forms silver mirror with ammonical silver nitrate - Tollen's reagent (q), forms cyanohydrin with CN^- (s).

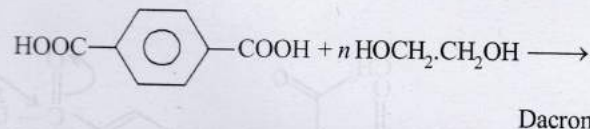
(B) $CH_3C \equiv CH$ gives ppt. with $AgNO_3$ (q)

(C) CN^- reacts with $AgNO_3$ to form ppt. of $AgCN$ (q), it is a nucleophile (r) and forms cyanohydrin (s)

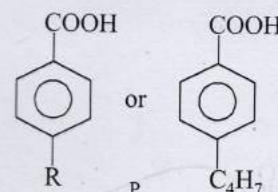
(D) I^- gives ppt. of AgI with $AgNO_3$ (q), and it is a nucleophile (r)

For 43-44 (Passage-I)

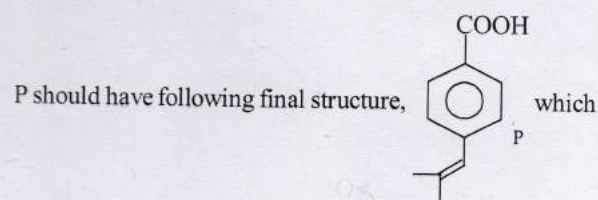
(i) The oxidation product (a dibasic acid) of the compound P reacts with ethylene glycol and gives polymer dacron (a very well known reaction) points out that the oxidation product i.e. the dibasic acid is terephthalic acid.



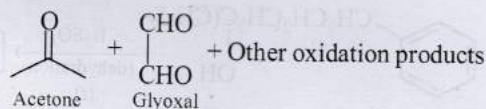
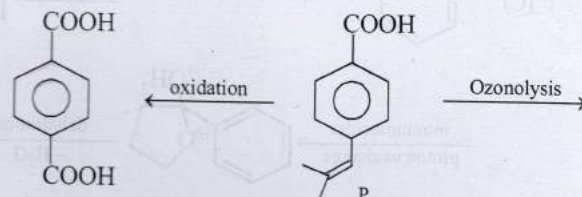
(ii) Now since terephthalic acid is obtained by the oxidation of a carboxylic acid $P(C_{11}H_{12}O_2)$, P must have following partial structure ($C_{11}H_{12}O_2 - COOH - C_6H_4 = C_4H_7$)



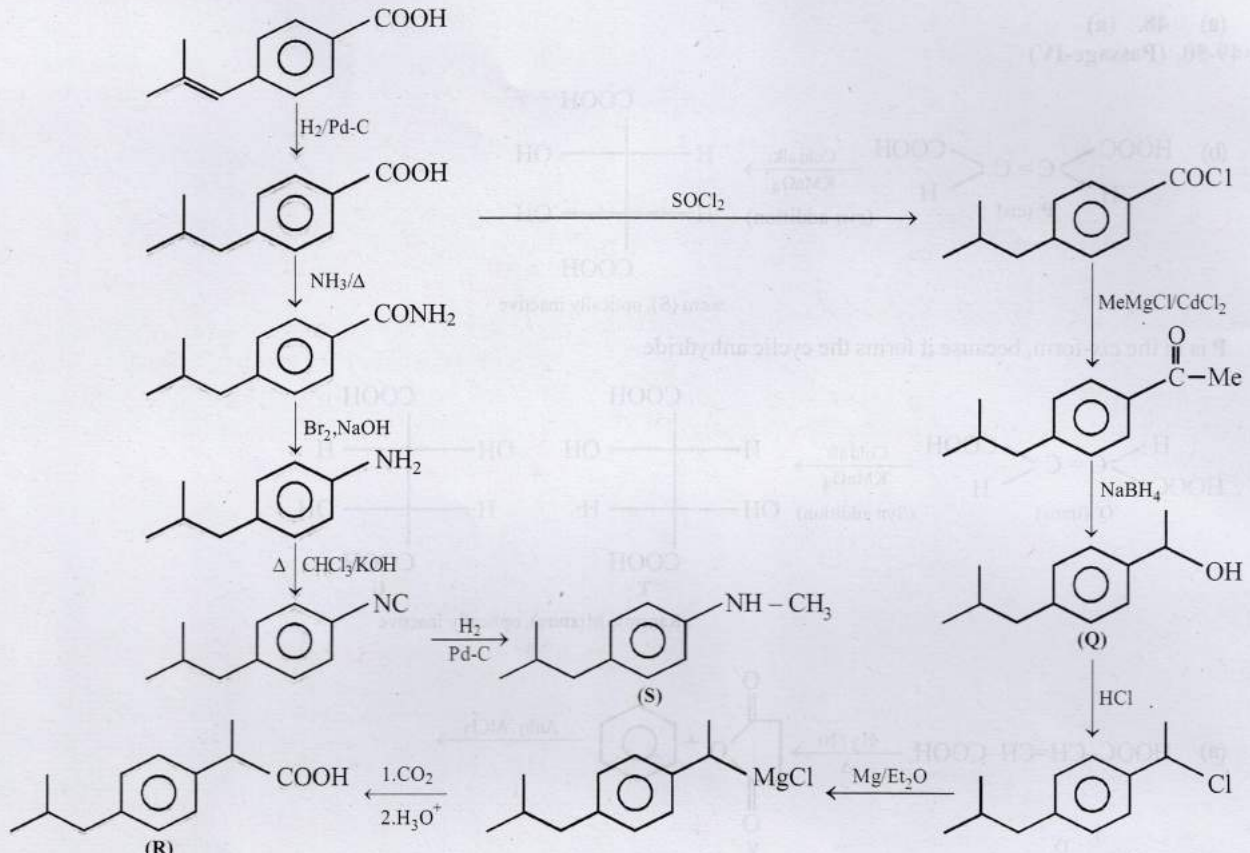
(iii) The compound P undergoes reduction by means of H_2/Pd and also undergoes ozonolysis, it must have an unsaturated linkage. Further ozonolysis of P to form an aliphatic ketone indicates = $C(R_2)$ type of linkage for which



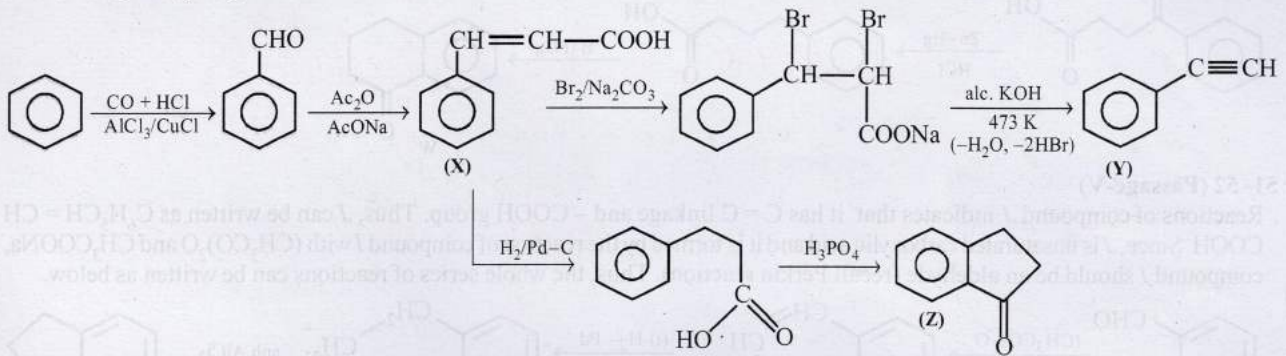
explains all the given reactions.



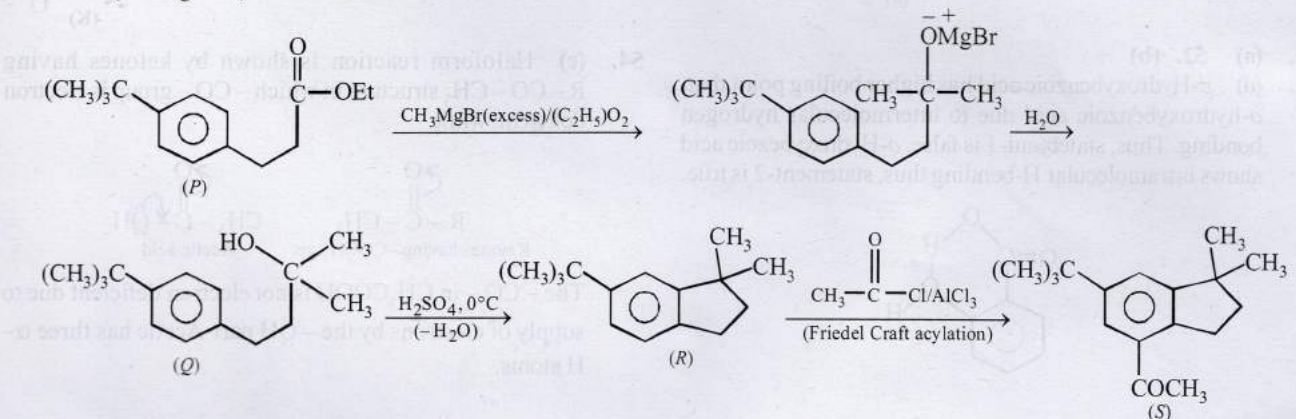
The above structure of P also explains other given reactions.



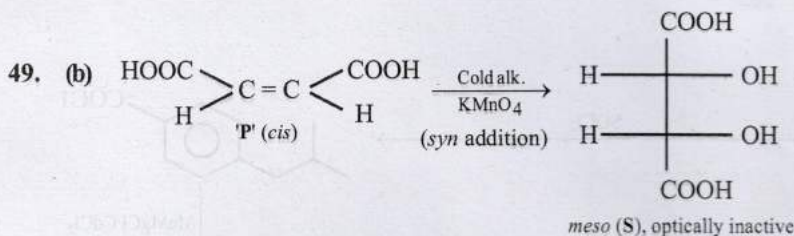
43. (a) 44. (b)
For 45-46 (Passage-II)



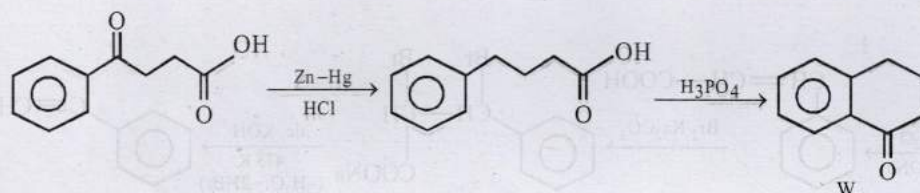
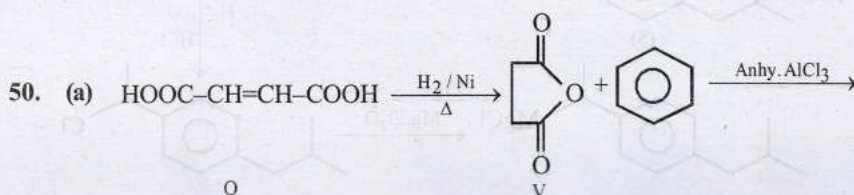
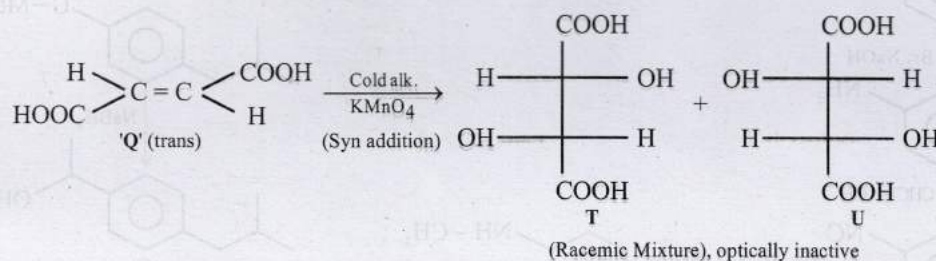
45. (c) 46. (a)
For 47-48 (Passage-III)



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

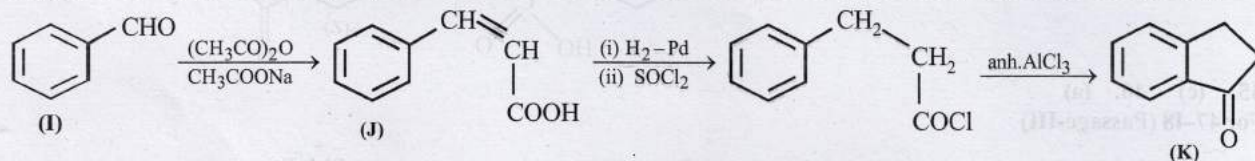


P is in the *cis*-form, because it forms the cyclic anhydride.



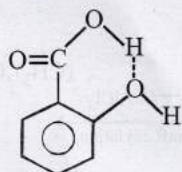
For 51-52 (Passage-V)

Reactions of compound *J* indicates that it has C = C linkage and -COOH group. Thus, *J* can be written as C₆H₅CH = CHCOOH. Since, *J* is unsaturated carboxylic acid and it is formed by the reaction of compound *I* with (CH₃CO)₂O and CH₃COONa, compound *I* should be an aldehyde (recall Perkin reaction). Thus, the whole series of reactions can be written as below.

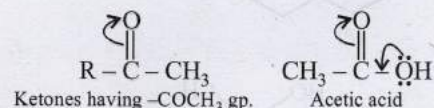


51. (a) 52. (b)

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

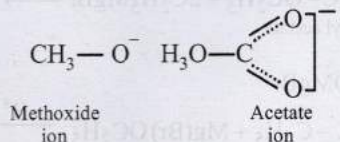


54. (c) Haloform reaction is shown by ketones having R-CO-CH₃ structure in which -CO- group is electron deficient, while



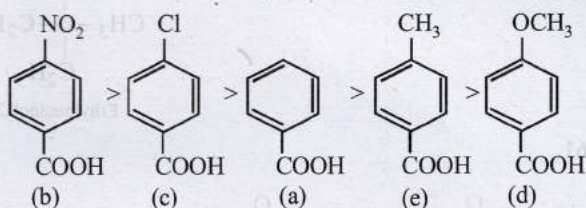
The -CO- in CH₃COOH is not electron deficient due to supply of electrons by the -OH part-Acetic has three α-H atoms.

55. (d) Acetate ion is resonance stabilized while methoxide ion is not.



Hence, acetate ion is less basic than methoxide ion.

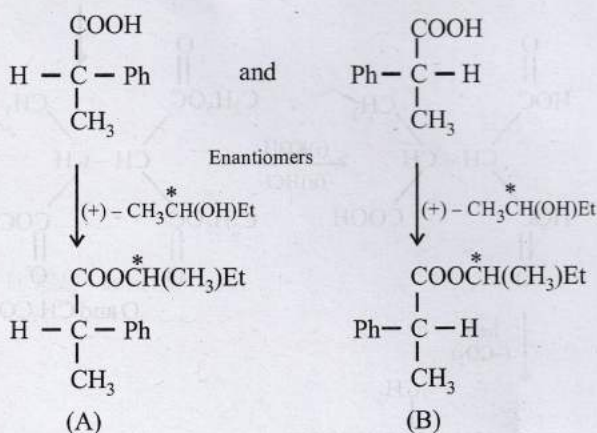
56. Higher the K_a value, more stronger is the acid.
Correct order of acidic strength of the given acids is



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.

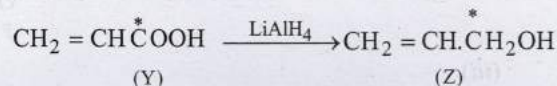
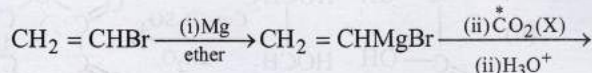
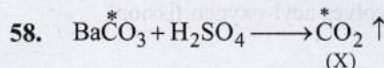
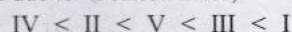


(A) and (B) are diastereomers.

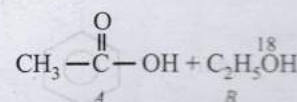
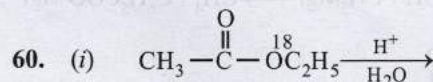
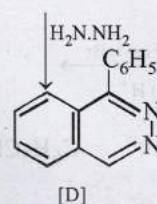
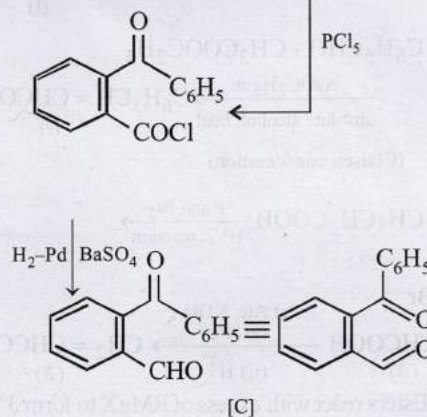
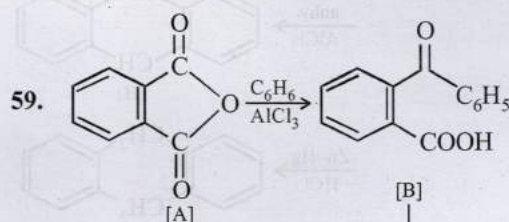
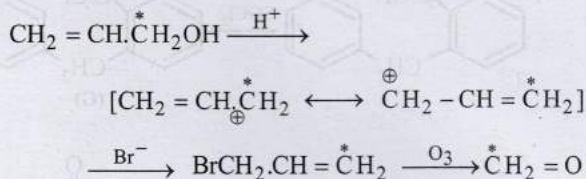
The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction.

(+) - Acid reacts with (+) -alcohol to give an (+)-(+) -ester, while (-) acid reacts with (+) alcohol to give (-)-(+) -ester. These two esters are diastereoisomers.

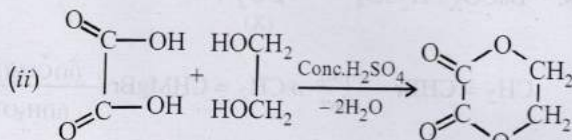
(iv) Presence of electron withdrawing group increases the acidic character of the -COOH due to -I effect, Further the -I group (-Cl) from -COOH group, weaker is the acid, thus III is weaker than I while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect.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



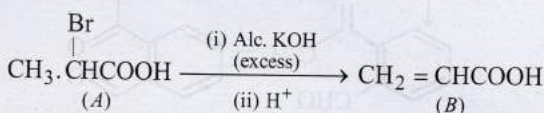
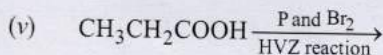
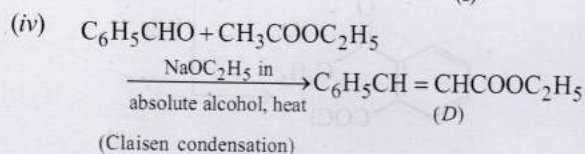
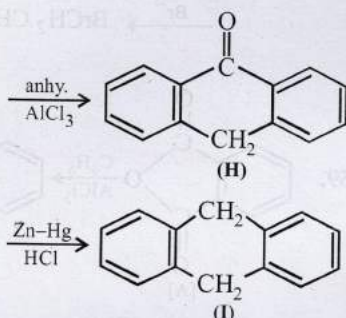
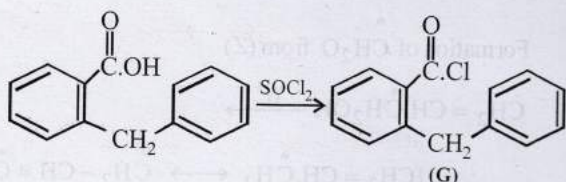
Formation of CH_2O from (Z)



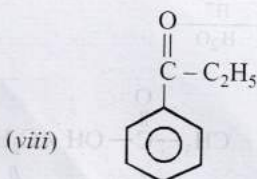
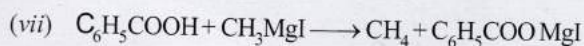
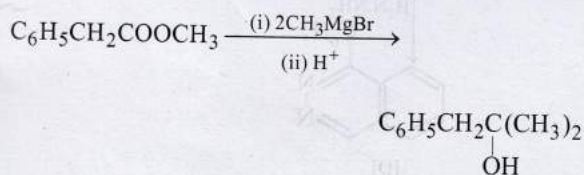
(Ester hydrolysis involves acyl-oxygen fission)



(iii)

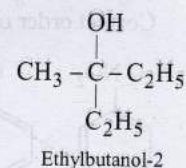
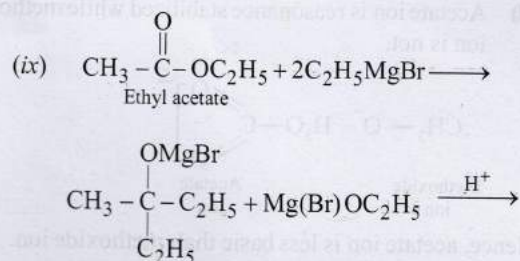


(vi) Esters react with excess of RMgX to form 3° alcohols having two alkyl groups corresponding to R of RMgX . Thus,

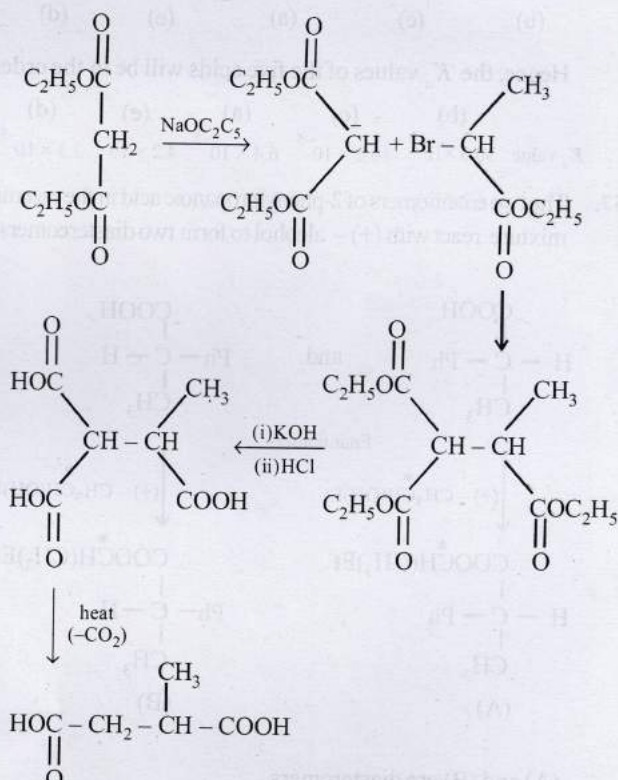


(viii)

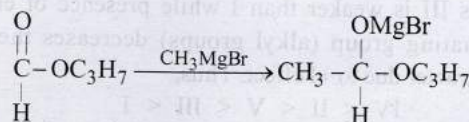
Phenyl ethyl ketone

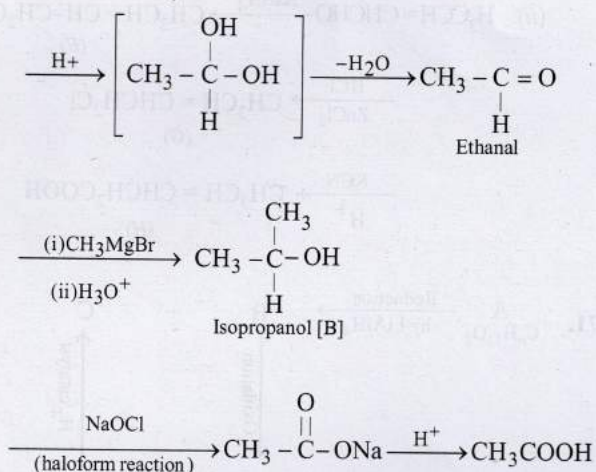


61.

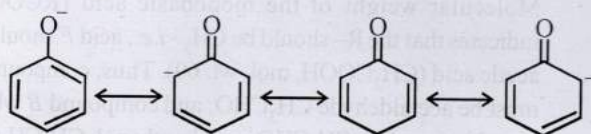


62. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formates) or tertiary alcohols (from esters other than formates). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence, ester A ($\text{C}_4\text{H}_8\text{O}_2$) should be HCOOC_3H_7 . Thus the various reactions and nature of compound B can be established as below.

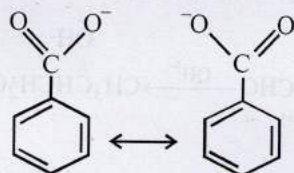




63. (i) Both of the resonating structures of benzoate ion are equivalent, while it is not so in phenoxide ion.

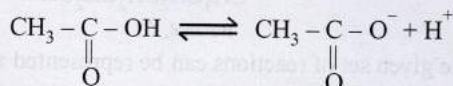
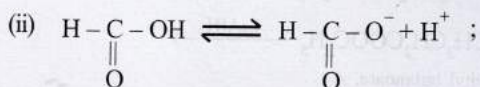


Resonating structures of phenoxide ion



Resonating structures of benzoate ion

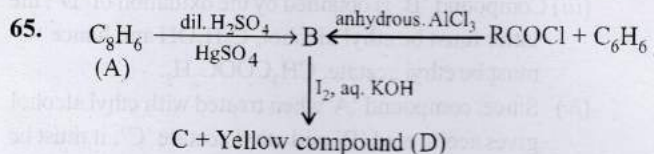
The benzoate ion is more stabilized because the negative charge on both structures is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms.



- (iii) Presence of CH_3 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 CH_3COOH .

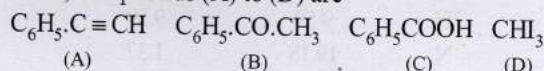
Formic acid has no alkyl group i.e. no α -H atom, hence it does not undergo halogenation, while acetic acid has a methyl group (i.e. three α -H atoms) on which halogenation takes place.

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

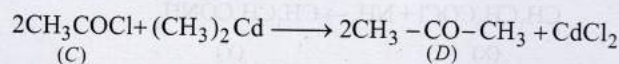
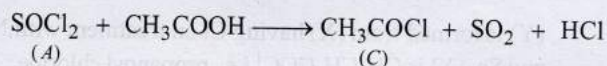
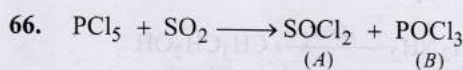
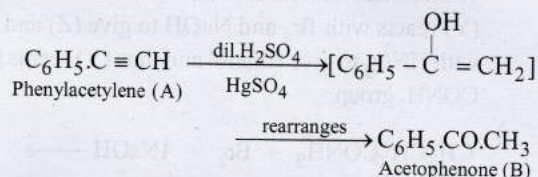


- (i) Formation of (B) from benzene and acid chloride in presence of anhydrous $AlCl_3$ (Friedel-Craft reaction) indicates that it is a ketone, C_6H_5COR .
- (ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone (B) is $-CH_3$. Hence, (B) should be $C_6H_5.CO.CH_3$.
- (iii) Since ketone (B) is also formed from the hydrocarbon C_8H_6 (A) by reaction with $\text{dil. } H_2SO_4$ and $HgSO_4$, the hydrocarbon (A) must have an acetylenic hydrogen atom, i.e. $\equiv C-H$ grouping. Hence, (A) must be $C_6H_5C \equiv CH$.

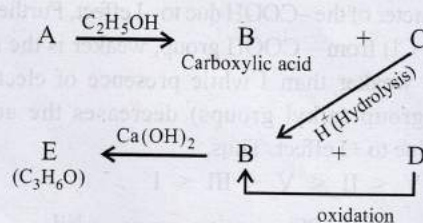
Thus, compounds (A) to (D) are



Formation of (B) from (A)

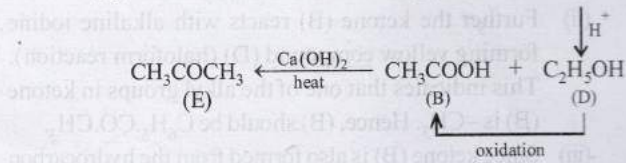
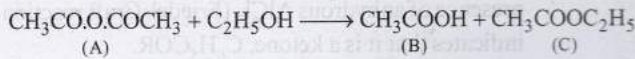


67.



- (i) Since, 'E' (C_3H_6O) forms a 2,4-dinitrophenylhydrazone but does not reduce Tollen's reagent and Fehling solution, it must be a ketone, $CH_3.CO.CH_3$.

- (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.

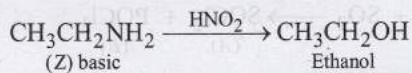
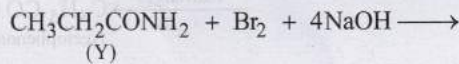


68. For empirical formula of (Y)

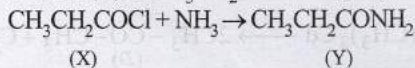
Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.10	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.92	1.37	1

∴ Empirical formula of (Y) is C₃H₇NO.

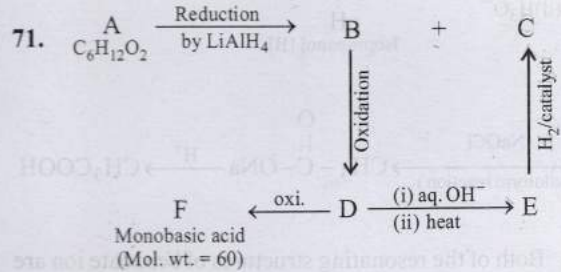
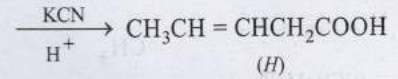
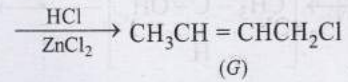
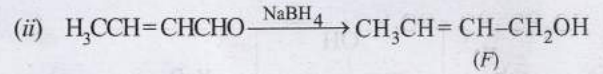
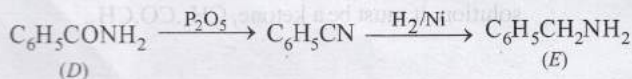
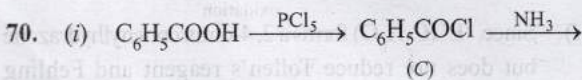
(Y) reacts with Br₂ and NaOH to give (Z) and (Z) reacts with HNO₂ to give ethanol and thus (Y) seems to have —CONH₂ group.



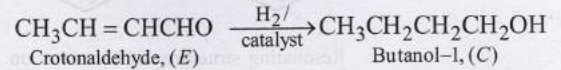
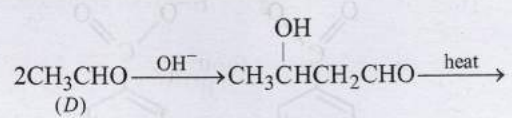
(Y) is formed from (X) having Cl on treatment with NH₃ and So, (X) is CH₃CH₂COCl *i.e.*, propanoyl chloride.



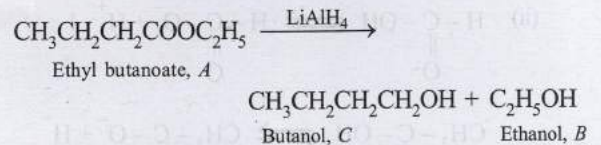
69. Presence of electron withdrawing group increases the acidic character of the —COOH due to —I effect, Further the —I group (—Cl) from —COOH group, weaker is the acid, thus III is weaker than I while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect.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



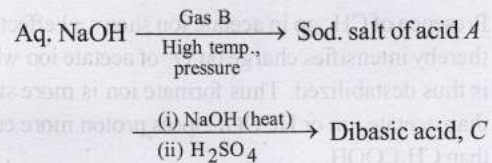
Molecular weight of the monobasic acid (RCOOH) indicates that the R— should be CH₃— *i.e.*, acid F should be acetic acid (CH₃COOH, mol. wt. 60). Thus, compound D must be acetaldehyde CH₃CHO, and compound B which on oxidation gives CH₃CHO must be ethanol, CH₃CH₂OH. Acetaldehyde (D) on treating with aqueous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



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 (CH₃CH₂CH₂COOC₂H₅).



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



Calculation of molecular formula of C

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

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

$$\% \text{ of O} = 100 - (2.22 + 27.30) = 71.48\%$$

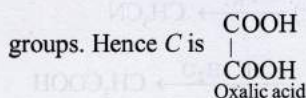
By usual method, empirical formula of acid $C = \text{CHO}_2$

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

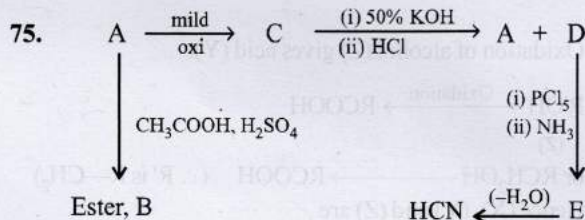
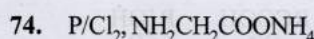
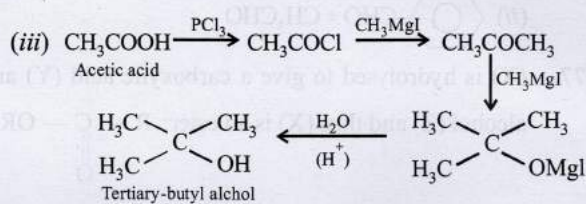
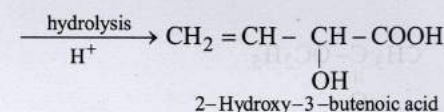
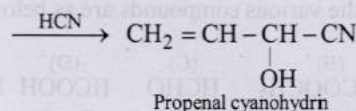
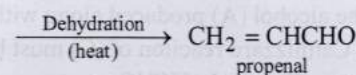
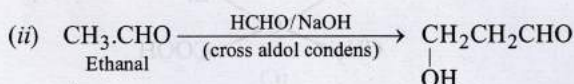
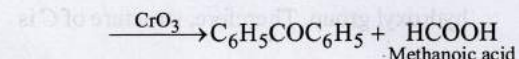
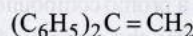
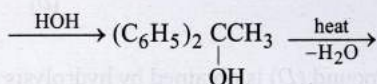
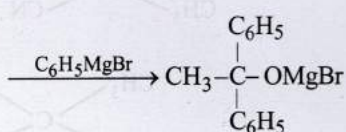
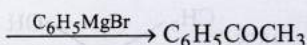
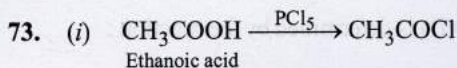
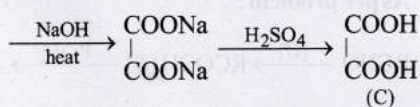
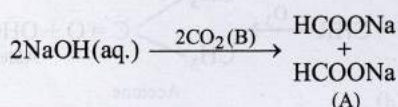
$$\text{Mol. wt. of acid } C = 45 \times 2 = 90$$

$$\therefore \text{ Mol. formula of } C = \text{C}_2\text{H}_2\text{O}_4$$

Since it is dicarboxylic acid, it must have two $-\text{COOH}$

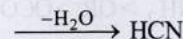
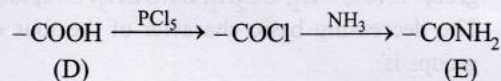


Going back, compound C must be produced from sodium oxalate which in turn is produced from sodium formate. Hence A is formic acid and B is CO_2 . Thus the complete series of reactions can be written as below.



The above reactions lead to following conclusions.

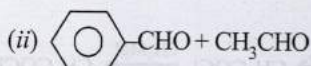
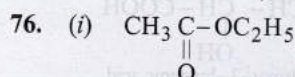
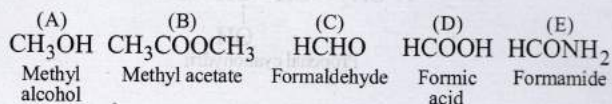
- Reaction of (A) with CH_3COOH in presence of H_2SO_4 to form ester (B) indicates that (A) is an alcohol.
- Reaction of (C) with 50% KOH followed by acidification to give alcohol (A) and the compound (D) seems to be the Cannizzaro reaction. Hence, (C) must be an aldehyde and (D) must be an acid. The 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.
- Structure of acid (D) is established by its given facts.



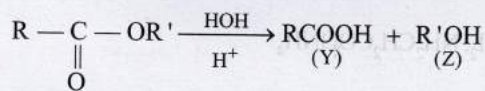
Formation of HCN by the dehydration of (E) establishes that (E) is HCONH_2 and hence (D) is HCOOH .

(iv) Thus the alcohol (A) produced along with HCOOH during Cannizzaro reaction of (C) must be CH_3OH and hence, (C) must be HCHO.

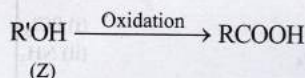
Thus, the various compounds are as below :



77. (X) is hydrolysed to give a carboxylic acid (Y) and an alcohol (Z) and thus (X) is an ester; $\text{R}-\text{C}(\text{O})-\text{OR}'$.

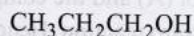
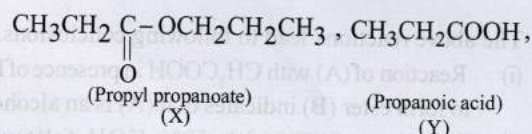


Oxidation of alcohol (Z) gives acid (Y).



or $\text{RCH}_2\text{OH} \longrightarrow \text{RCOOH}$ (\therefore R' is $\text{R}-\text{CH}_2$)

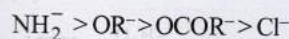
Hence (X), (Y) and (Z) are



(Propan-1-ol)
(Z)

78. The weaker a base better is its leaving ability.

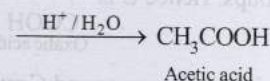
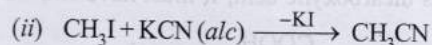
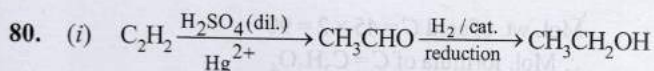
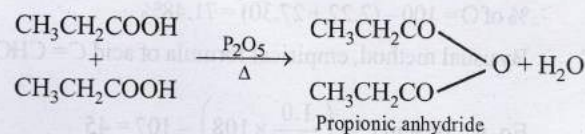
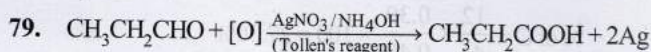
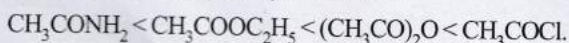
This is an example of nucleophilic substitution where the group X (Cl , NH_2 , OC_2H_5 , OCOCH_3) is replaced by OH. The decreasing basic character of the four concerned groups is:



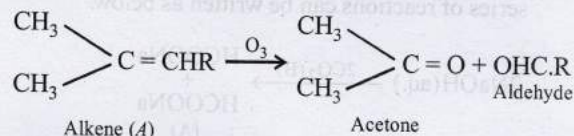
Hence, Cl^- (the weakest base) will be lost most easily, while

NH_2^- (the strongest base) will be lost with most difficulty.

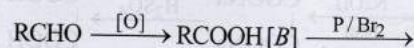
Thus, the order of hydrolysis becomes:



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

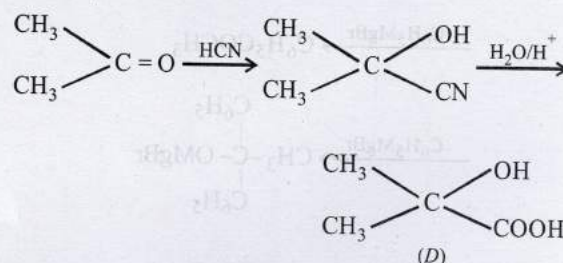


As per problem :

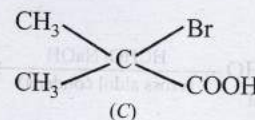


Bromo compound [C] $\xrightarrow{\text{H}_2\text{O}}$ Hydroxy acid [D]

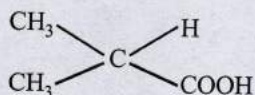
Structure of (D) is determined by the reaction :



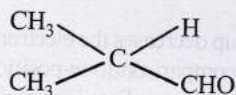
The compound (D) is obtained by hydrolysis of (C) with aqueous alkali. Since (C) is a bromo compound, therefore it has a bromo group whereas the compound (D) has a hydroxyl group. Therefore, structure of C is



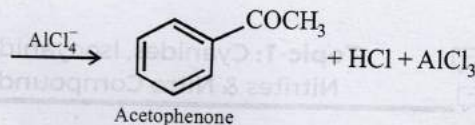
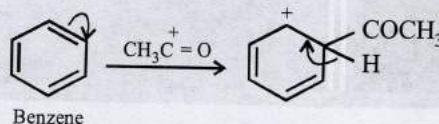
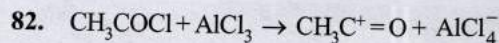
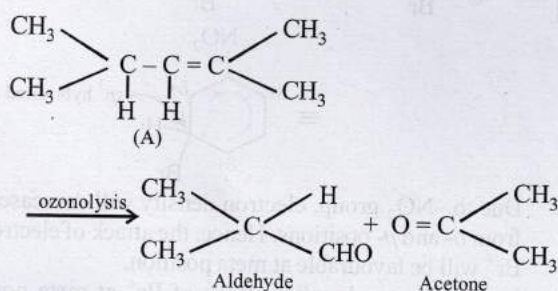
The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is



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



83. First step is Claisen condensation.

