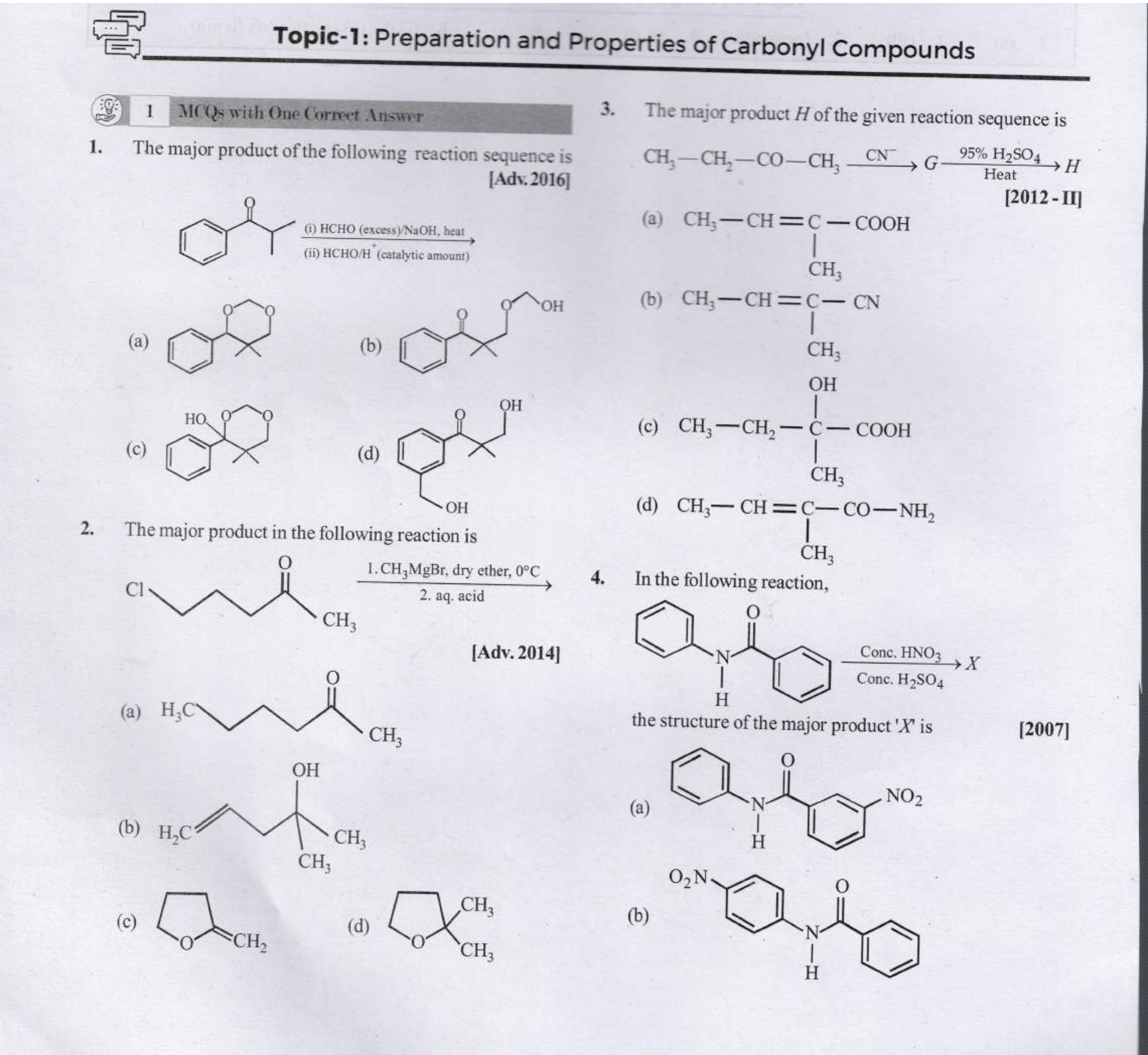
Chapter
Aldehydes Ketones and Carboxylic Acids



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]

$\xrightarrow[\text{(ii) HCHO/}H^+\text{ (catalytic amount)}]{\text{(i) HCHO (excess)/NaOH, heat}}$

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

2. The major product in the following reaction is

$\xrightarrow[\text{2. aq. acid}]{\text{1. }CH_3MgBr\text{, dry ether, 0°C}}$

[Adv. 2014]

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

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

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

[2012 - II]

(a) $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH$

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

(c) $CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-COOH$

(d) $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-NH_2$

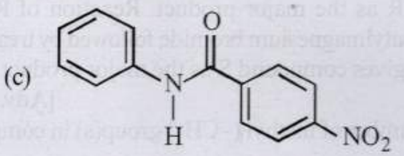
4. In the following reaction,

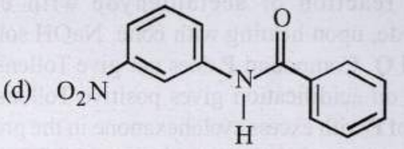
$\xrightarrow[\text{Conc. }H_2SO_4]{\text{Conc. }HNO_3} X$

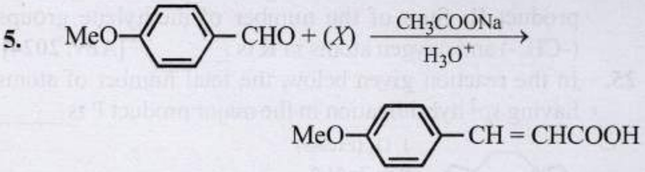
the structure of the major product 'X' is [2007]

(a)

(b)

(c) 

(d) 

5. 

$MeO-C_6H_4-CHO + (X) \xrightarrow[H_3O^+]{CH_3COONa} MeO-C_6H_4-CH=CHCOOH$

The compound (*X*) is **[2005S]**

(a) CH_3COOH (b) $BrCH_2-COOH$

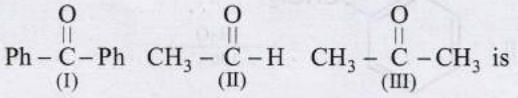
(c) $(CH_3CO)_2O$ (d) $CHO-COOH$

6. How will you convert butan–2–one to propanoic acid? **[2005S]**

(a) Tollen's reagent (b) Fehling's solution

(c) $NaOH/I_2/H^+$ (d) $NaOH/NaI/H^+$

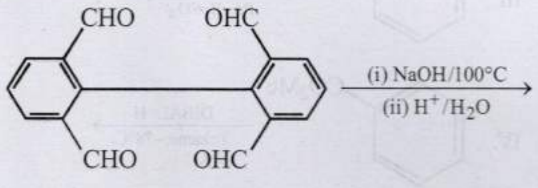
7. The correct order of reactivity of PhMgBr with **[2004S]**



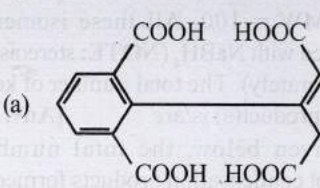
$\underset{(I)}{Ph-\overset{O}{\overset{\|}{C}}-Ph}$ $\underset{(II)}{CH_3-\overset{O}{\overset{\|}{C}}-H}$ $\underset{(III)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$ is

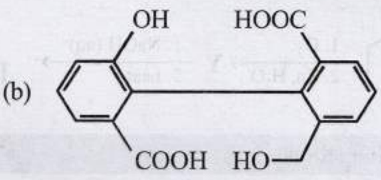
(a) (I) > (II) > (III) (b) (III) > (II) > (I)

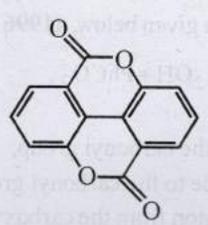
(c) (II) > (III) > (I) (d) (I) > (III) > (II)

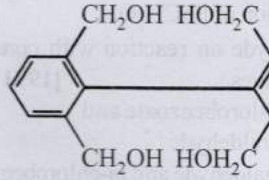
8. 

Major product is : **[2003S]**

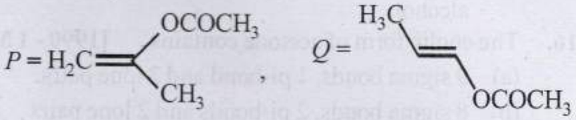
(a) 

(b) 

(c) 

(d) 

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]**

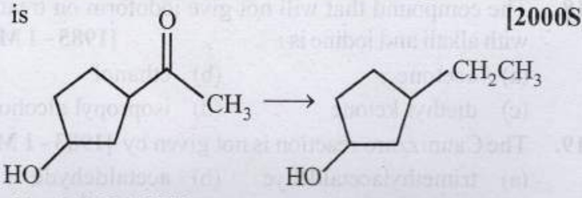
(a) benzyl alcohol and sodium formate

(b) sodium benzoate and methyl alcohol

(c) sodium benzoate and sodium formate

(d) benzyl alcohol and methyl alcohol

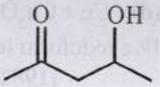
11. The appropriate reagent for the following transformation is **[2000S]**

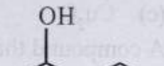


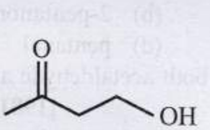
(a) Zn(Hg), HCl (b) NH_2NH_2/OH^-

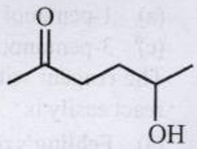
(c) H_2/Ni (d) $NaBH_4$

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

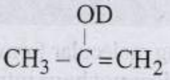
(a) 

(b) 

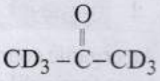
(c) 

(d) 

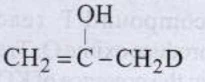
13. The enol form of acetone, after treatment with D_2O, gives. **[1999 - 2 Marks]**

(a) 

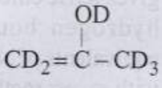
$CH_3-\overset{OD}{\overset{|}{C}}=CH_2$

(b) 

$CD_3-\overset{O}{\overset{\|}{C}}-CD_3$

(c) 

$CH_2=\overset{OH}{\overset{|}{C}}-CH_2D$

(d) 

$CD_2=\overset{OD}{\overset{|}{C}}-CD_3$

14. In the Cannizzaro reaction given below, **[1996 - 1 Mark]**

$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^-$,

the slowest step is

(a) the attack of ^-OH at the carbonyl group,

(b) the transfer of hydride to the carbonyl group,

(c) the abstraction of proton from the carboxylic acid,

(d) the deprotonation of $PhCH_2OH$.

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) $\overset{\delta^-}{C}H_2=CH-\overset{\delta^+}{C}H=O$ (b) $\overset{\delta^-}{C}H_2=CH-CH=\overset{\delta^+}{O}$

(c) $\overset{\delta^-}{C}H_2=\overset{\delta^+}{C}H-CH=O$ (d) $\overset{\delta^+}{C}H_2=CH-CH=\overset{\delta^-}{O}$

18. The compound that will not give iodoform on treatment with alkali and iodine is : **[1985 - 1 Mark]**

(a) acetone (b) ethanol

(c) diethyl ketone (d) isopropyl alcohol

19. The Cannizzaro reaction is not given by **[1983 - 1 Mark]**

(a) trimethylacetaldehye (b) acetaldehyde

(c) benzaldehyde (d) formaldehyde

20. When acetaldehyde is heated with Fehling's solution it gives a precipitate of **[1983 - 1 Mark]**

(a) Cu (b) CuO

(c) Cu_2O (d) $Cu + Cu_2O + CuO$

21. A compound that gives a positive iodoform test is **[1982 - 1 Mark]**

(a) 1-pentanol (b) 2-pentanone

(c) 3-pentanone (d) pentanal

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

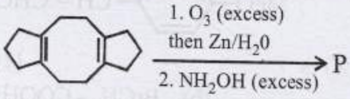
2 Integer Value Answer

23. An organic compound P having molecular formula $C_6H_6O_3$ 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 ($-CH_3$) group(s) in compound S is _____.

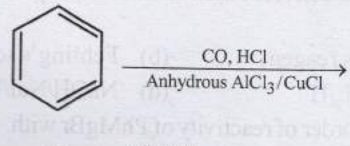
24. Complete reaction of acetaldehyde with excess formaldehyde, upon heating with conc. NaOH solution, gives **P** and **Q**. Compound **P** does not give Tollens' test, whereas **Q** on acidification gives positive Tollens' test. Treatment of **P** with excess cyclohexanone in the presence of catalytic amount of *p*-toluenesulfonic acid (PTSA) gives product **R**. Sum of the number of methylene groups ($-CH_2-$) and oxygen atoms in **R** is _____. **[Adv. 2024]**

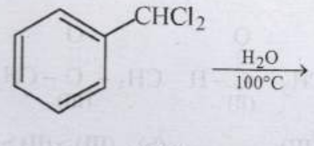
25. In the reaction given below, the total number of atoms having sp^2 hybridization in the major product P is _____

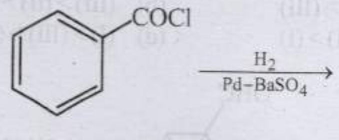


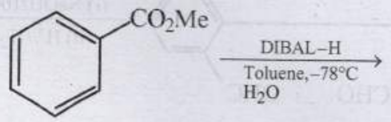
[Adv. 2021]

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

I. 

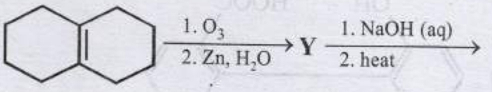
II. 

III. 

IV. 

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 $CH_3-CO-CH_2-CO-CH_3$ 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

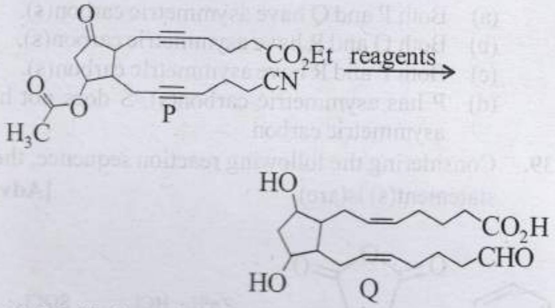
33. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. **[1987 - 1 Mark]**

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^+

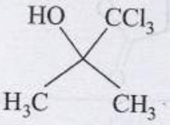
(b) (i) Lindlar's catalyst, H_2; (ii) H_3O^+; (iii) $SnCl_2/HCl$; (iv) $NaBH_4$

(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 $Ca(OH)_2$ produces compound **R** and calcium salt **S**. The correct statement(s) regarding **P**, **Q**, **R** and **S** is(are) **[Adv. 2024]**

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



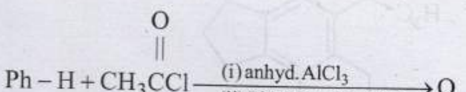
(b) Reaction of **R** with O_2 in the presence of light gives phosgene gas

(c) **Q** reacts with aqueous NaOH to produce Cl_3CCH_2OH and $Cl_3CCOONa$

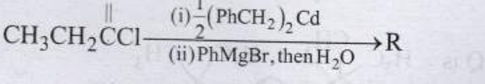
(d) **S** on heating gives **P**

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

$$CH_3CH_2CH(CH_3)CH_2CN \xrightarrow[\text{(ii) PhMgBr, then } H_2O]{\text{(i) PhMgBr, then } H_3O^{\oplus}} P$$



$$Ph-H+CH_3\overset{\overset{O}{\|}}{C}Cl \xrightarrow[\text{(ii) PhMgBr, then } H_2O]{\text{(i) anhyd. } AlCl_3} Q$$



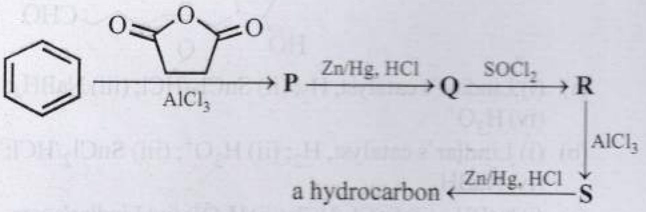
$$CH_3CH_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow[\text{(ii) PhMgBr, then } H_2O]{\text{(i) } \frac{1}{2}(PhCH_2)_2Cd} R$$

$$PhCH_2CHO \xrightarrow[\substack{\text{(iii) HCN} \\ \text{(iv) } H_2SO_4,\Delta}]{\substack{\text{(i) PhMgBr, then } H_2O \\ \text{(ii) } CrO_3, \text{ dil. } H_2SO_4}} S$$

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

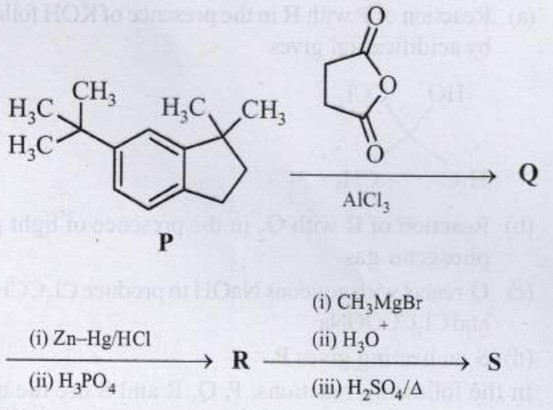
(a) Both P and Q have asymmetric carbon(s).
(b) Both Q and R have asymmetric carbon(s).
(c) Both P and R have asymmetric carbon(s).
(d) P has asymmetric carbon(s), S does not have any asymmetric carbon.

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



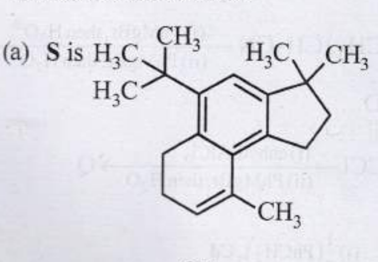
(a) Compounds **P** and **Q** are carboxylic acids.
(b) Compound **S** decolorizes bromine water.
(c) Compounds **P** and **S** react with hydroxylamine to give the corresponding oximes.
(d) Compound **R** reacts with dialkylcadmium to give the corresponding tertiary alcohol.

40. In the reaction scheme shown below, **Q, R,** and **S** are the major products. **[Adv. 2020]**

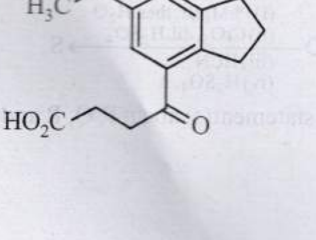


The correct structure of

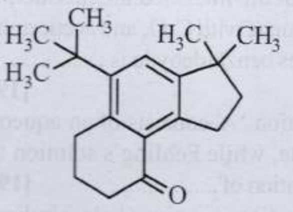
(a) **S** is



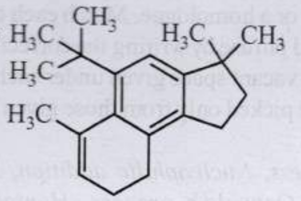
(b) **Q** is



(c) **R** is



(d) **S** is

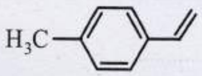
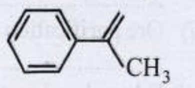


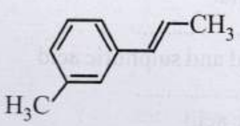
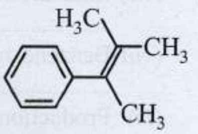
41. Compounds *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is C_8H_8O. *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction

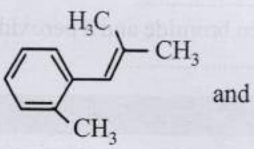
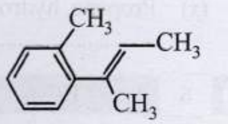
(i) $P \xrightarrow[\text{ii) Zn/H}_2\text{O}]{\text{i) O}_3/\text{CH}_2\text{Cl}_2} \underset{(C_8H_8O)}{Q}$

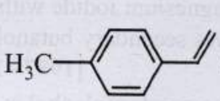
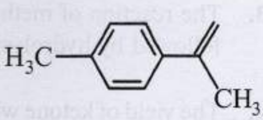
(ii) $R \xrightarrow[\text{ii) Zn/H}_2\text{O}]{\text{i) O}_3/\text{CH}_2\text{Cl}_2} \underset{(C_8H_8O)}{S}$

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]**

$$\text{Cumene}(C_9H_{12}) \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}O_2} \mathbf{P} \xrightarrow{CHCl_3/NaOH} \mathbf{Q}\text{ (major)} + \mathbf{R}\text{ (minor)}$$

$$\mathbf{Q} \xrightarrow[PhCH_2Br]{NaOH} \mathbf{S}$$

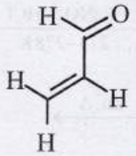
(a) **R** is steam volatile

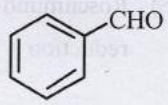
(b) **Q** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

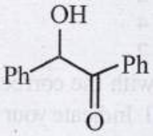
(c) **S** gives yellow precipitate with 2, 4–dinitrophenylhydrazine

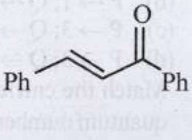
(d) **S** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

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

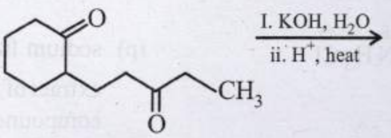
(a) 

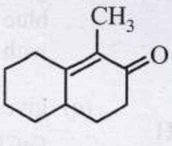
(b) 

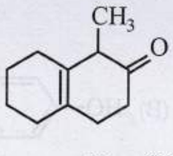
(c) 

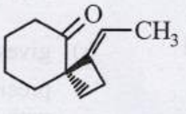
(d) 

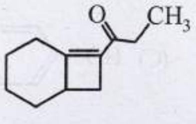
44. The major product of the following reaction is **[Adv. 2015]**



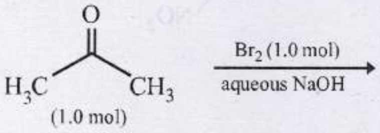
(a) 

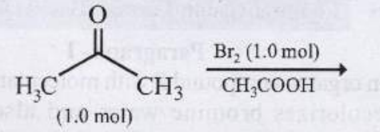
(b) 

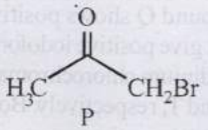
(c) 

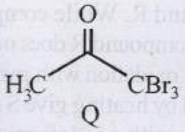
(d) 

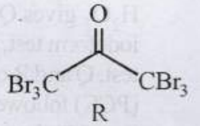
45. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are) **[Adv. 2013]**

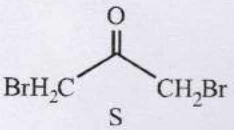
Reaction I : 

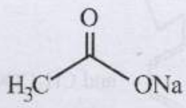
Reaction II : 


P


Q


R


S


T

$CHBr_3$
U

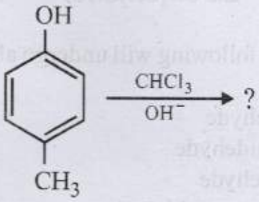
(a) Reaction I : *P* and Reaction II : *P*

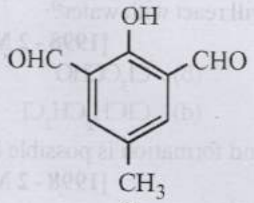
(b) Reaction I : *U*, acetone and Reaction II : *Q*, acetone

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

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

46. In the following reaction, the product(s) formed is (are) **[Adv. 2013]**

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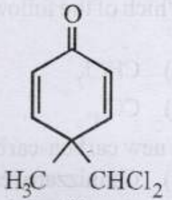
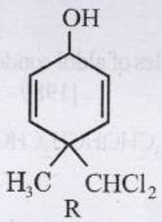
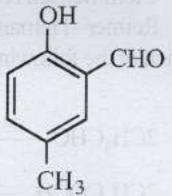

Q


R


S

(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

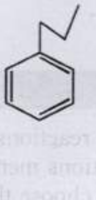
(c) Two oximes formed are optically active

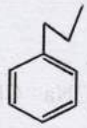
(d) All oximes formed are optically active

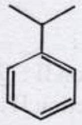
48.  $+ Cl-CH_2CH_2CH_3$

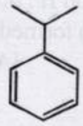
$$\xrightarrow{AlCl_3} P \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2/\Delta} Q + \text{Phenol}$$

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

(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

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) $ClCH_2CH_2Cl$

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]**

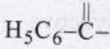
(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$

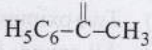
(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3COH(CH_3)CH_2COCH_3$

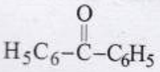
(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$

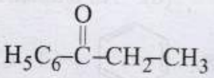
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

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

(a)  $H_5C_6-\overset{O}{\overset{\|}{C}}-H$

(b)  $H_5C_6-\overset{O}{\overset{\|}{C}}-CH_3$

(c)  $H_5C_6-\overset{O}{\overset{\|}{C}}-C_6H_5$

(d)  $H_5C_6-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

54. Base catalysed aldol condensation occurs with : **[1984 - 1 Mark]**

(a) propionaldehyde
(b) benzaldehyde
(c) 2-methylpropionaldehyde
(d) 2, 2-dimethylpropionaldehyde

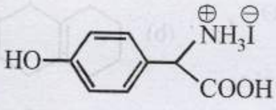
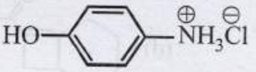
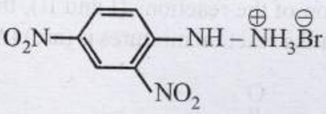
7 Match the Following

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	List-II
(P) Etard reaction	(1) Acetophenone $\xrightarrow{Zn-Hg, HCl}$
(Q) Gattermann reaction	(2) Toluene $\xrightarrow[(ii)\,SOCl_2]{(i)\,KMnO_4, KOH, \Delta}$
(R) Gattermann–Koch reaction	(3) Benzene $\xrightarrow[\text{anhyd. }AlCl_3]{CH_3Cl}$
(S) Rosenmund reduction	(4) Aniline $\xrightarrow[273-278K]{NaNO_2/HCl}$
	(5) Phenol $\xrightarrow{Zn, \Delta}$

(a) P → 2; Q → 4; R → 1; S → 3
(b) P → 1; Q → 3; R → 5; S → 2
(c) P → 3; Q → 2; R → 1; S → 4
(d) P → 3; Q → 4; R → 5; S → 2

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

Column I	Column II
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B) 	(q) gives positive $FeCl_3$ test
(C) 	(r) gives white precipitate with $AgNO_3$
(D) 	(s) reacts with aldehydes to form the corresponding hydrazone derivative

8 Comprehension/Passage Based Questions

Paragraph - I

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

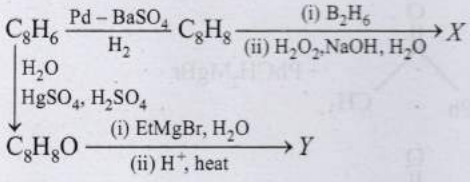
Complete copolymerization of 500 moles of Q and 500 moles of R gives one mole of a single acyclic copolymer U.
[Given, atomic mass: H = 1, C = 12, O = 16]

57. Sum of number of oxygen atoms in S and T is ______. **[Adv. 2024]**

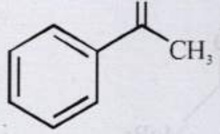
58. The molecular weight of U is ______. **[Adv. 2024]**

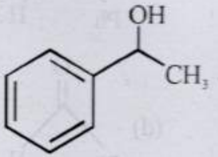
Passage-I

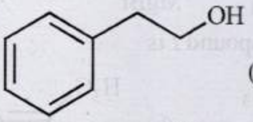
In the following reactions **[Adv. 2015]**

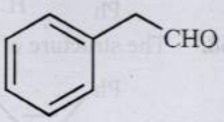


59. Compound *X* is

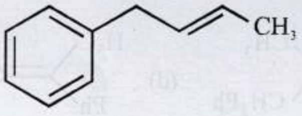
(a) 

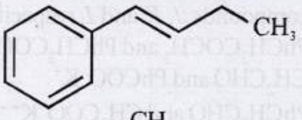
(b) 

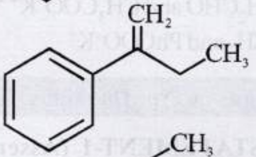
(c) 

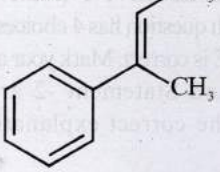
(d) 

60. The major compound *Y* is

(a) 

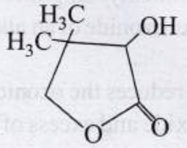
(b) 

(c) 

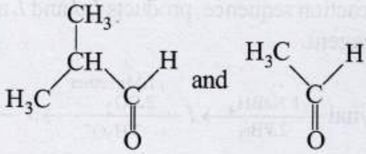
(d) 

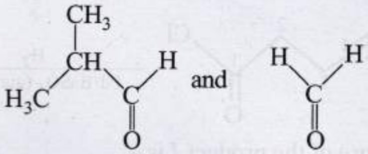
Passage-II

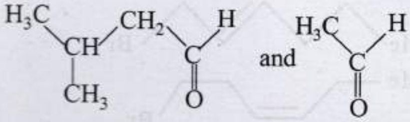
Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below. **[2010]**

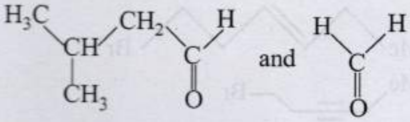


61. The compounds *P* and *Q* respectively are :

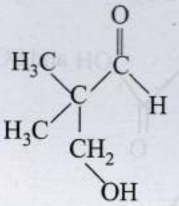
(a) 

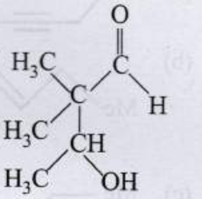
(b) 

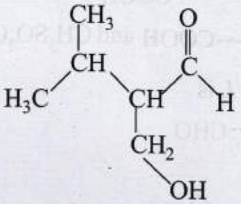
(c) 

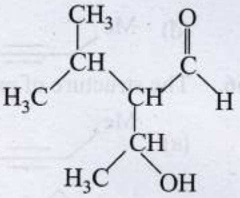
(d) 

62. The compound *R* is :

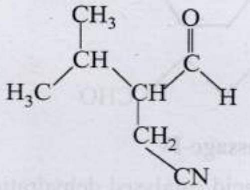
(a) 

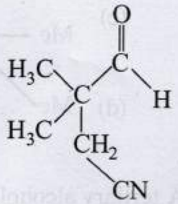
(b) 

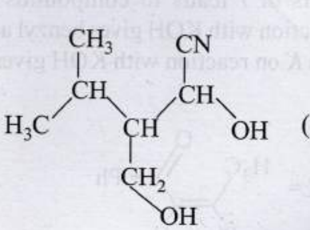
(c) 

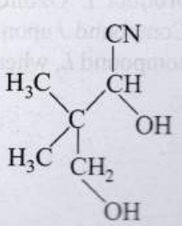
(d) 

63. The compound *S* is :

(a) 

(b) 

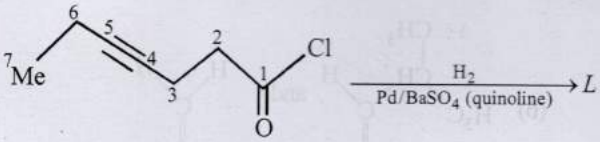
(c) 

(d) 

Passage-III

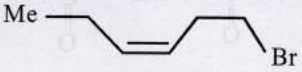
In the following reaction sequence, products *I*, *J* and *L* are formed. *K* represents a reagent. **[2008]**

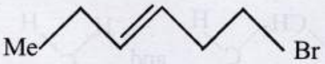
$$\text{Hex}-3-\text{ynal}\xrightarrow[2.PBr_3]{1.NaBH_4} I \xrightarrow[3.H_3O^+]{\substack{1.Mg/ether\\2.CO_2}} J \xrightarrow{K}$$

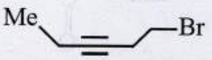


64. The structure of the product *I* is –

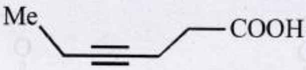
(a) 

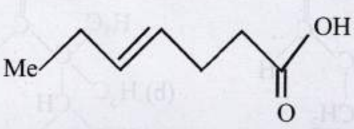
(b) 

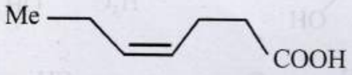
(c) 

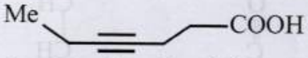
(d) 

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

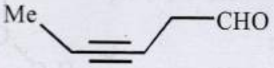
(a)  and $SOCl_2$

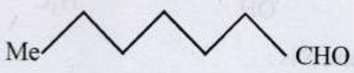
(b)  and $SOCl_2$

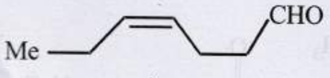
(c) 

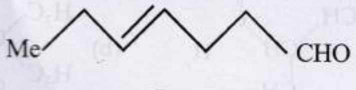
(d)  and CH_3SO_2Cl

66. The structure of product *L* is

(a) 

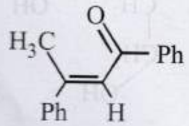
(b) 

(c) 

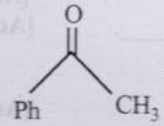
(d) 

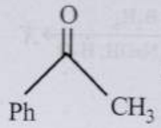
Passage-IV

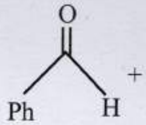
A tertiary alcohol *H* upon acid catalysed dehydration gives a product I. Ozonolysis of *I* leads to compounds *J* and *K*. Compound *J* upon reaction with KOH gives benzyl alcohol and compound *L*, whereas *K* on reaction with KOH gives only *M*. **[2008]**

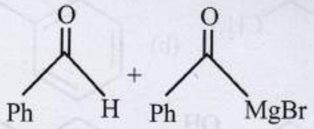
M = 

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

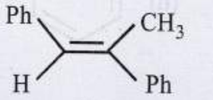
(a)  + PhMgBr

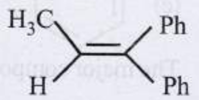
(b)  + $PhCH_2MgBr$

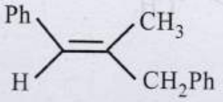
(c)  + $PhCH_2MgBr$

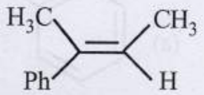
(d) 

68. The structure of compound *I* is

(a) 

(b) 

(c) 

(d) 

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

(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

(d) PhCHO, $PhCOCH_3$ 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. $A(C_6H_{12})\xrightarrow{HCl}\underset{(C_6H_{13}Cl)}{B+C}$ **[2003 - 4 Marks]**

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

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

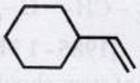
$A\xrightarrow{Ozonolysis}F+G$ (both gives positive Tollen's test but do not give iodoform test).

$F+G\xrightarrow{conc.\ NaOH}HCOONa + A$ primary alochol.

Identify from A to G.

73. Compound 'A' of molecular formula $C_9H_7O_2Cl$ 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]**



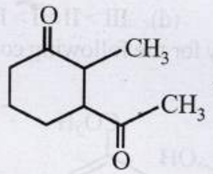
$\xrightarrow{Br_2/CCl_4}(A)\xrightarrow{NaNH_2}(B)\xrightarrow{HgSO_4/H_2SO_4}(C)\xrightarrow{NH_2NHCONH_2}(D)$

$[C]\xrightarrow{NaOD/D_2O(excess)}(E)$

75. An organic compound **A**, $C_6H_{10}O$ 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.

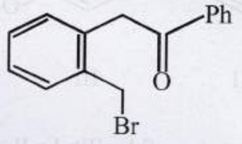


$\xrightarrow[NaOH]{Br_2}(A)\ +\ (B)$

$\xrightarrow[\Delta]{H^+}(C)\ C_7H_{12}O$

[2000 - 3 Marks]

(*ii*)

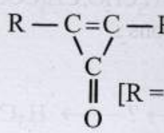


$\xrightarrow{base}$ **[2000 - 1 Mark]**

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

(*iv*) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow ----$ **[1997 - 1 Mark]**

(*v*)



$R-\underset{\underset{O}{\overset{\|}{C}}}{C=C}-R + HClO_4 \longrightarrow -----$ [R = n-Pr]

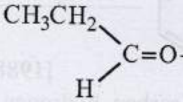
[1997 - 1 Mark]

(*vi*)

$+\ Ph_3P=CH_2 \longrightarrow \overset{E}{----}$

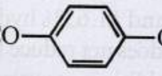
[1997 - 1 Mark]

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



$\begin{matrix}CH_3CH_2 & \\ & C=O\\ H & \end{matrix}\xrightarrow[2.LiAlH_4]{1.KCN/H_2SO_4}D$

(*viii*) H_3CO-



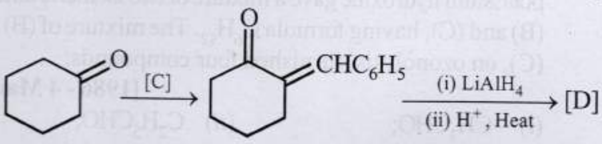
$-CHO + HCHO\xrightarrow{KOH}$

[1992 - 1 Mark]

(*ix*) propanal $\xrightarrow[heat]{NaOH}$ **[1985 - 1 Mark]**

(*x*) methanal reacts with ammonia **[1981 - ½ Mark]**

77. Complete the following reaction with appropriate structures of products/reagents : **[1998 - 2 + 2 Marks]**



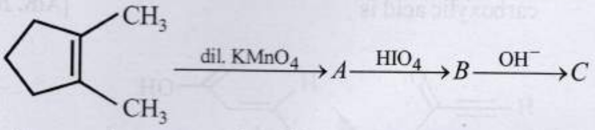
78. Write the intermediate steps for the following reaction.

$$C_6H_5CH(OH)C\equiv CH\xrightarrow{H_3O^+}C_6H_5CH=CHCHO$$

[1998 - 2 Marks]

79. An aldehyde A ($C_{11}H_8O$), 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 appopriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.) **[1996 - 3 Marks]**

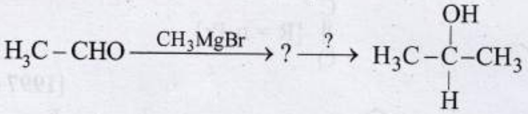


81. An organic compound A, C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous 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]**

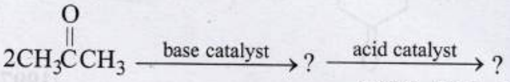
$CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, CH_3COCH_2COCH_3$

83. Complete the following reactions :

(*i*) 

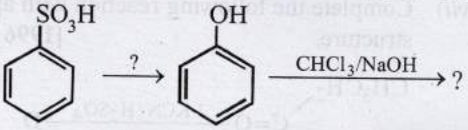
$H_3C-CHO \xrightarrow{CH_3MgBr} ? \xrightarrow{?} H_3C-\overset{OH}{\underset{H}{C}}-CH_3$

[1988 - 1 Mark]

(*ii*) 

$2CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{\text{base catalyst}} ? \xrightarrow{\text{acid catalyst}} ?$

[1988 - 1 Mark]

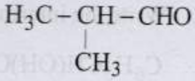
(*iii*) 

[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 $C_6H_{13}Cl$. 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]**

(*i*) CH_3CHO; (*ii*) C_2H_5CHO;

(*iii*) CH_3COCH_3 and (*iv*) 

$H_3C-\underset{CH_3}{\underset{|}{CH}}-CHO$

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]**

$CH_3CHO,\ CH_3COCH_3,\ HCHO,\ C_2H_5COCH_3$

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 $R-C\equiv O^+$ is more stable than $R-C^+=O$. **[1994 - 1 Mark]**

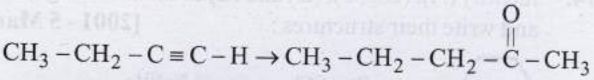
(*iii*) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion. **[1991 - 1 Mark]**

(*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]**



$CH_3-CH_2-C\equiv C-H \rightarrow CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

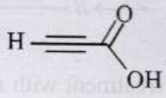
(*ii*) acetylene to acetone **[1985 - 1 Mark]**

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

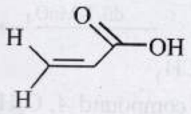
Topic-2: Preparation and Properties of Carboxylic Acids and its Derivatives

1 MCQs with One Correct Answer

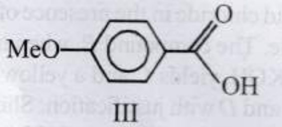
1. The correct order of acid strength of the following carboxylic acid is **[Adv. 2019]**



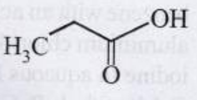
I



II



III

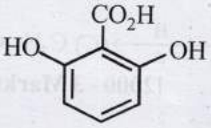


IV

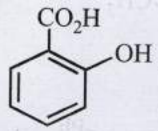
(a) I > II > III > IV (b) II > I > IV > III

(c) I > III > II > IV (d) III > II > I > IV

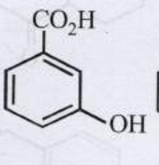
2. The correct order of acidity for the following compounds is



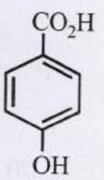
I



II



III



IV

[Adv. 2016]

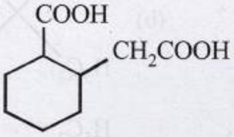
(a) I > II > III > IV (b) III > I > II > IV

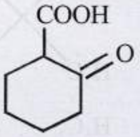
(c) III > IV > II > I (d) I > III > IV > II

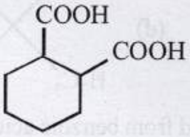
3. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is **[Adv. 2013]**

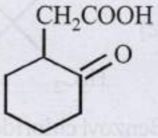
(a) Benzoic acid (b) Benzenesulphonic acid
(c) Salicylic acid (d) Carbolic acid (Phenol)

4. The compound that undergoes decarboxylation most readily under mild condition is **[2012]**

(a) 

(b) 

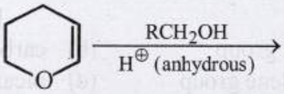
(c) 

(d) 

5. The carboxyl functional group (– COOH) is present in **[2012]**

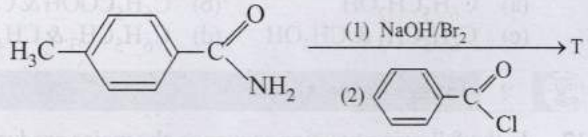
(a) picric acid (b) barbituric acid
(c) ascorbic acid (d) aspirin

6. The major product of the following reaction is **[2011]**

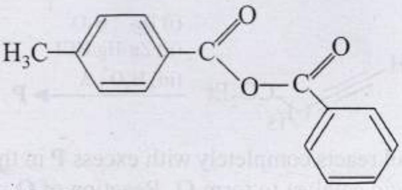


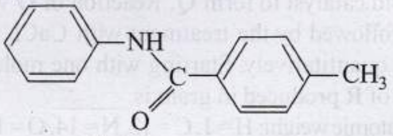
(a) a hemiacetal (b) an acetal
(c) an ether (d) an ester

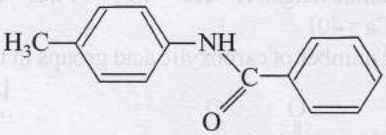
7. In the reaction

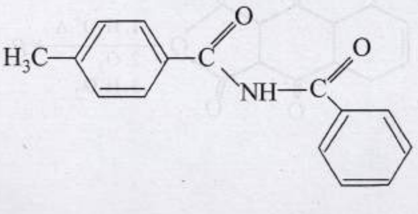


the structure of the product T is : **[2010]**

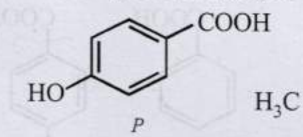
(a) 

(b) 

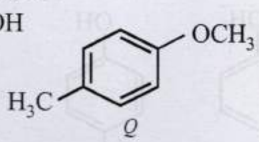
(c) 

(d) 

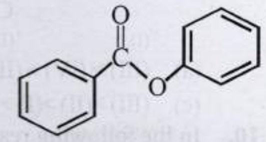
8. The compounds *P*, *Q* and *S*



P

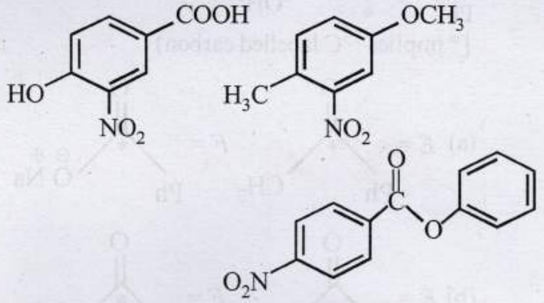


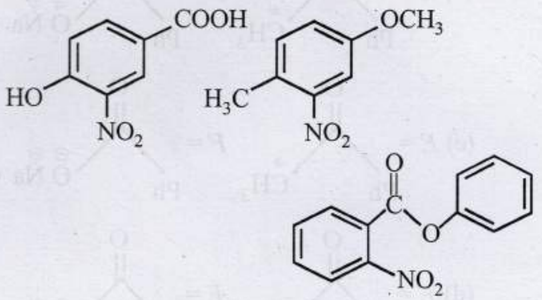
Q

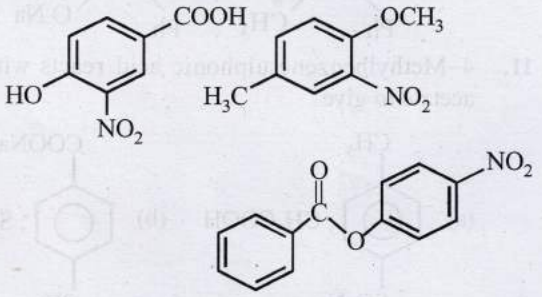


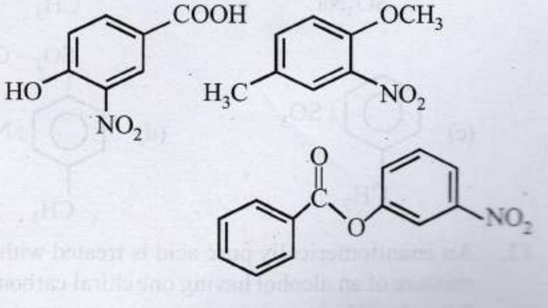
S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is : **[2010]**

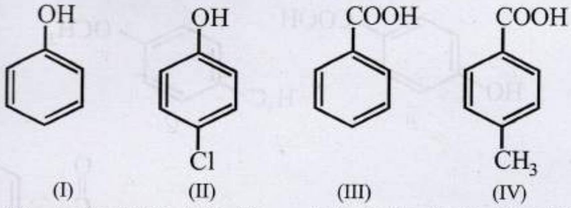
(a) 

(b) 

(c) 

(d) 

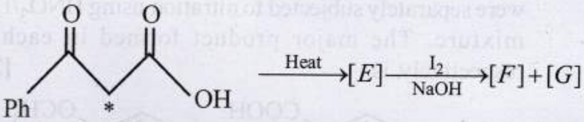
9. The correct acidity order of the following is **[2009S]**



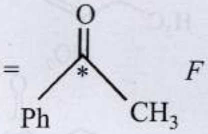
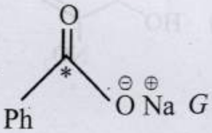
(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)

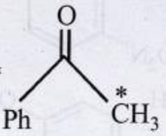
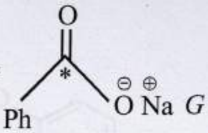
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

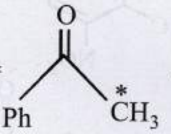
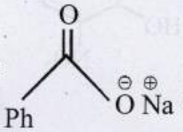
10. In the following reaction sequence, the correct structures of E, F and G are

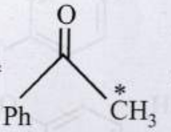
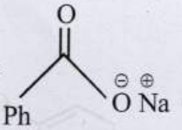


[* implies ^{13}C labelled carbon) **[2008]**

(a) $E =$  $F =$  $G = CHI_3$

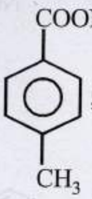
(b) $E =$  $F =$  $G = CHI_3$

(c) $E =$  $F =$  $G = \overset{*}{C}HI_3$

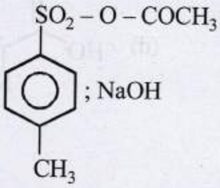
(d) $E =$  $F =$  $G \overset{*}{=} CH_3I$

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

(a)  ; CH_3COOH

(b)  ; SO_3

(c)  ; SO_3

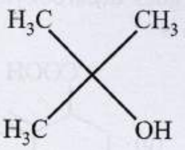
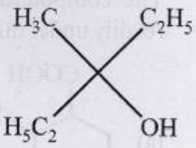
(d)  ; NaOH

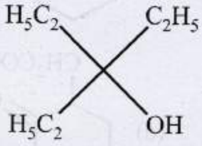
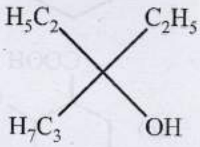
12. An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be **[2003S]**

(a) Optically active mixture (b) Pure enantiomer

(c) Meso compound (d) Racemic mixture

13. Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr} P$. The product P will be **[2003S]**

(a)  (b) 

(c)  (d) 

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

(a) $Cl_2, h\nu$ (b) SO_2Cl_2

(c) $SOCl_2$ (d) Cl_2, H_2O

15. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The 'C' of CO_2 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]**

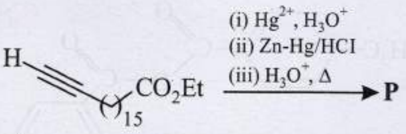
$$C_6H_5COOH \xrightarrow[\text{II } H_3O^+]{\text{I LiAlH}_4}$$

(a) $C_6H_5CH_2OH$ (b) C_6H_5COOH & CH_4

(c) $C_6H_5CH_3$ & CH_3OH (d) $C_6H_5CH_3$ & CH_4

2 Integer Value Answer

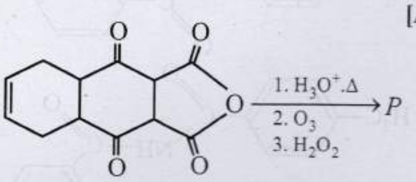
17. In the following reaction sequence, the major product **P** is formed. **[Adv. 2024]**



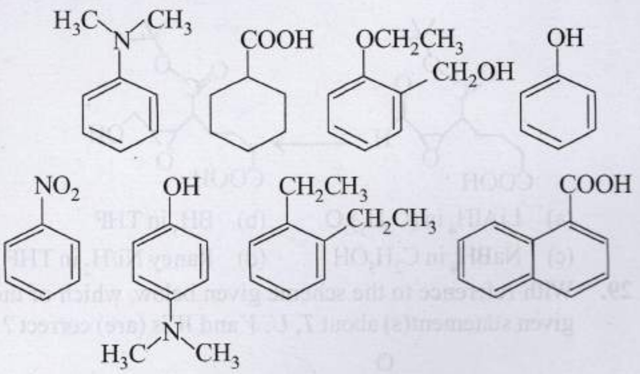
Glycerol reacts completely with excess **P** in the presence of an acid catalyst to form **Q**. Reaction of **Q** with excess NaOH followed by the treatment with $CaCl_2$ yields Ca-soap **R**, quantitatively. Starting with one mole of **Q**, the amount of **R** produced in gram is ______.

[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]**

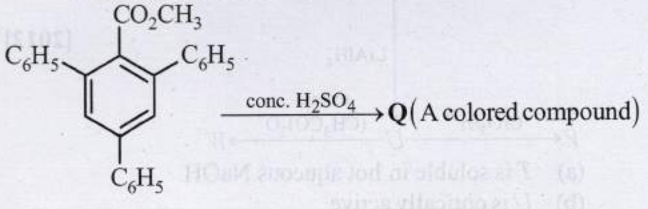


19. Amongst the following, the total number of compounds soluble in aqueous NaOH is **[2010]**



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]**

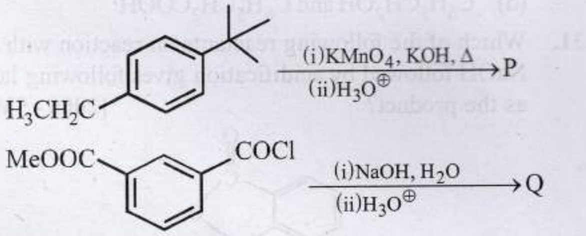
5 True / False

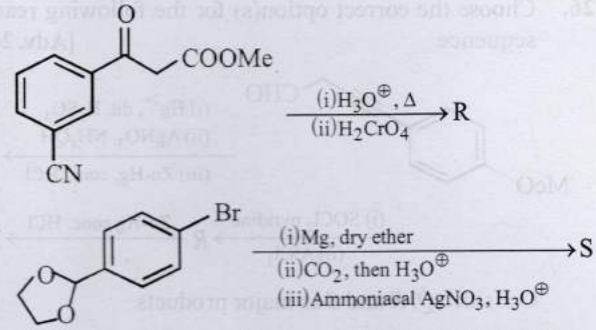
22. The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. **[1991 - 1 Mark]**

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.

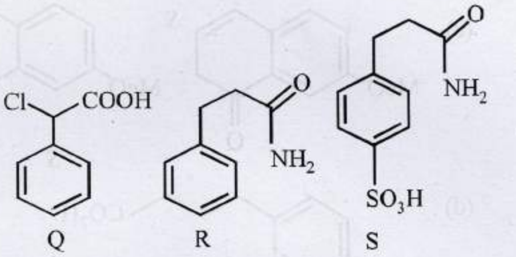
25. Consider the following reaction scheme and choose the correct option(s) for the major products Q, R and S.

$$\text{Styrene} \xrightarrow[\text{(ii) NaOH, } H_2O_2, H_2O]{\text{(i) } B_2H_6} P \xrightarrow[\text{(ii) } Cl_2\text{, Red phosphorus (iii) } H_2O]{\text{(i) } CrO_3, H_2SO_4} Q$$

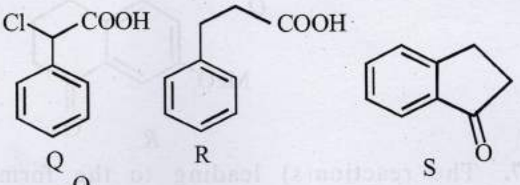
$$P \xrightarrow[\text{(ii) NaCN (iii) } H_3O^+, \Delta]{\text{(i) } SOCl_2} R \xrightarrow{\text{conc. } H_2SO_4} S$$

[Adv. 2023]

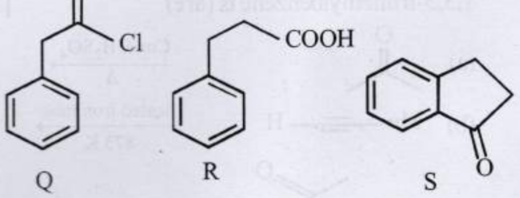
(a)



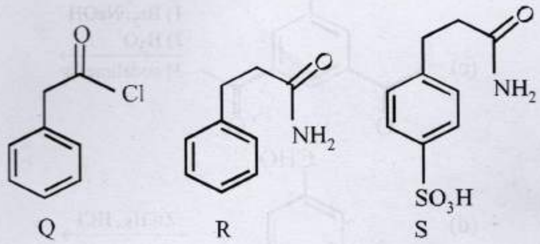
(b)



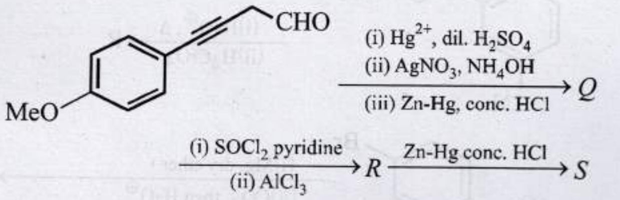
(c)



(d)

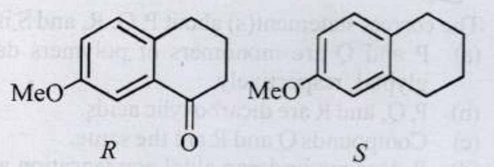


26. Choose the correct option(s) for the following reaction sequence **[Adv. 2019]**



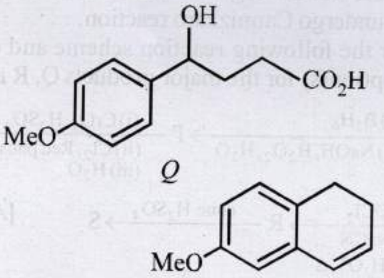
Consider *Q*, *R* and *S* as major products.

(a)



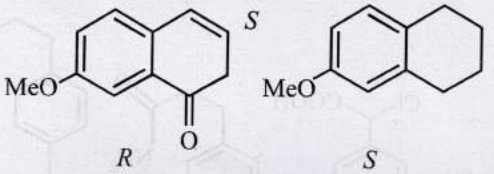
R *S*

(b)



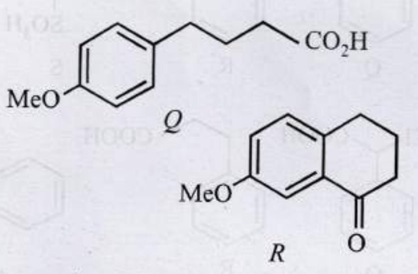
Q *S*

(c)



R *S*

(d)



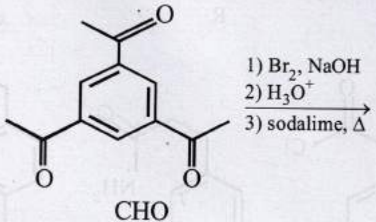
Q *R*

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

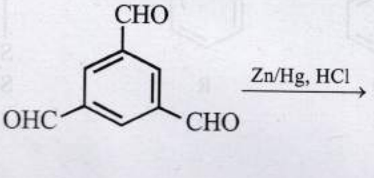
(a)

(b)

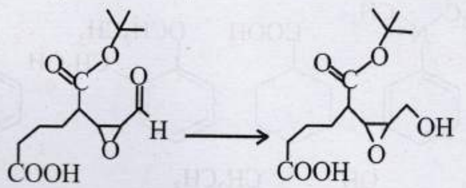
(c)



(d)



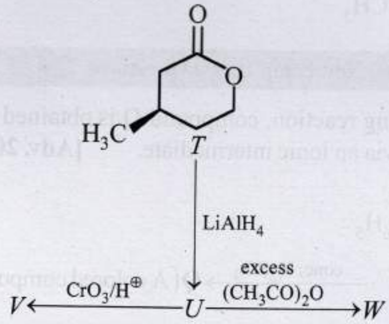
28. Reagent(s) which can be used to bring about the following transformation is (are) **[Adv. 2016]**



(a) $LiAlH_4$ in $(C_2H_5)_2O$ (b) BH_3 in THF

(c) $NaBH_4$ in C_2H_5OH (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]**



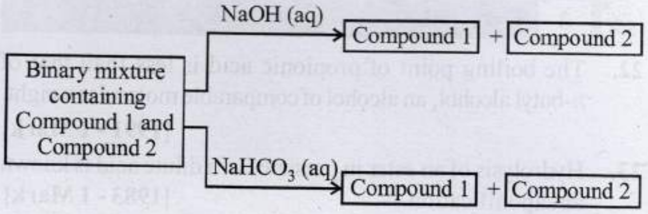
(a) *T* is soluble in hot aqueous NaOH

(b) *U* is optically active

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

(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]**



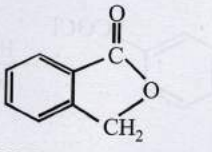
(a) C_6H_5OH and C_6H_5COOH

(b) C_6H_5COOH and $C_6H_5CH_2OH$

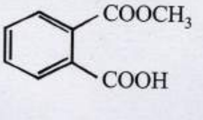
(c) $C_6H_5CH_2OH$ and C_6H_5OH

(d) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

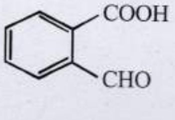
31. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? **[2006 - 5M, –1]**

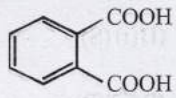


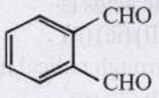
(a)



(b)



(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]**

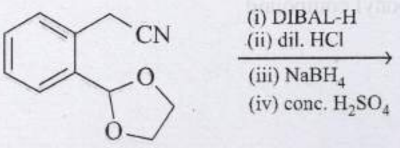
(a) 2-Hydroxypropane (b) acetophenone

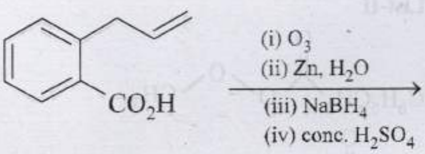
(c) methyl acetate (d) acetamide

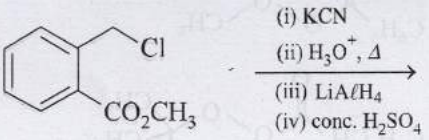
7 Match the Following

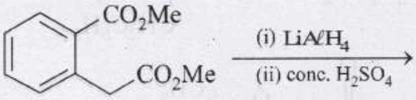
Directions [Qs. 34-35] : Answer the following by appropriately matching the lists based on the information given in the paragraph. List–I includes starting materials and reagents of selected chemical reactions. List–II gives structures of compounds that may be formed as intermediate products and/ or final products from the reactions of List–I. **[Adv. 2019]**

List–I

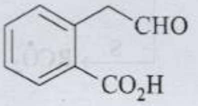
(I) 

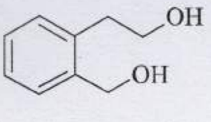
(II) 

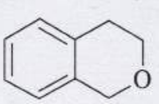
(III) 

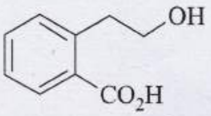
(IV) 

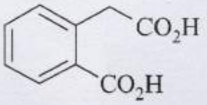
List–II

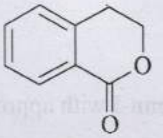
(P) 

(Q) 

(R) 

(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/hv	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O/CH_3COOK$	(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)

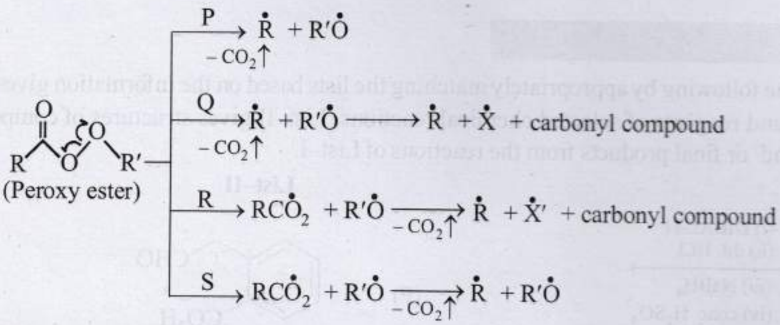
37. The only CORRECT combination that gives two different carboxylic acids is

(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

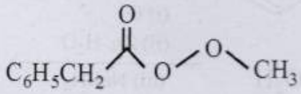
P. Pathway P

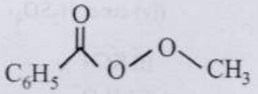
Q. Pathway Q

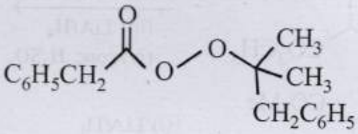
R. Pathway R

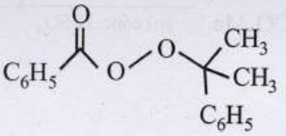
S. Pathway S

List-II

1.


2.


3.


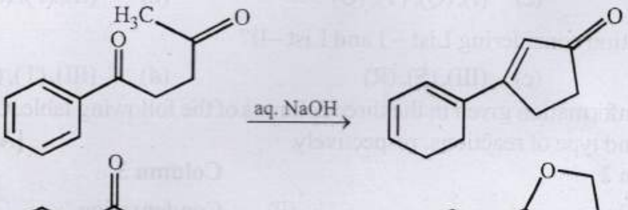
4.


Code :

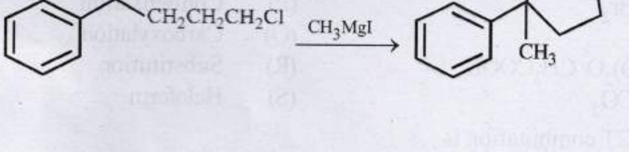
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

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

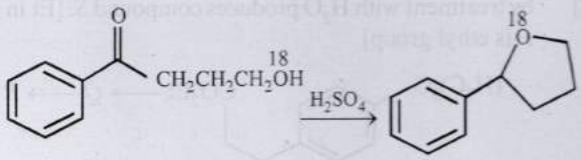
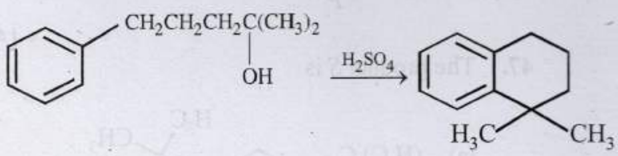
Column-I **Column-II**

(A)


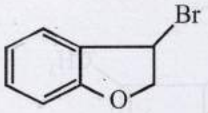
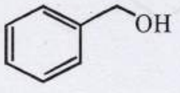
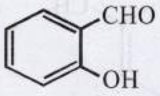
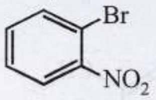
(p) Nucleophilic substitution

(B)


(q) Electrophilic substitution

(C) 	(r) Dehydration
(D) 	(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**
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(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**
(A) C_6H_5CHO	(p) gives precipitate with 2, 4-dinitrophenylhydrazine
(B) $CH_3C\equiv CH$	(q) gives precipitate with $AgNO_3$
(C) CN^-	(r) is a nucleophile
(D) I^-	(s) is involved in cyanohydrin formation

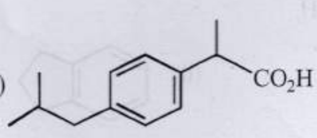
8 Comprehension/Passage Based Questions

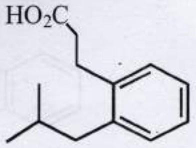
Passage-I

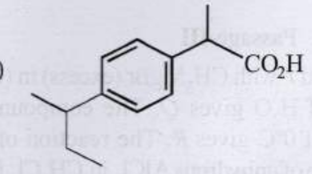
An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** *via* **Q**. The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

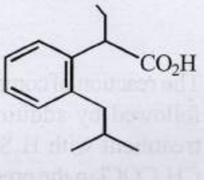
$$\mathbf{S} \xleftarrow[\substack{\text{4) } CHCl_3,\text{ KOH, }\Delta \\ \text{5) } H_2/\text{ Pd-C}}]{\substack{\text{1) } H_2/\text{Pd-C} \\ \text{2) } NH_3/\Delta \\ \text{3) } Br_2/\text{NaOH}}} \mathbf{P} \xrightarrow[\substack{\text{3) MeMgBr, } CdCl_2 \\ \text{4) } NaBH_4}]{\substack{\text{1) } H_2/\text{Pd-C} \\ \text{2) } SOCl_2}} \mathbf{Q} \xrightarrow[\substack{\text{3) } CO_2\text{ (dry ice)} \\ \text{4) } H_3O^+}]{\substack{\text{1) HCl} \\ \text{2) Mg/}Et_2O}} \mathbf{R}$$

43. The compound **R** is

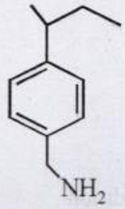
(a) 

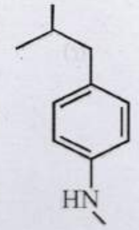
(b) 

(c) 

(d) 

44. The compound **S** is **[Adv. 2018]**

(a)


(b)


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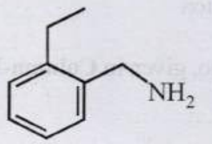

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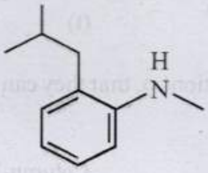
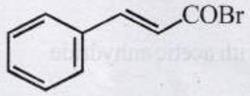


Passage-II

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

(a)


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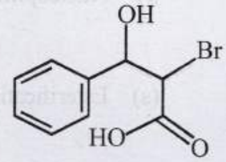

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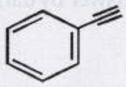

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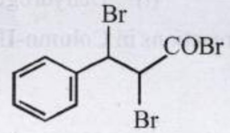
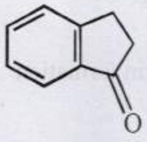
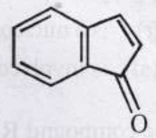


46. The compound **Z** is

(a)


(b)


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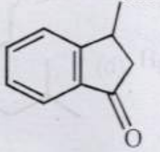

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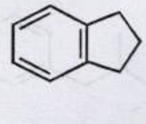
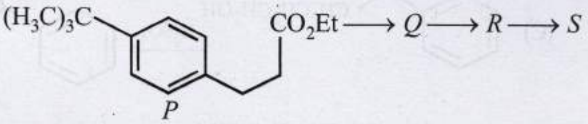


Passage-III

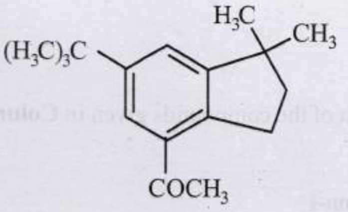
The reaction of compound *P* with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives *Q*. The compound *Q* on treatment with H_2SO_4 at 0°C gives *R*. The reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound *S*. [Et in compound *P* is ethyl group]



P

[Adv. 2017]

47. The product *S* is

(a)


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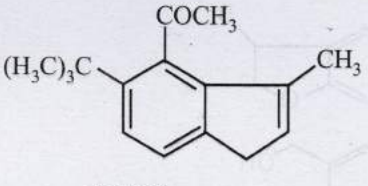

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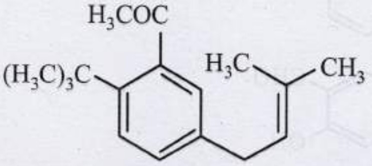

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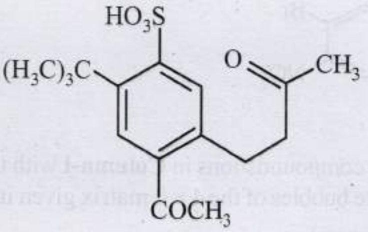
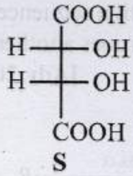


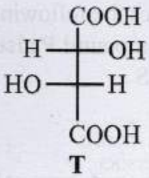
48. The reactions, *Q* to *R* and *R* to *S*, are
(a) Dehydration and Friedel–Craft's acylation
(b) Aromatic sulfonation and Friedel–Craft's acylation
(c) Friedel–Craft's alkylation, dehydration and Friedel–Craft's acylation
(d) Friedel–Craft's alkylation and Friedel–Craft's acylation

Passage-IV

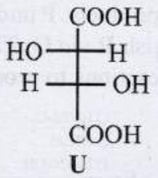
P and **Q** are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O. On heating, **P** forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, **P** as well as **Q** could produce one or more than one from **S**, **T** and **U**.



S



T



U

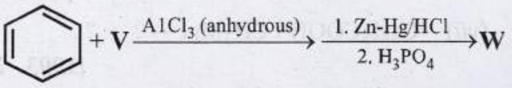
[Adv. 2013]

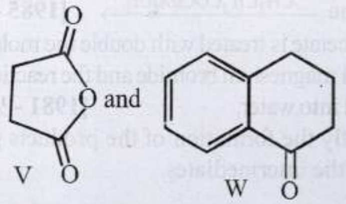
49. Compounds formed from **P** and **Q** are, respectively

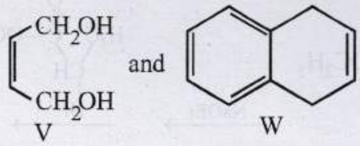
(a) Optically active S and optically active pair **[T, U]**
(b) Optically inactive S and optically inactive pair **[T, U]**
(c) Optically active pair **[T, U]** and optically active **S**
(d) Optically inactive pair **[T, U]** and optically inactive **S**

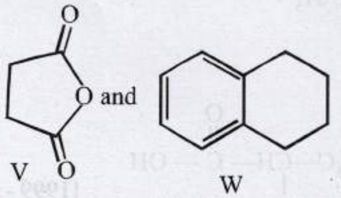
50. In the following reaction sequences **V** and **W** are respectively

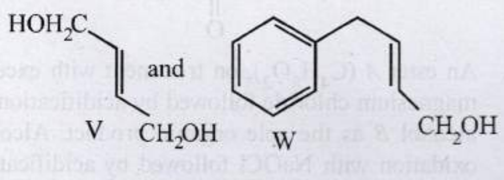
$$\mathbf{Q} \xrightarrow[\Delta]{H_2/Ni} \mathbf{V}$$



(a)


(b)


(c)


(d)


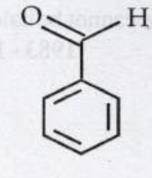
Passage-V

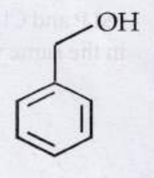
In the following reaction sequence, the compound **J** is an intermediate.

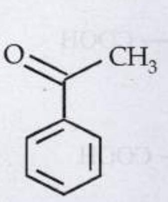
$$\mathbf{I} \xrightarrow[CH_3COONa]{(CH_3CO)_2O} \mathbf{J} \xrightarrow[\text{(ii) } SOCl_2 \text{ (iii) anhyd. } AlCl_3]{\text{(i) } H_2, Pd/C} \mathbf{K}$$

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

(a)


(b)


(c)


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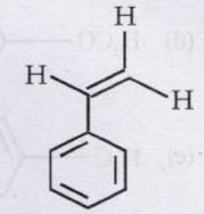
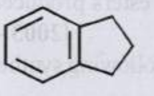


52. The compound **K** is

(a)


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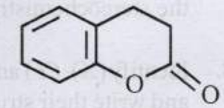
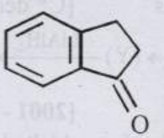
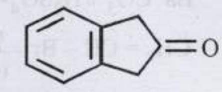


(b)


(d)


9 Assertion and Reason Type Questions

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

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

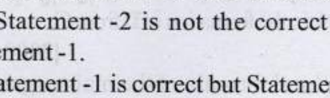
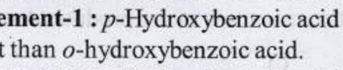
53. **Statement-1 :** *p*-Hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.
Statement-2 : *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. **[2007]**

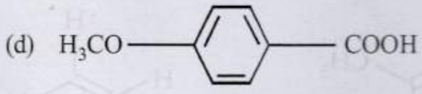
54. **Statement-1 :** Acetic acid does not undergo haloform reaction.
Statement-2 : Acetic acid has no alpha hydrogens. **[1998 - 2 Marks]**

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

10 Subjective Problems

56. Match the K_a values **[2003]**

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

(d)  3.3×10^{-5}

(e)  4.2×10^{-5}

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

[2003 - 2 Marks]

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

$Ba^*CO_3 + H_2SO_4 \longrightarrow (X)$ gas [C* denotes C^{14}]

$CH_2 = CH - Br \xrightarrow[\text{(ii) X (iii) } H_3O^+]{\text{(i) Mg/ether}} (Y) \xrightarrow{LiAlH_4} (Z)$

[2001 - 5 Marks]

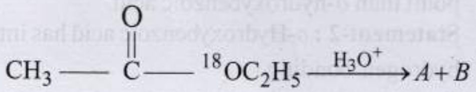
Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

59. An organic compound **A**, $C_8H_4O_3$, 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** ($C_{14}H_{10}N_2$). Identify **A, B, C** and **D**. Explain the formation of **D** from **C**.

[2000 - 5 Marks]

60. Write the structural formula of the main organic product formed when :

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



$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - {}^{18}OC_2H_5 \xrightarrow{H_3O^+} A + B$$

[2000 - 2 Marks]

(*ii*) $(COOH)_2 + (CH_2OH)_2 + \text{Conc.} H_2SO_4 \xrightarrow{} \overset{\textbf{F}}{- - - -}$ **[1997 - 1 Mark]**

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

$\xrightarrow{SOCl_2} \overset{\textbf{G}}{- - - - - -} \xrightarrow[AlCl_3]{\text{anhydrous}} \overset{\textbf{H}}{- - - - - -}$

$\textbf{H} \xrightarrow[HCl]{Zn-Hg} \overset{\textbf{I}}{- - - - - -}.$ **[1995 - 2 Marks]**

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

$\xrightarrow[C_2H_5\,OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}} \overset{\textbf{D}}{- - - - - -}$

[1995 - 1 Mark]

(*v*) $CH_3 - CH_2 - COOH \xrightarrow[\text{bromine}]{\text{P and}} \overset{\textbf{A}}{- - - - -}$

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

[1995 - 2 Marks]

(*vi*) $C_6H_5CH_2CO_2CH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr\text{(excess)}}$

[1994 - 1 Mark]

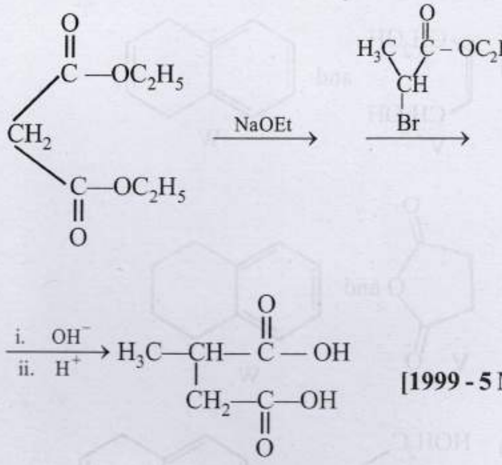
(*vii*) $C_6H_5COOH + CH_3MgI \rightarrow ? + ?$

[1993 - 2 Marks]

(*viii*) benzene $\xrightarrow{CH_3CH_2COCl/AlCl_3}$ **[1985 - 1 Mark]**

(*ix*) ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water. **[1981 - ½ Mark]**

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



[1999 - 5 Marks]

62. An ester *A* ($C_4H_8O_2$), 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;

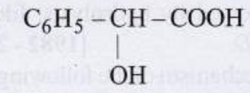
[1985 - 1 Mark]

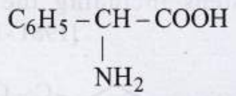
(*iii*) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. **[1983 - 1 Mark]**

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

(*i*) $C_6H_5-CO-CH_2-COOH$

(*ii*) $C_6H_5-CO-COOH$

(*iii*)

$C_6H_5-\underset{\underset{\displaystyle OH}{|}}{CH}-COOH$

(*iv*)

$C_6H_5-\underset{\underset{\displaystyle NH_2}{|}}{CH}-COOH$

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]**

$$PCl_5 + SO_2 \longrightarrow A + B$$
$$A + CH_3COOH \longrightarrow C + SO_2 + HCl$$
$$2C + (CH_3)_2Cd \longrightarrow 2D + CdCl_2$$

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]**

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

$$\xrightarrow[ZnCl_2]{HCl} G \xrightarrow[H^+]{KCN} H;$$

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 - 2Marks]**

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

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

74. Complete the following reactions :

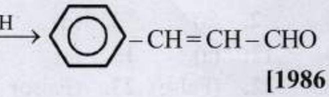
$$CH_3COOH \xrightarrow{?} ClCH_2COOH \xrightarrow{\text{excess ammonia}} ?$$

[1988 - 1 Mark]

75. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B), (A) on mild oxidation gives (C), (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D), (D) with phosphorus pentachloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid.
Identify the compounds A, B, C, D and E. **[1987 - 5 Marks]**

76. Complete the following with appropriate structures :

(*i*) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$ **[1986 - 1 Mark]**

(*ii*) $? \xrightarrow{\text{NaOH}}$

[1986 - 1 Mark]

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]**

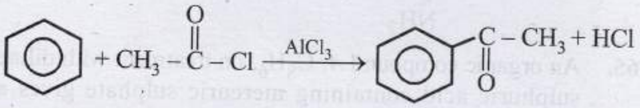
80. State the conditions under which the following preparations are carried out. Give the necessary equations which need not be balanced.

(*i*) Ethanol from acetylene **[1983 - 1 Mark]**

(*ii*) Acetic acid from methyl iodide **[1983 - 1 Mark]**

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

82. Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates. **[1981 - 3 Marks]**



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)

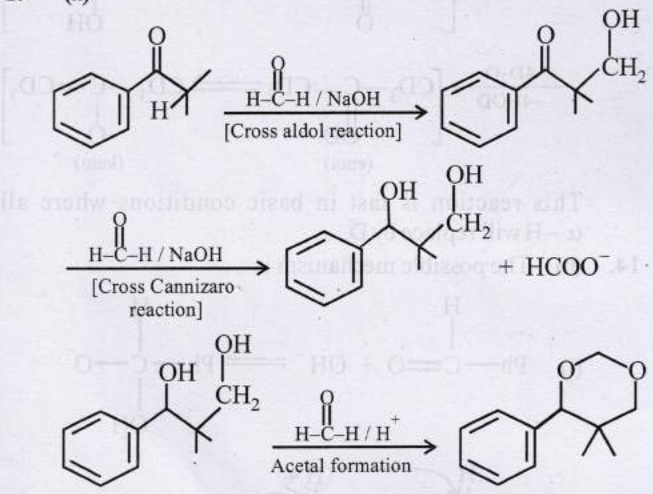
Topic-2 : Preparation and Properties of Carboxylic Acids and its Derivatives

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)

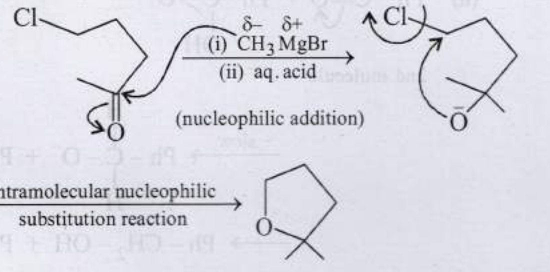
Hints & Solutions

Topic-1: Preparation and Properties of Carbonyl Compounds

1. (a)

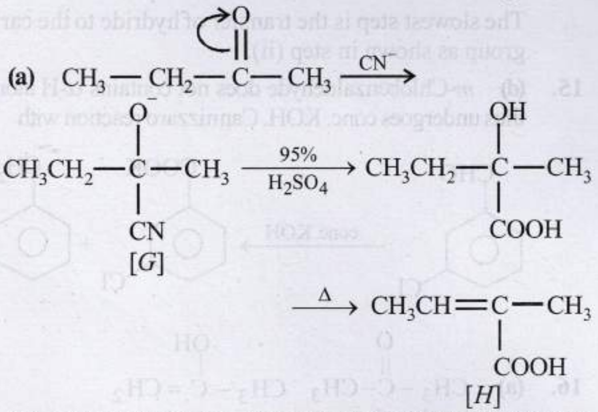


2. (d)



5-Keto-2-methylhexanal

3. (a)



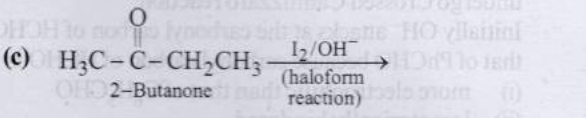
$$CH_3-CH_2-\overset{\overset{\curvearrowright}{O}}{\overset{\|}{C}}-CH_3 \xrightarrow{CN^-} \underset{[G]}{CH_3CH_2-\underset{CN}{\overset{O^-}{C}}-CH_3} \xrightarrow[H_2SO_4]{95\%} CH_3CH_2-\underset{COOH}{\overset{OH}{C}}-CH_3$$

$$\xrightarrow{\Delta} \underset{[H]}{CH_3CH{=}\underset{COOH}{C}-CH_3}$$

4. **(b)** The ring to which –NH group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which –C=O is attached is deactivated. Hence, the electrophile 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 $(CH_3CO)_2O$. 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.

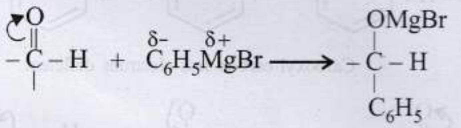
6. **(c)**



$$\underset{\text{2-Butanone}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3} \xrightarrow[\text{(haloform reaction)}]{I_2/OH^-}$$

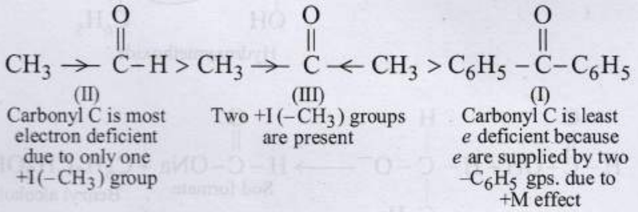
$$CHI_3\downarrow + CH_3CH_2COO^-Na^+ \xrightarrow{H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

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.



$$-\overset{\overset{O}{\|}}{\underset{|}{C}}-H + \overset{\delta-}{C_6H_5}\overset{\delta+}{MgBr} \longrightarrow -\underset{C_6H_5}{\overset{OMgBr}{C}}-H$$

Thus the decreasing order should be



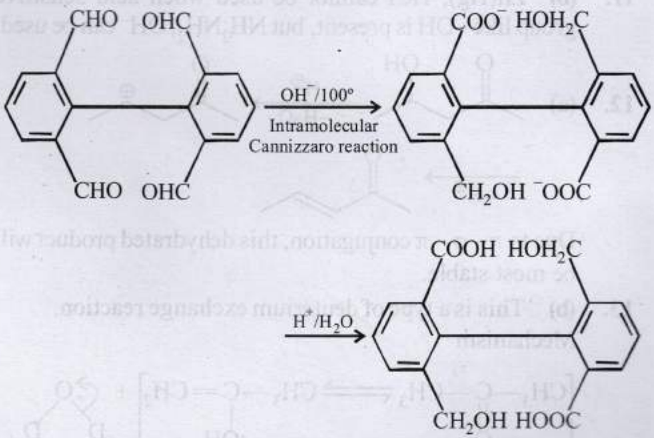
$$\underset{(II)}{CH_3\rightarrow\overset{\overset{O}{\|}}{C}-H} > \underset{(III)}{CH_3\rightarrow\overset{\overset{O}{\|}}{C}\leftarrow CH_3} > \underset{(I)}{C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5}$$

(II) Carbonyl C is most electron deficient due to only one +I($-CH_3$) group

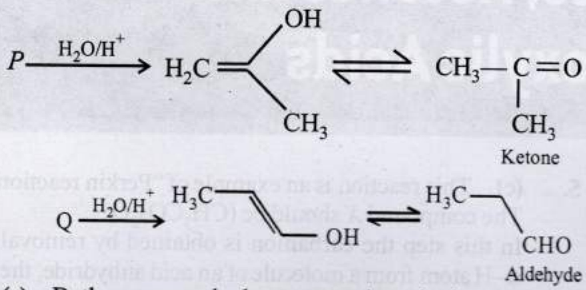
(III) Two +I ($-CH_3$) groups are present

(I) Carbonyl C is least *e* deficient because *e* are supplied by two $-C_6H_5$ gps. due to +M effect

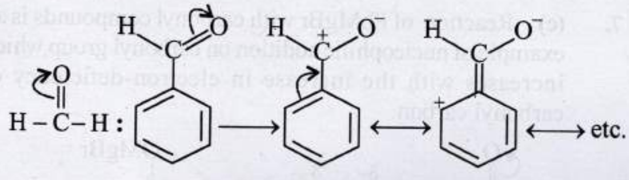
8. **(b)**



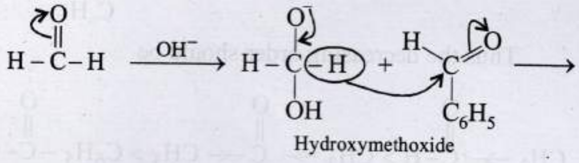
9. **(c)** Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.

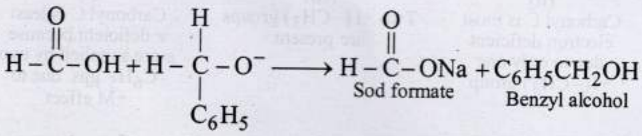


10. **(a)** Both compounds do not contain α-hydrogen hence undergo Crossed Cannizzaro reaction.
Initially OH^- attacks at the carbonyl carbon of HCHO than that of PhCHO because carbonyl carbon of HCHO is
(i) more electrophilic than that of C_6H_5CHO
(ii) less sterically hindered
to give hydroxymethoxide which acts as hydride donor in next step to give sodium formate.



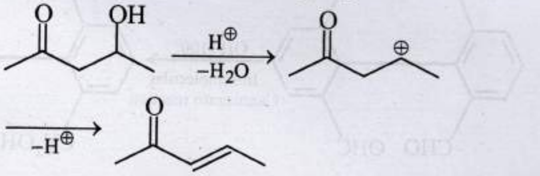
Carboxyl carbon less electrons deficient





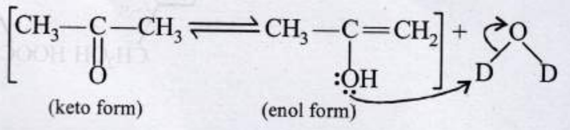
11. **(b)** Zn(Hg), HCl cannot be used when acid sensitive group like –OH is present, but NH_2NH_2, OH^- can be used.

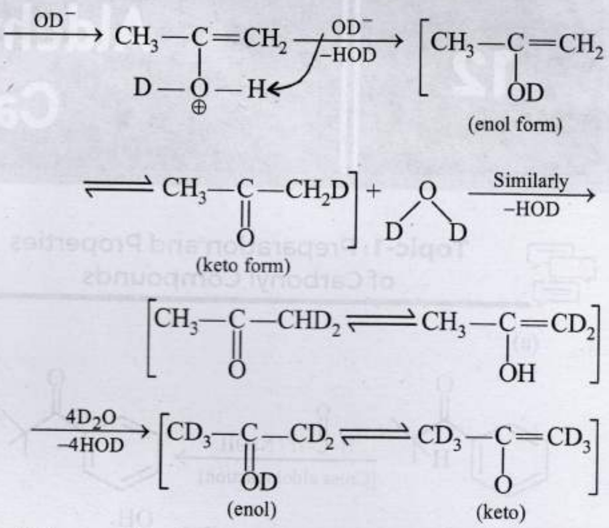
12. **(a)**



Due to π – σ – π conjugation, this dehydrated product will be most stable.

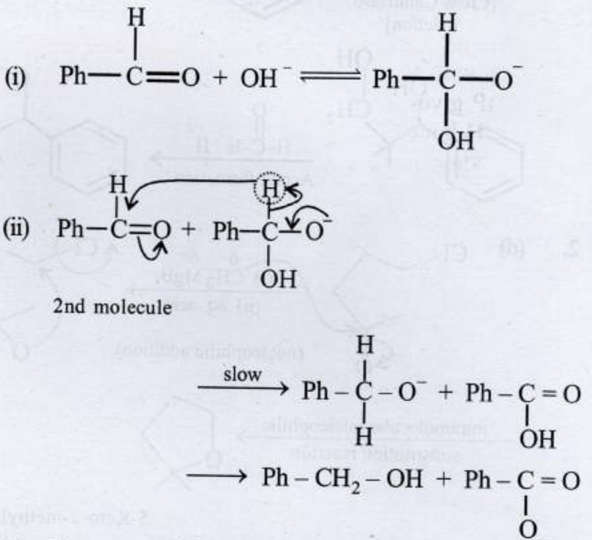
13. **(b)** This is a type of deuterium exchange reaction.
Mechanism





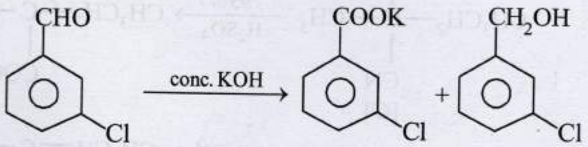
This reaction is fast in basic conditions where all α – H will replace by D.

14. **(b)** The possible mechanism is

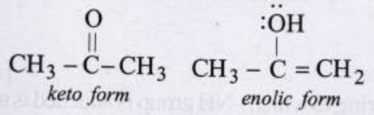


The slowest step is the transfer of hydride to the carbonyl group as shown in step (ii).

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



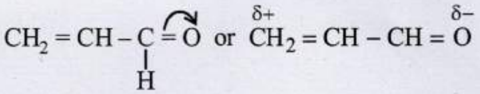
16. **(a)**



$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ *keto form* $CH_3-\overset{\overset{:\ddot{O}H}{|}}{C}=CH_2$ *enolic form*

No. of σ bonds in enolic form : 3 + 1 + 1 + 1 + 1 + 2 = 9
No. of π bonds in enolic form : 1
No. of lone pairs of electrons in enolic form = 2

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



$$CH_2 = CH - \underset{\displaystyle H}{\underset{|}{C}} = O \text{ or } CH_2 = CH - CH = \overset{\delta-}{O}$$

18. (c) Iodoform test is given by compounds having $-COCH_3$, $CHOHCH_3$ and CH_3CH_2OH.
Thus diethyl ketone does not give this test.

19. (b) The compound containing α-H atom (CH_3CHO) does not undergo Cannizzaro's reaction. The other three reaction α-hydrogen.

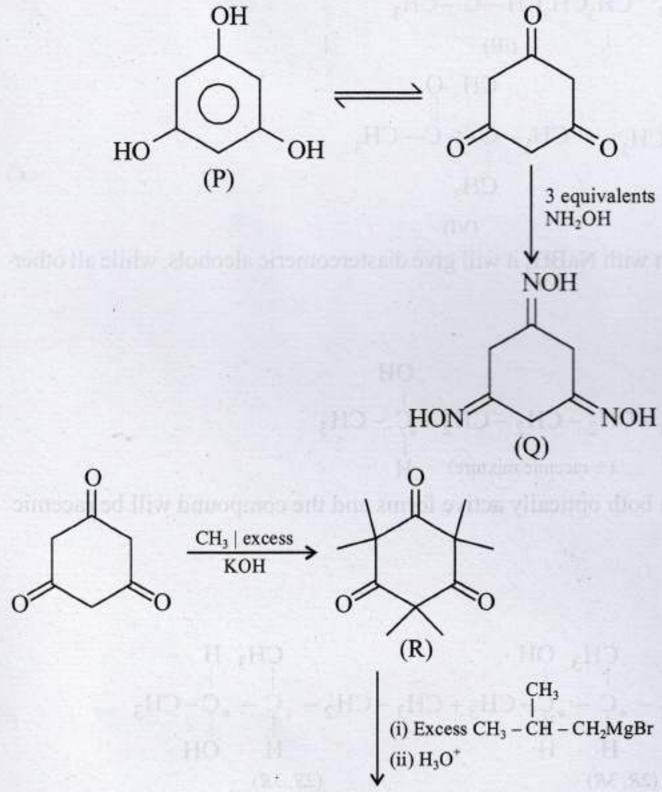
20. (c) $\underset{\text{Fehling solution}}{CH_3CHO + 2Cu^{2+} + OH^-} \rightarrow CH_3COOH + \underset{\text{(red)}}{Cu_2O}\downarrow$

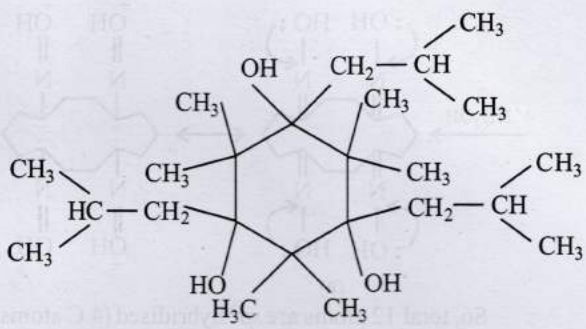
21. (b) Compounds having $-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$ groups, show positive iodoform test.

Hence, $CH_3 - CH_2 - CH_2 - \underset{\underset{\displaystyle O}{\|}}{C} - CH_3$ (pentanone-2) gives this test.

22. (b) Fehling solution, Schiff's reagent & Tollen's reagent react only with aldehydes, but Grignard reagents react both with aldehydes and ketones.

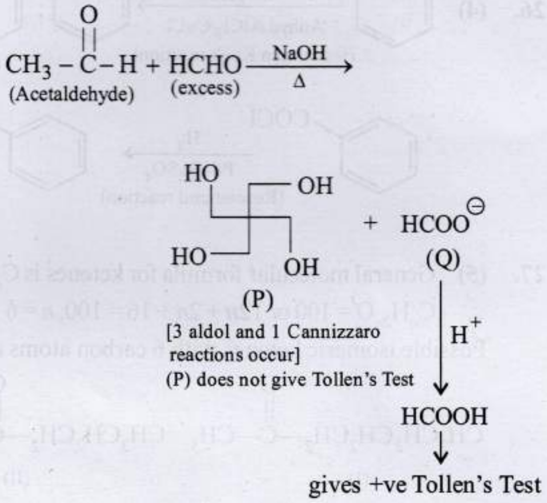
23. (12) P gives $FeCl_3$ test and there are no intramolecular H-bonds.
Thus, P wil be a trihydric phenol.

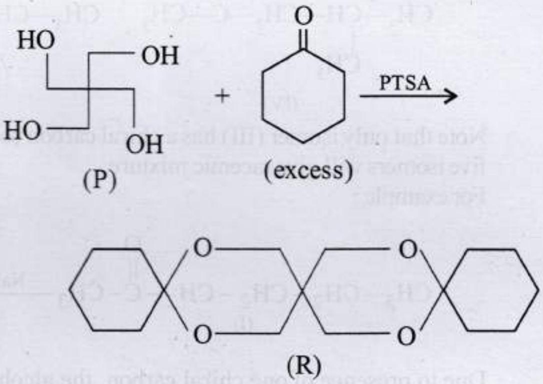




Number of CH_3 groups = 12

24. (18) Reactions taking place as:



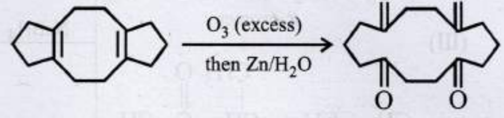


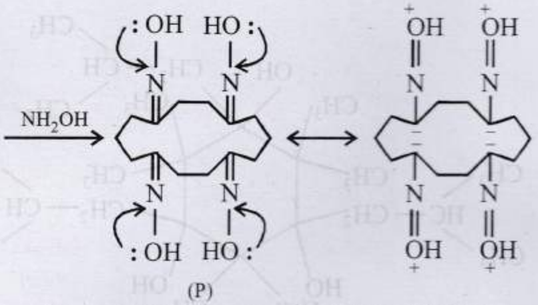
Number of CH_2 groups in R = 14

Number of O-atoms = 4

Required Answer = 14 + 4 = 18

25. (12)

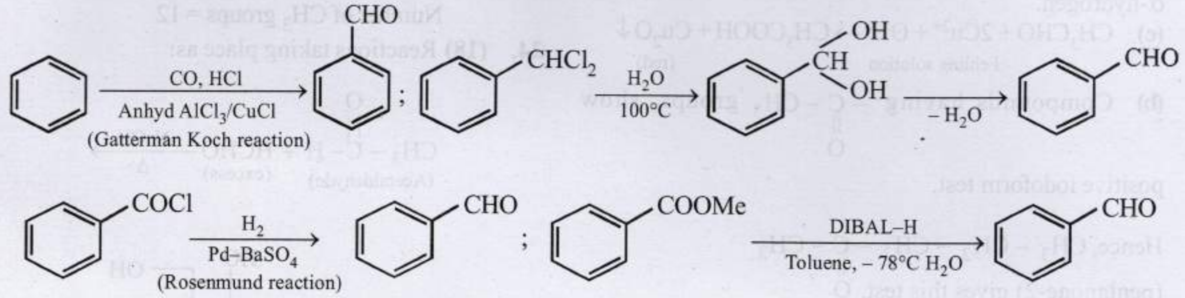




(P)

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

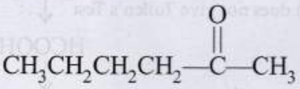
26. **(4)**



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

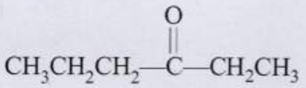
$\therefore$ $C_nH_{2n}O = 100$ or $12n + 2n + 16 = 100, n = 6$

Possible isomeric ketones with 6 carbon atoms are



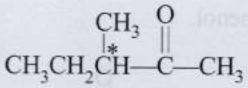
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(I)



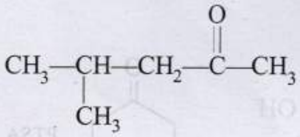
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(II)



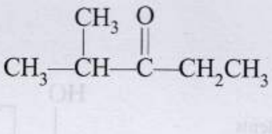
$CH_3CH_2\overset{CH_3}{\overset{|*}{C}}H-\overset{O}{\overset{\|}{C}}-CH_3$

(III)



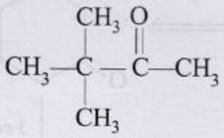
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(IV)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(V)

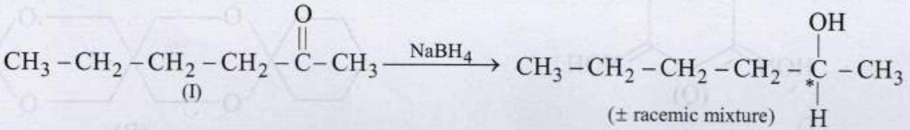


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH_3$

(VI)

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.

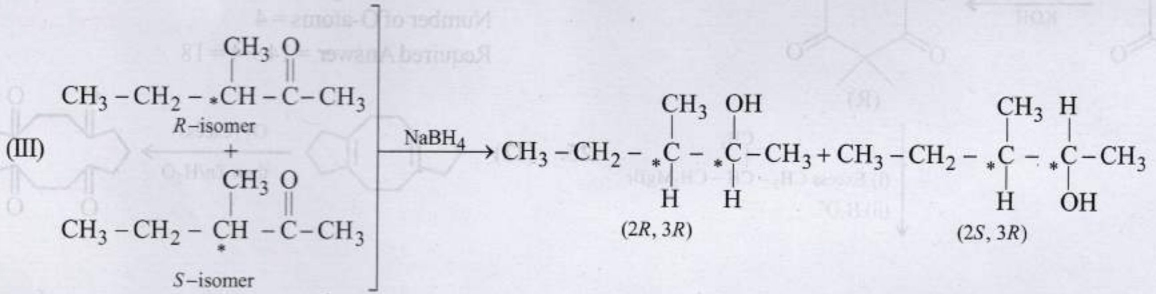
For example :



$$\underset{(I)}{CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{NaBH_4} CH_3-CH_2-CH_2-CH_2-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{\underset{*}{C}}}}}-CH_3$$

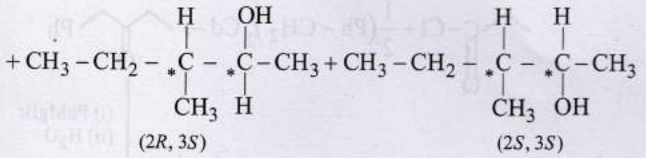
(± racemic mixture)

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



$$(III)\left.\begin{array}{c} CH_3-CH_2-{}_*\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-CH_3 \\ R\text{–isomer} \\ + \\ CH_3-CH_2-\underset{*}{\overset{CH_3}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-CH_3 \\ S\text{–isomer} \end{array}\right] \xrightarrow{NaBH_4} \underset{(2R,\,3R)}{CH_3-CH_2-{}_*\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-{}_*\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_3} + \underset{(2S,\,3R)}{CH_3-CH_2-{}_*\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-{}_*\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3}$$

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



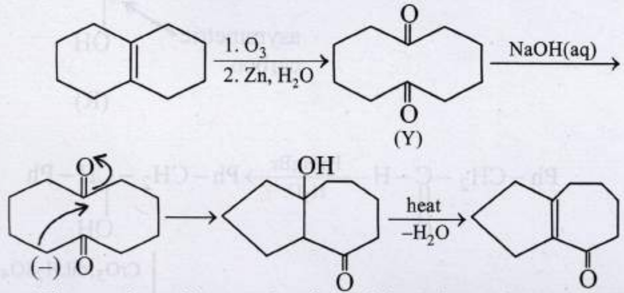
$$+CH_3-CH_2-{}_{*}\overset{H}{\underset{CH_3}{C}}-{}_{*}\overset{OH}{\underset{H}{C}}-CH_3+CH_3-CH_2-{}_{*}\overset{H}{\underset{CH_3}{C}}-{}_{*}\overset{H}{\underset{OH}{C}}-CH_3$$

$(2R, 3S)$ $(2S, 3S)$

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

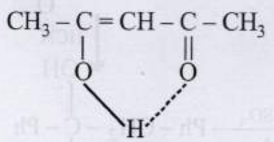
Note : All stereoisomers are reacted separately.

28. **(1)**



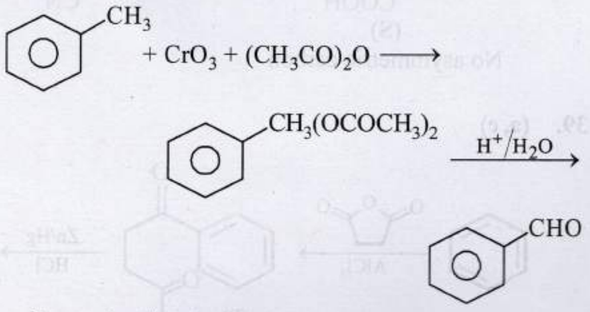
The number of intra molecular aldol condensation products (α, β –unsaturated carbonyl compound formed from **Y** is 1.

29.



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

30. **$C_6H_5CH(OCOCH_3)_2$ benzylidene acetate;**



31. **sodium potassium tartarate.**

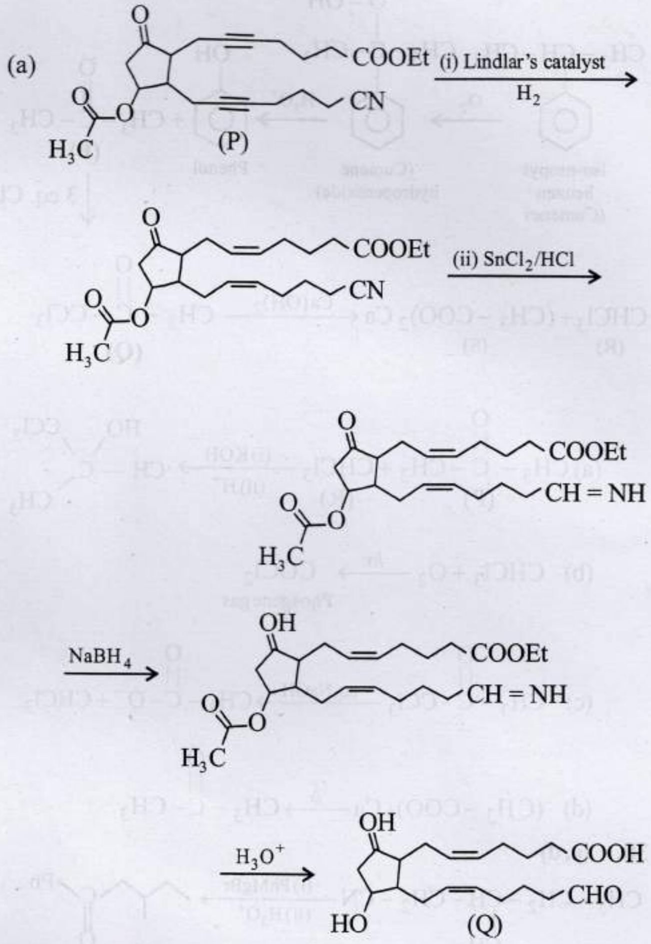
32. (*i*) Free radical substitution (*ii*) Thermite process
(*iii*) Nucleophilic addition (*iv*) Cyanamide process;
(*v*) Nucleophilic subsitution (*vi*) Bayer's process
(*vii*) Homologous pair
(*viii*) Electrophilic substitution (*ix*) Ostwald's process
(*x*) Homolytic addition.

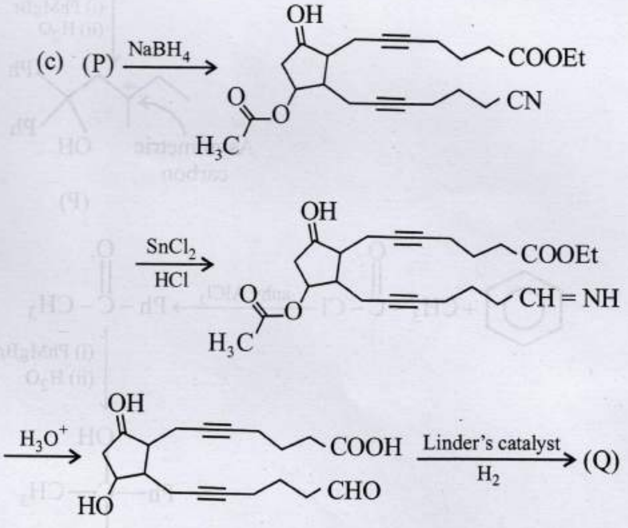
33. **False.** Grignard reagents react with ketones to form *ter*-alcohols; hence here, *ter*-butanol will be formed.

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

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

36. **(a, c, d)**

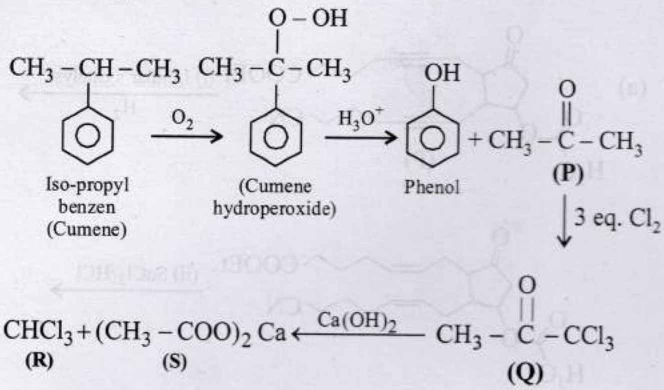


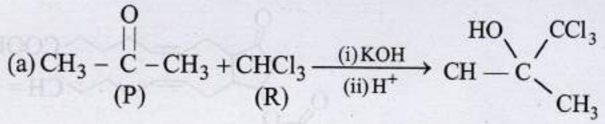


(d) Similarly, (P) $\xrightarrow[\text{(iii) SnCl}_2\text{/HCl, (iv) H}_3\text{O}^+]{\text{(i) Lindlar's catalyst, H}_2\text{, (ii) NaBH}_4\text{,}}$ (Q)

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

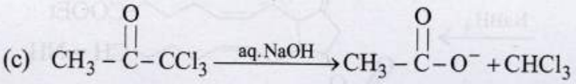
37. (a, b, d)



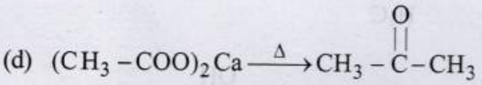


$$\text{(a) } \underset{(P)}{CH_3-\overset{\overset{O}{||}}{C}-CH_3} + \underset{(R)}{CHCl_3} \xrightarrow[\text{(ii) } H^+]{\text{(i) KOH}} CH-\underset{\diagdown\, CH_3}{\overset{HO\ \diagup\ CCl_3}{C}}$$

(b) $CHCl_3 + O_2 \xrightarrow{h\nu} \underset{\text{Phosgene gas}}{COCl_2}$

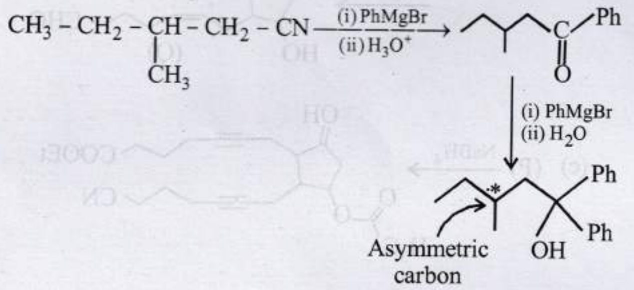


$$\text{(c) } CH_3-\overset{\overset{O}{||}}{C}-CCl_3 \xrightarrow{\text{aq. NaOH}} CH_3-\overset{\overset{O}{||}}{C}-O^- + CHCl_3$$

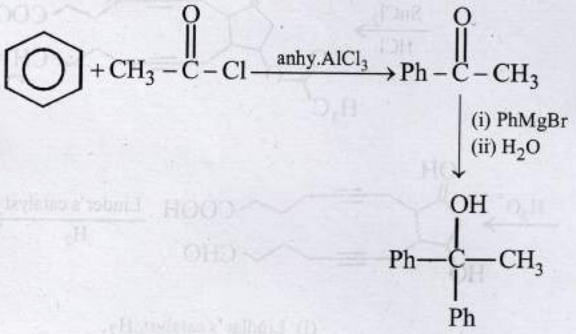


$$\text{(d) } (CH_3-COO)_2Ca \xrightarrow{\Delta} CH_3-\overset{\overset{O}{||}}{C}-CH_3$$

38. (c, d)

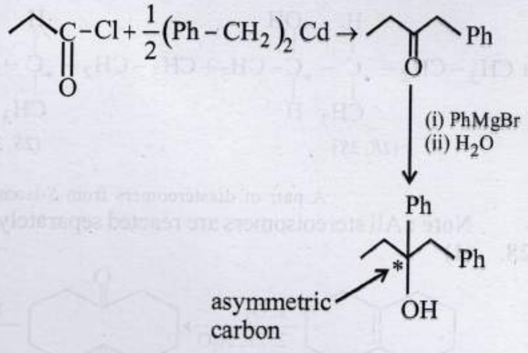


(P)

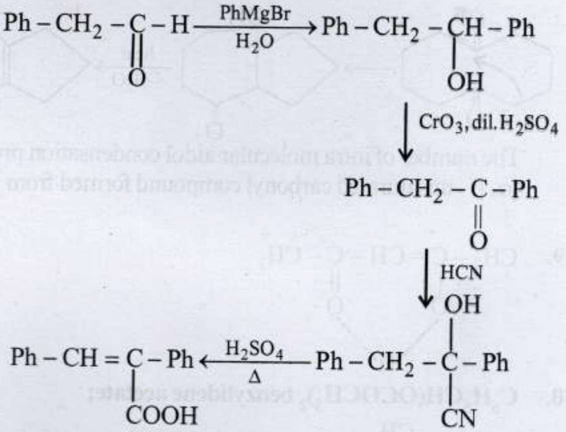


(Q)

No asymmetric carbon



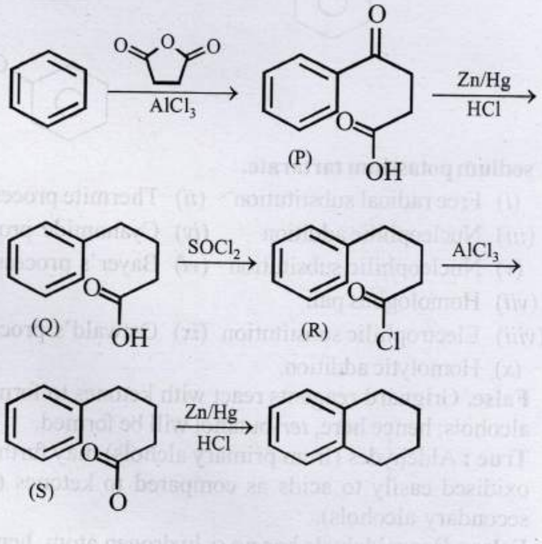
(R)



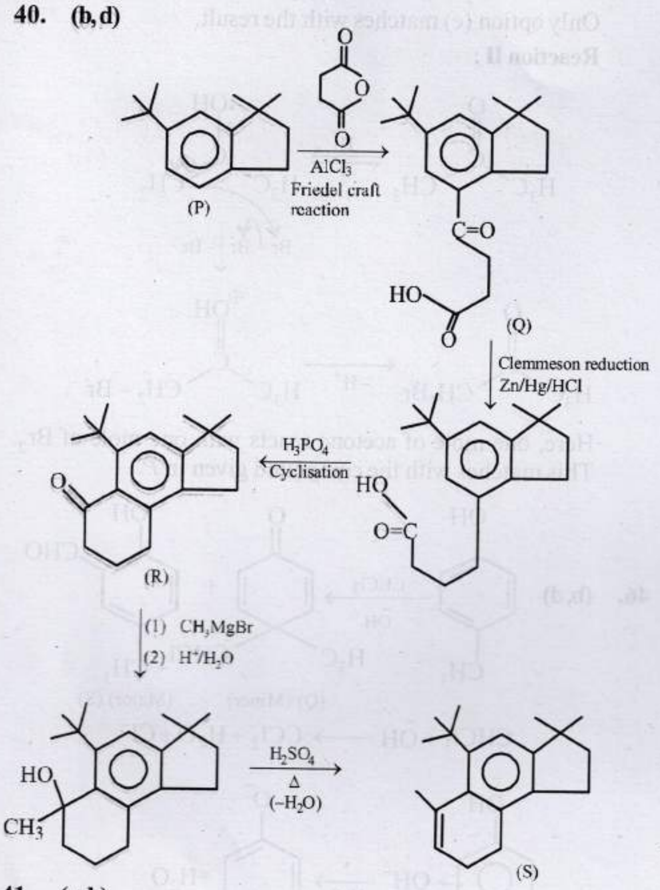
(S)

No asymmetric carbon

39. (a, c)

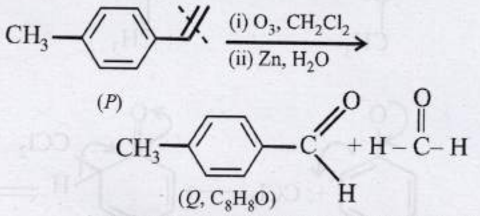


40. **(b,d)**

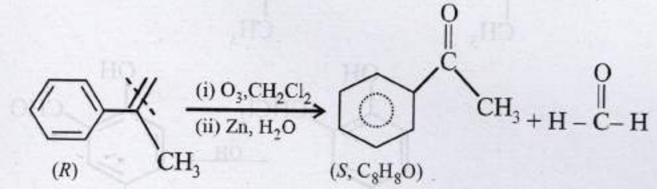


41. **(a,b)**

(a)

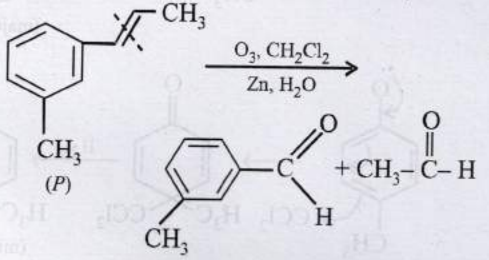


(+ve Cannizaro reaction, no haloform reaction)

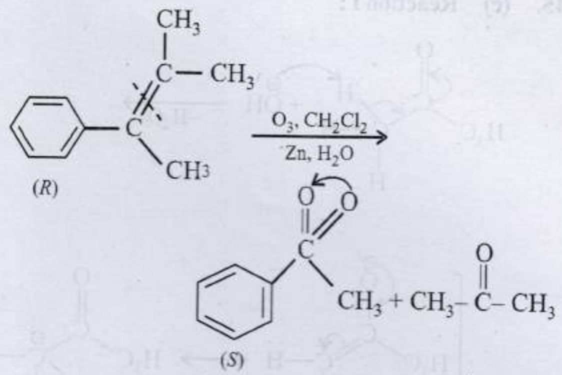


(+ve haloform reaction, not Cannizzaro reaction)

(b)

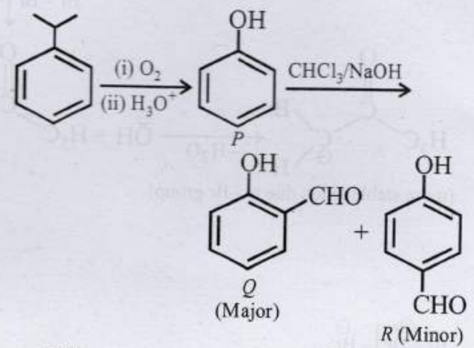


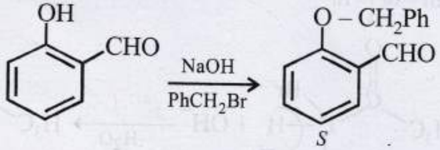
(Q) (+ve Cannizaro reaction, not haloform reaction)



(+ve haloform reaction, not Cannizzaro reaction)

42. **(b, c)**

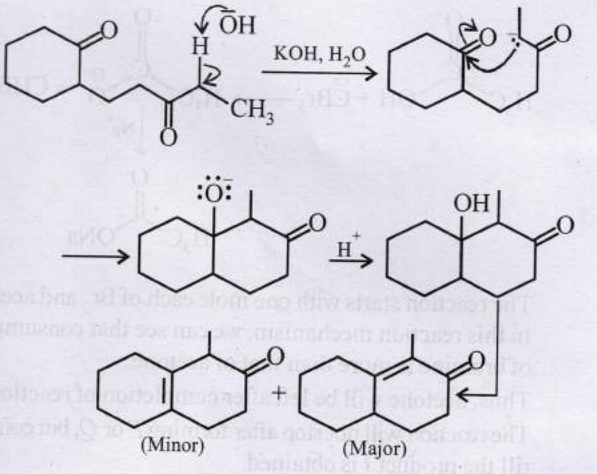




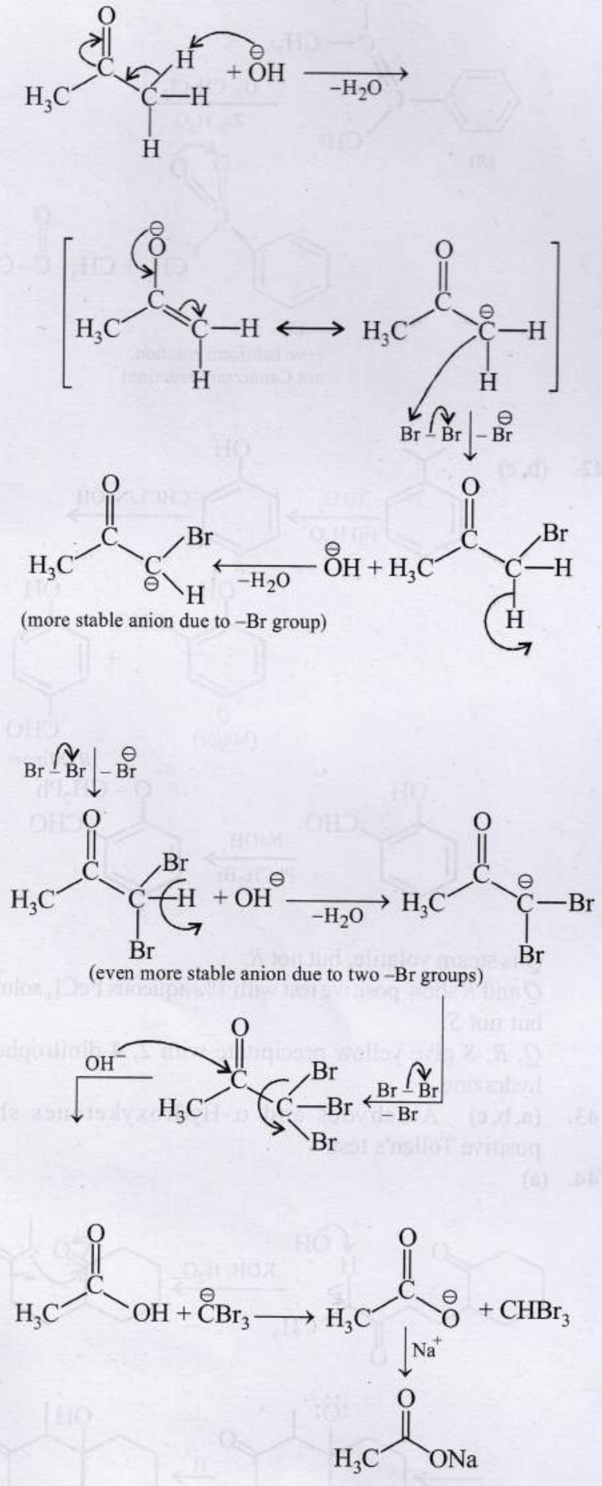
Q is steam volatile, but not R.
Q and R show positive test with 1% aqueous FeCl$_3$ solution but not S.
Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

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

44. **(a)**



45. (c) Reaction I :



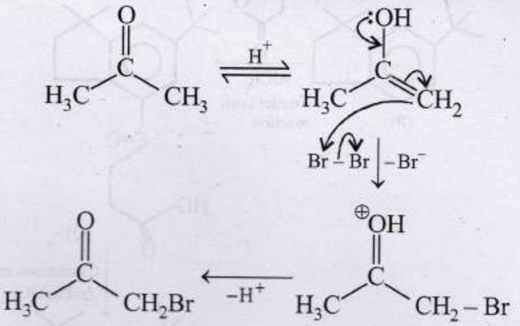
The reaction starts with one mole each of Br_2 and acetone. In this reaction mechanism, we can see that consumption of bromine is more than that of acetone.

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.

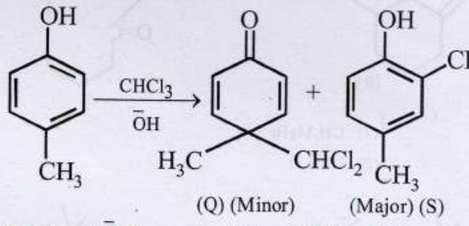
Only option (c) matches with the result.

Reaction II :

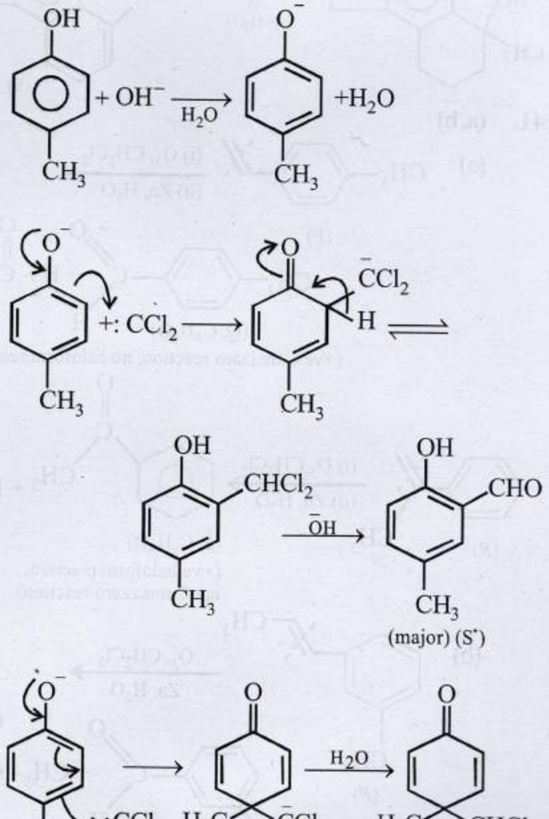


Here, one mole of acetone reacts with one mole of Br_2. This matches with the compound given in *P*.

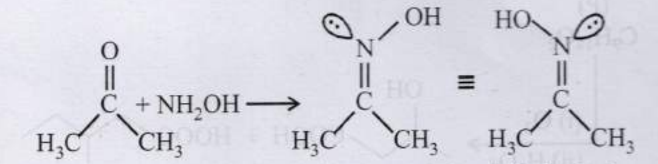
46. (b,d)



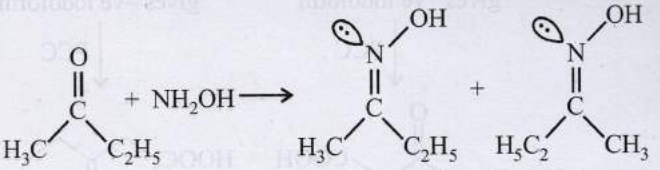
$$CHCl_3 + \bar{O}H \longrightarrow :CCl_2 + H_2O + Cl^-$$



47. (b, c)

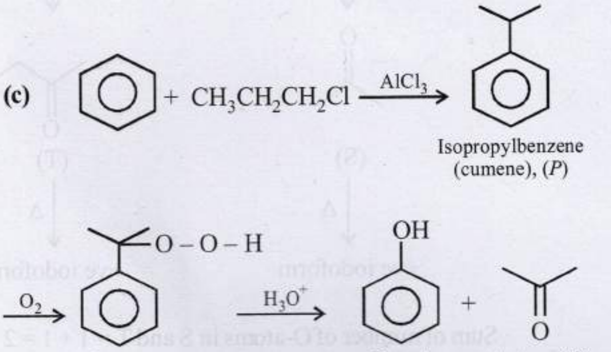


(same compound optically inactive)
(methyl–methyl ketoxime)



(syn-ethyl methyl ketoxime) (anti-ethyl methyl ketoxime)
geometrical isomers

48. (c)



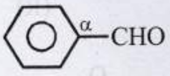
Isopropylbenzene (cumene), (*P*)

Cumene hydroperoxide Phenol Acetone (Q)

49. (a, b, d) Carbonyl compounds having α – H or α - D undergo aldol condensation.

(a) $\overset{\alpha}{C}H_3CHO$ (b) $CH_3\overset{\alpha}{C}H_2CHO$

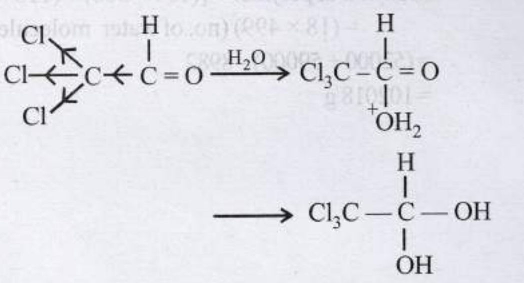
(c)



(No α – H)

(d) $\overset{\alpha}{C}D_3CHO$ (α–D present)

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, $CCl_3CH(OH)_2$, which is quite stable due to intramolecular H–bonding between two – OH groups.



51. (b, d)

(a) $HCHO \xrightarrow{OH^-} CH_3OH + HCOO^-$

(No new C – C bond is formed)

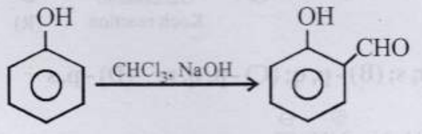
(b) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5 - CH_3$

(New C – C bond is formed)

(c) $\rangle C=O \xrightarrow[HCl]{Na/H_g} \rangle CH_2$

(No new C – C bond is formed)

(d)



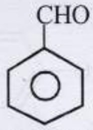
(New C – C bond is formed)

52. (a, b) Aldehydes and ketones containing α-hydrogen atom undergo aldol condensation.

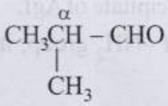
53. (b, d) Keto-enol tautomerism is shown in compounds having α-hydrogen on the C adjacent to the CO group.

54. (a, c) Aldehydes having at least one α-hydrogen atom undergo aldol condensation.

$CH_3\overset{\alpha}{C}H_2CHO$
propionaldehyde
(a)

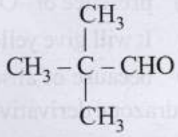


benzaldehyde
(no α- hydrogen atom)
(b)



$$CH_3\overset{\alpha}{C}H\underset{CH_3}{|}-CHO$$

2-methylpropionaldehyde
(c)

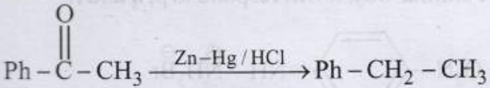


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHO$$

2, 2-dimethylpropionaldehyde
(no α-hydrogen atom)
(d)

55. (d) P → 3, Q → 4, R → 5, S → 2

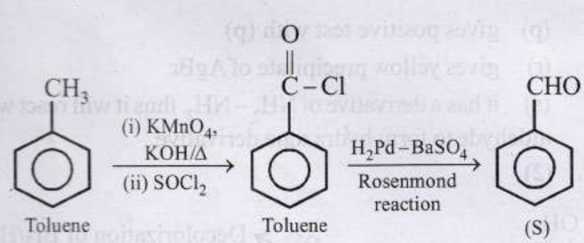
(1)



$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Zn-Hg/HCl} Ph-CH_2-CH_3$$

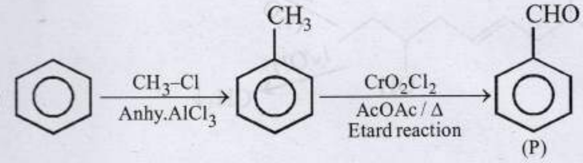
Acetophenone

(2)



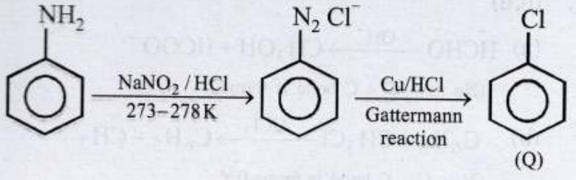
Toluene Toluene (S)

(3)

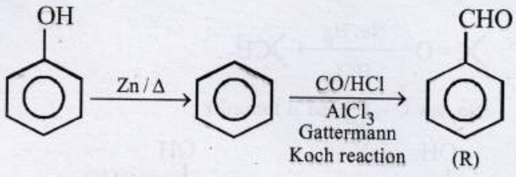


(P)

(4)



(5)



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

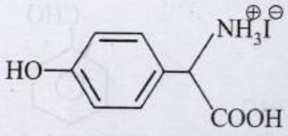
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$

(p) does not have carbon thus, will not respond to (p).

(r) because of presence of $Cl^{\ominus}$ ion, it will give white precipitate of AgCl with $AgNO_3$.

(s) because of $-NH_2$ group it will react with aldehydes to form hydrazone derivative.

(B)



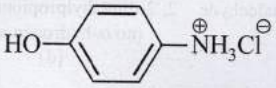
(p) because of presence of C – N bond, it will form prussian blue colour with $FeSO_4$.

(q) presence of –OH group will give positive $FeCl_3$ test.

(r) It will give yellow precipitate of AgI.

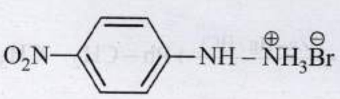
(s) because of absence of $-NH_2$ group, it will not give hydrazone derivative.

(C)



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

(D)

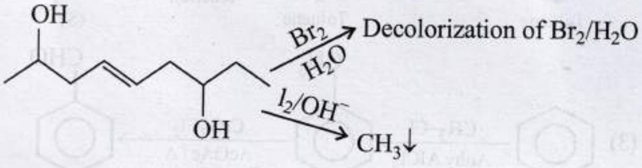


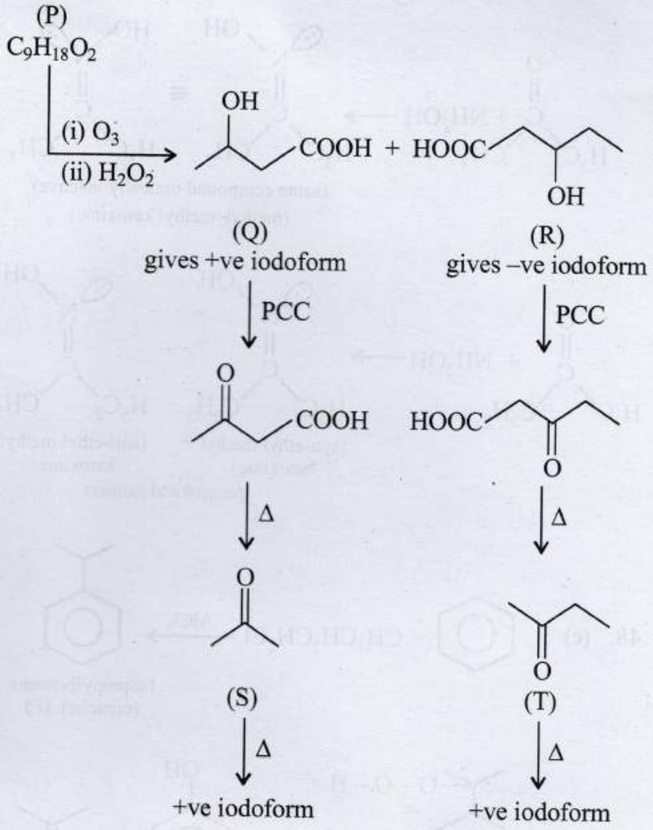
(p) gives positive test with (p)

(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.

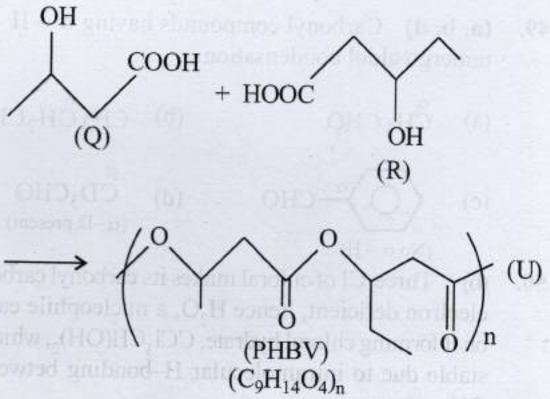
57. (2)





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

58. (102018)

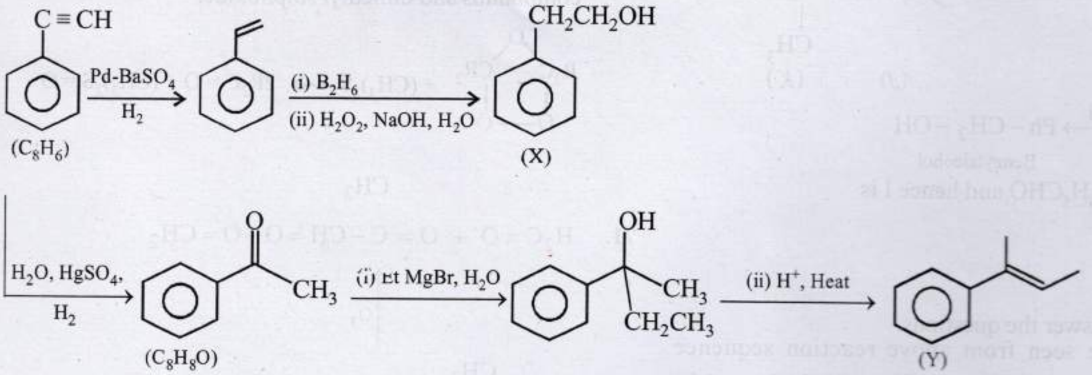


Mol. Wt. of polymer = [(104 × 500) + (118 × 500)] – (18 × 499) (no. of water molecules released)

= (52000 + 59000) – 8982

= 102018 g

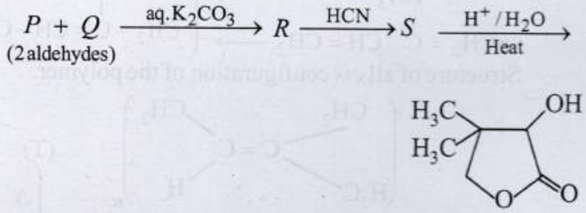
For 59-60. (Passage-I)



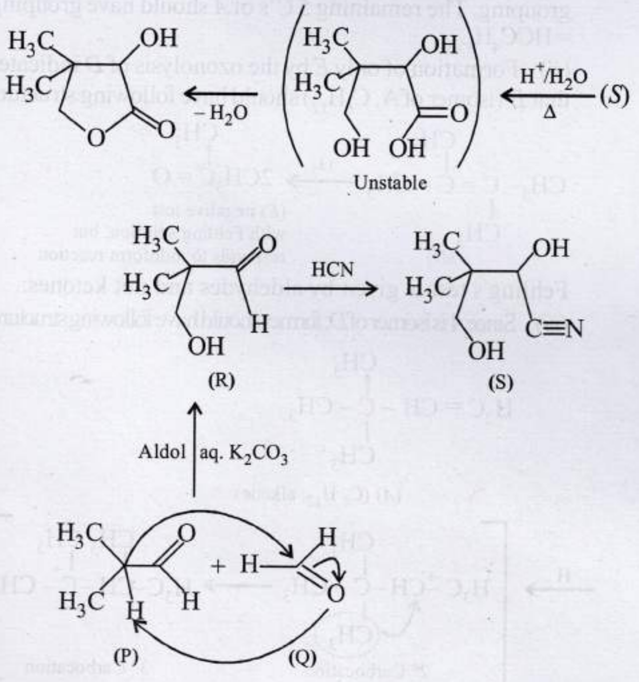
59. (c) **60.** (d)

For 61-63. (Passage-II)

Let us summarize the given facts of the problem.



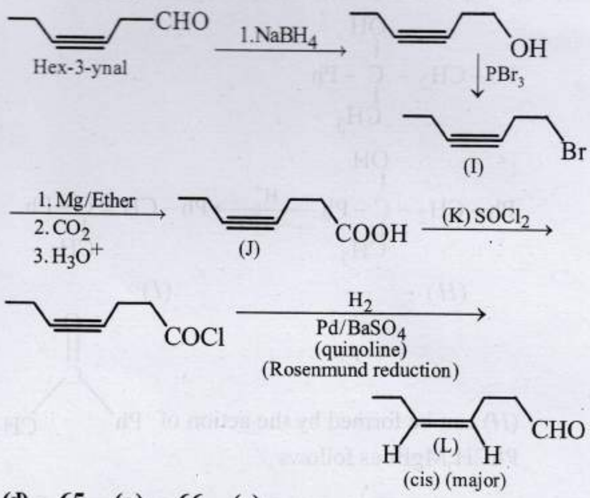
Structures of *P*, *Q*, *R* and *S* can be established on going backward from the known final product.



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)

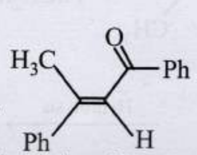


64. (d) **65.** (a) **66.** (c)

For 67-69. (Passage-IV)

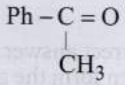
Before answering these question let us complete the sequence of reactions given in data.

The given compound (*M*) *i.e.*

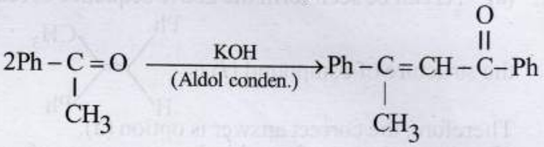


is the only product formed by the action of KOH on compound *K*.

The compound *K* is

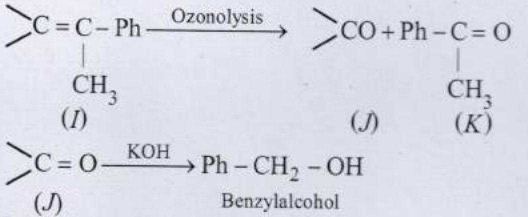


$$\underset{\displaystyle CH_3}{Ph-\underset{|}{C}=O}$$



$$2\,Ph-\underset{\underset{\displaystyle CH_3}{|}}{C}=O \xrightarrow[\text{(Aldol conden.)}]{KOH} Ph-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{||}}{C}-Ph$$

Compound *K* (*i.e.* $Ph-\underset{\underset{\displaystyle CH_3}{|}}{C}=O$) is one of the products of ozonolysis of compound *I*. Therefore the compound *I* may be



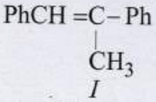
$$>C=\underset{\underset{(I)}{CH_3}}{C}-Ph \xrightarrow{\text{Ozonolysis}} >CO + Ph-\underset{CH_3}{C}=O$$

(J) (K)

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

(J) Benzylalcohol

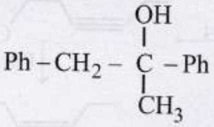
Thus J seems to be C_6H_5CHO and hence I is



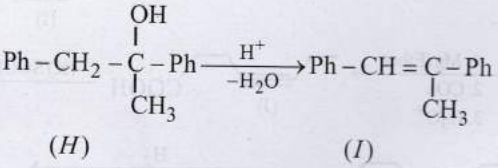
$$\underset{I}{PhCH=\underset{CH_3}{C}-Ph}$$

Now we will try to answer the questions.

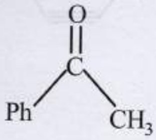
67. **(b)** As can be seen from above reaction sequence compound (I) is $Ph-CH=\underset{CH_3}{C}-Ph$ and it is formed by catalytic dehydration (acid catalysed) of a tertiary alcohol (compound *H*). Therefore, compound *H* is

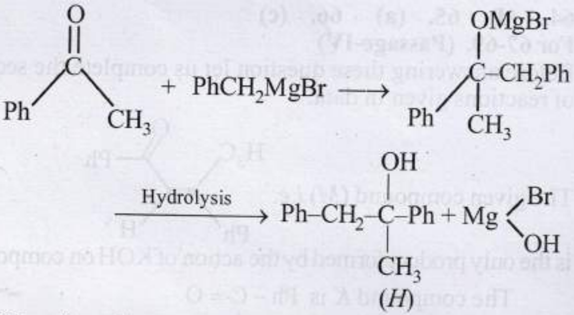


$$Ph-CH_2-\overset{OH}{\underset{CH_3}{C}}-Ph$$



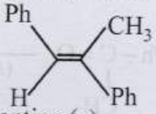
$$\underset{(H)}{Ph-CH_2-\overset{OH}{\underset{CH_3}{C}}-Ph} \xrightarrow[-H_2O]{H^+} \underset{(I)}{Ph-CH=\underset{CH_3}{C}-Ph}$$

(*H*) can be formed by the action of  with $PhCH_2MgBr$ as follows



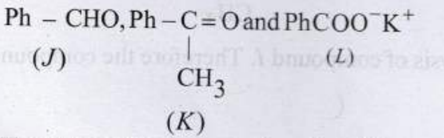
$$Ph\overset{O}{\overset{\|}{C}}CH_3 + PhCH_2MgBr \longrightarrow Ph\overset{OMgBr}{C}(CH_3)-CH_2Ph \xrightarrow{\text{Hydrolysis}} \underset{(H)}{Ph-CH_2-\overset{OH}{\underset{CH_3}{C}}-Ph} + Mg\langle^{Br}_{OH}$$

Therefore, the correct answer is option (b)

68. **(a)** As can be seen form the above sequence of reactions the structure of compound (*I*) is 

Therefore, the correct answer is option (a).

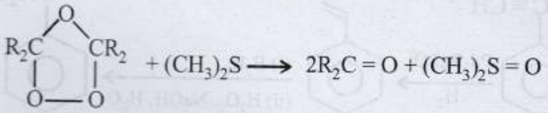
69. **(d)** As can be seen from the above sequence of reactions the structures of compounds *J*, *K* and *L* respectively are



$$\underset{(J)}{Ph-CHO}, \underset{(K)}{Ph-\underset{CH_3}{C}=O} \text{ and } \underset{(L)}{PhCOO^-K^+}$$

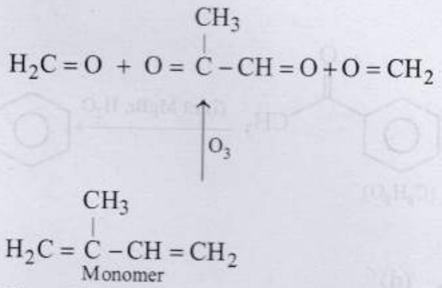
Thus, the correct answer is option (d),

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



$$R_2C(O_3)CR_2 + (CH_3)_2S \longrightarrow 2R_2C=O + (CH_3)_2S=O$$

71.

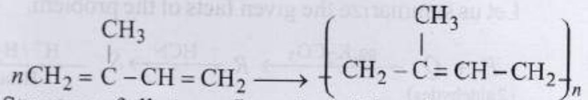


$$H_2C=O + O=\overset{CH_3}{C}-CH=O + O=CH_2$$

$$\uparrow O_3$$

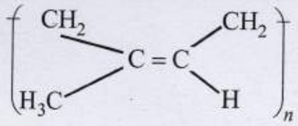
$$\underset{\text{Monomer}}{H_2C=\overset{CH_3}{C}-CH=CH_2}$$

Thus, the possible polymer should be



$$nCH_2=\overset{CH_3}{C}-CH=CH_2 \longrightarrow \left[CH_2-\overset{CH_3}{C}=CH-CH_2\right]_n$$

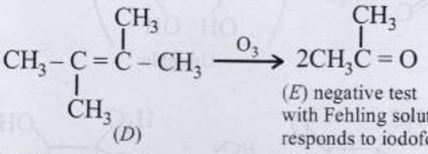
Structure of all *cis* configuration of the polymer.



All *cis* form

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

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

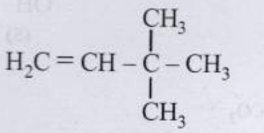


$$\underset{(D)}{CH_3-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3} \xrightarrow{O_3} 2CH_3\overset{CH_3}{C}=O$$

(*E*) negative test with Fehling solution, but responds to iodoform reaction

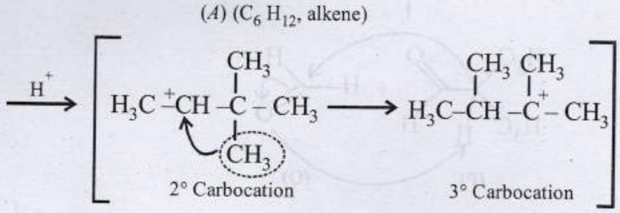
Fehling's test is given by aldehydes and not ketones.

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



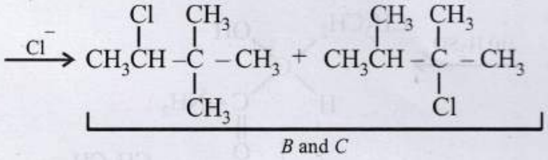
$$H_2C=CH-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

(*A*) (C_6H_{12}, alkene)

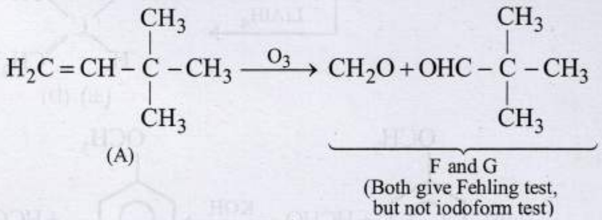


$$\xrightarrow{H^+} \left[H_3C-\overset{+}{C}H-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow H_3C-\overset{CH_3}{CH}-\overset{CH_3}{\overset{+}{C}}-CH_3\right]$$

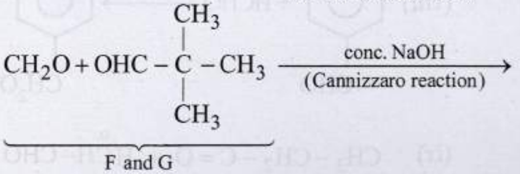
2° Carbocation 3° Carbocation



$$\xrightarrow{Cl^-} \underbrace{CH_3\overset{Cl}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + CH_3\overset{CH_3}{CH}-\overset{CH_3}{\underset{Cl}{C}}-CH_3}_{B\ and\ C}$$

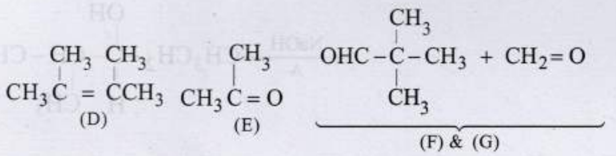


$$\underset{(A)}{H_2C=CH-\overset{CH_3}{\underset{CH_3}{C}}-CH_3} \xrightarrow{O_3} \underbrace{CH_2O + OHC-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}_{\substack{F\ and\ G\\ (Both\ give\ Fehling\ test,\\ but\ not\ iodoform\ test)}}$$



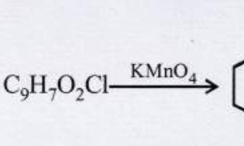
$$\underbrace{CH_2O + OHC-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}_{F\ and\ G} \xrightarrow[(Cannizzaro\ reaction)]{conc.\ NaOH}$$

$$HCOONa + \underset{1°\ Alcohol}{HOH_2C-C(CH_3)_3}$$

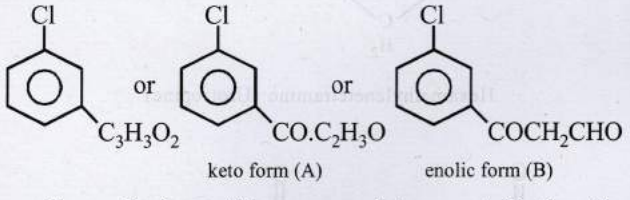


$$\underset{(D)}{CH_3\overset{CH_3}{C}=\overset{CH_3}{C}CH_3} \quad \underset{(E)}{CH_3\overset{CH_3}{C}=O} \quad \underbrace{OHC-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + CH_2=O}_{(F)\ \&\ (G)}$$

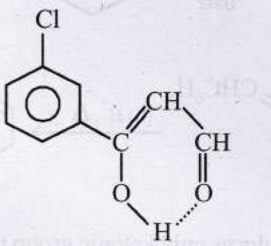
73. $C_9H_7O_2Cl \xrightarrow{KMnO_4}$



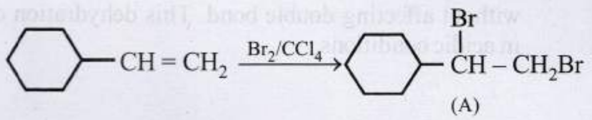
Hence, compound should have following part structure

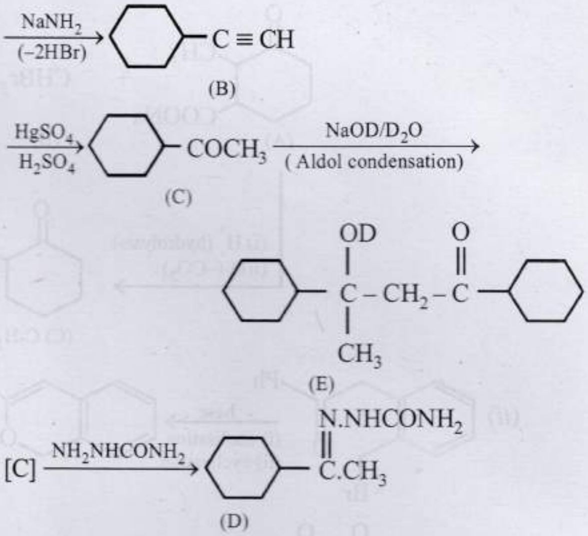


The enolic form of the compound is more stable than the keto form due to hydrogen bonding.

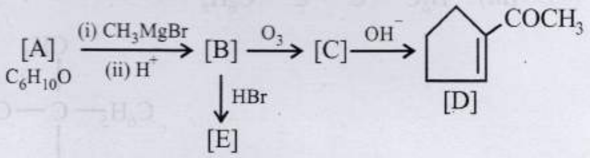


74.





75. The given reaction can be summarised as below :



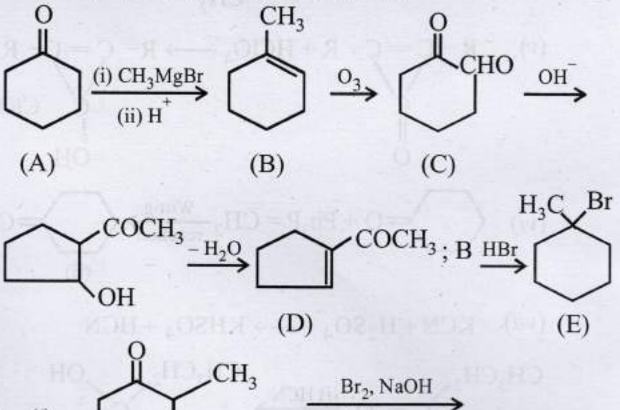
Conclusions from the set of reactions

(*i*) Carbon-hydrogen ratio in *A* indicates that it is a cyclic compound.

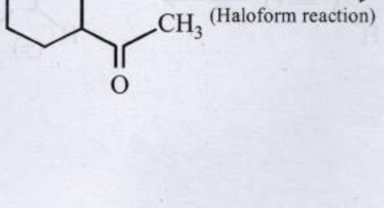
(*ii*) Reaction of *A* with CH_3MgBr indicates that it should have a ketonic group.

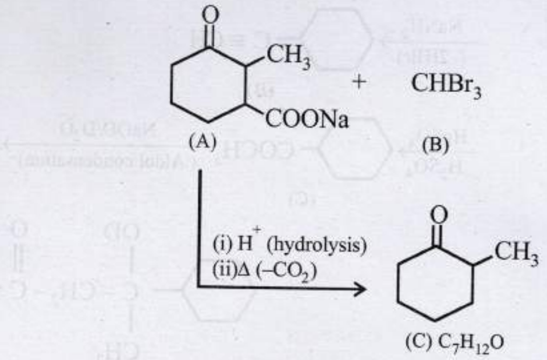
(*iii*) As *B* undergoes ozonolysis to form *C*, It must have a double bond, and *C* must have two carbonyl groups.

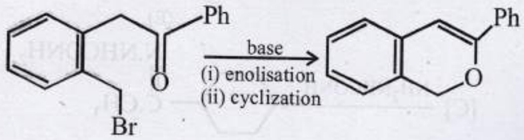
(*iv*) Reaction of *C* (a dicarbonyl compound) with a base gives a cyclic compound, it indicates that intramolecular condensation have occurred during this conversion. Thus, *A* is cyclohexanone which explains all the given reactions.

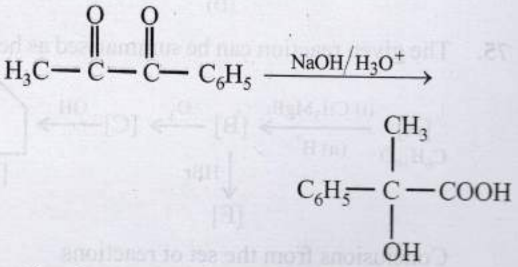


76. (*i*)





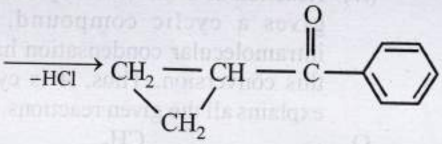
(*ii*)


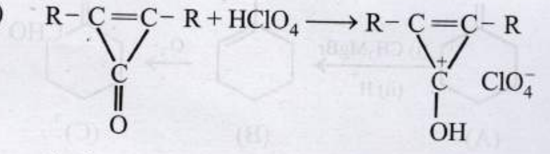
(*iii*)


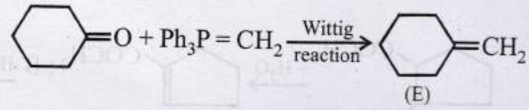
$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{NaOH/H_3O^+} C_6H_5-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-COOH$$

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

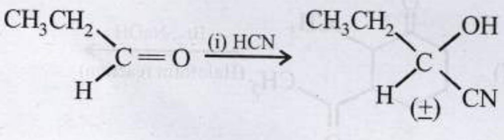
(*iv*) $ClCH_2CH_2CH_2COPh \xrightarrow{MeO^-} Cl\,CH_2CH_2\overset{-}{C}H_2COPh$

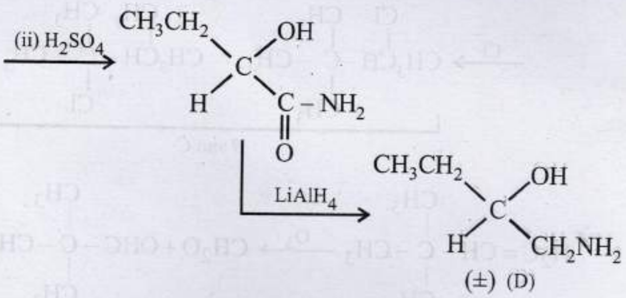


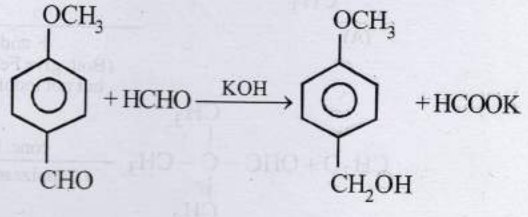
(*v*)


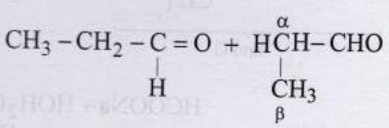
(*vi*)


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

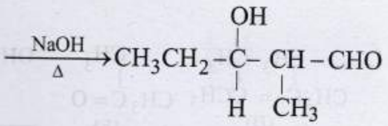




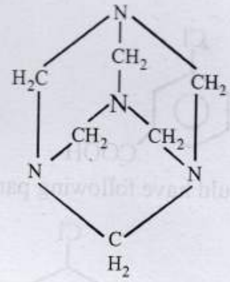
(*viii*)


(*ix*)


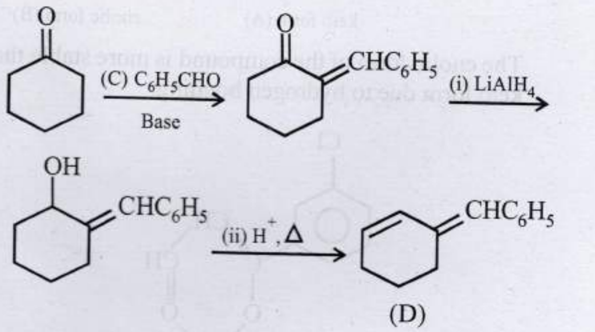
$$CH_3-CH_2-\underset{H}{\underset{|}{C}}=O+H\overset{\alpha}{C}H(\underset{\beta}{CH_3})-CHO$$



$$\xrightarrow[\Delta]{NaOH} CH_3CH_2-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{CH_3}{\underset{|}{CH}}-CHO$$

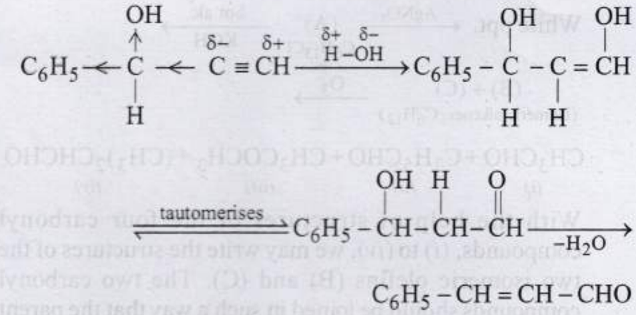
(*x*)


Hexamethylenetetramine (Urotropine)

77.


LiAlH$_4$ reduces only ketonic group to 2° alcoholic group without affecting double bond. This dehydration occurs in acidic conditions.

78.



$$C_6H_5 \leftarrow \overset{\overset{OH}{\uparrow}}{\underset{\underset{H}{|}}{C}} \leftarrow \overset{\delta-}{C} \equiv \overset{\delta+}{C}H \xrightarrow{\overset{\delta+\ \delta-}{H-OH}} C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}=CH$$

$$\xrightleftharpoons{\text{tautomerises}} C_6H_5-\overset{\overset{OH}{|}}{C}H-\overset{\overset{H}{|}}{C}H-\overset{\overset{O}{\|}}{C}H \xrightarrow{-H_2O} C_6H_5-CH=CH-CHO$$

79. Following informations are provided by the problem.

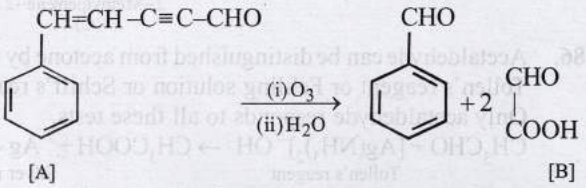
(i) Since aldehyde *A* ($C_{11}H_8O$) gives C_6H_5CHO on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon ($C_{11}-C_6=C_5$), three hydrogen ($H_8-H_5=H_3$) and one oxygen atom, *i.e.*, it should be C_5H_3O. Further the compound *A* has an aldehydic group, so the side chain can be written as C_4H_2CHO.

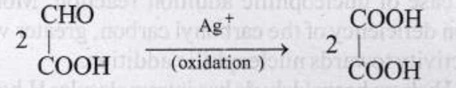
(ii) Formation of two moles of *B* from one mole of *A* by ozonolysis indicates that the side chain must possess two unsaturated linkages, one of which must be alkyne type, suggested by very low number of hydrogen atoms.

(iii) Further, since the aldehyde *A* does not undergo aldol condensation, α-hydrogen is absent and hence triple bond should be present between C_2 and C_3.

(iv) Thus the side chain C_4H_2CHO of *A* can be written as $-CH=CH-C\equiv C-CHO$.

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

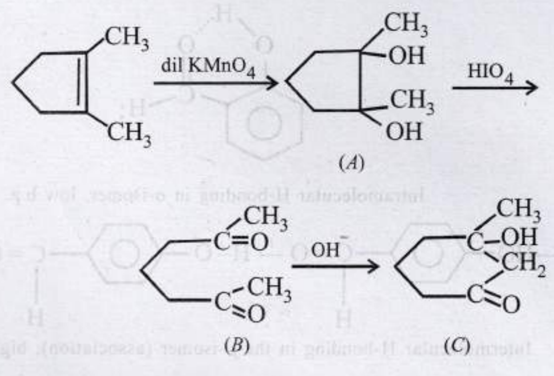




$$2\,\underset{COOH}{\overset{CHO}{|}} \xrightarrow[\text{(oxidation)}]{Ag^+} 2\,\underset{COOH}{\overset{COOH}{|}}$$

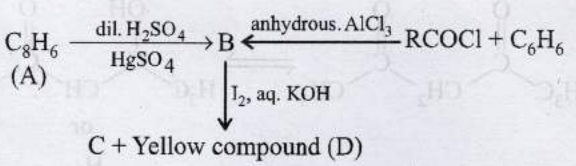
Glyoxalic acid Oxalic acid

80.



The last step is **intramolecular aldol condensation.**

81.



$$\underset{(A)}{C_8H_6} \xrightarrow[HgSO_4]{dil.\ H_2SO_4} B \xleftarrow{anhydrous.\ AlCl_3} RCOCl + C_6H_6$$

$$B \xrightarrow{I_2,\ aq.\ KOH} C + \text{Yellow compound (D)}$$

(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.

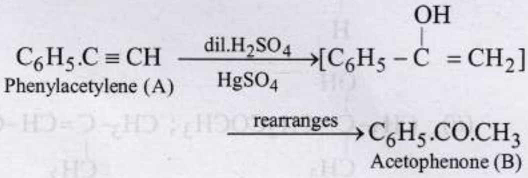
(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone (B) is $-CH_3$. Hence, (B) should be $C_6H_5.CO.CH_3$.

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

Thus, compounds (A) to (D) are

$\underset{(A)}{C_6H_5.C\equiv CH}$ $\underset{(B)}{C_6H_5.CO.CH_3}$ $\underset{(C)}{C_6H_5COOH}$ $\underset{(D)}{CHI_3}$

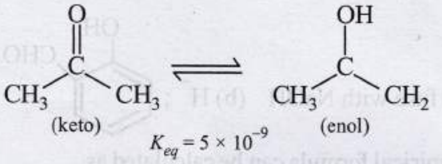
Formation of (B) from (A)



$$\underset{\text{Phenylacetylene (A)}}{C_6H_5.C\equiv CH} \xrightarrow[HgSO_4]{dil.H_2SO_4} [C_6H_5-\overset{\overset{OH}{|}}{C}=CH_2]$$

$$\xrightarrow{\text{rearranges}} \underset{\text{Acetophenone (B)}}{C_6H_5.CO.CH_3}$$

82.



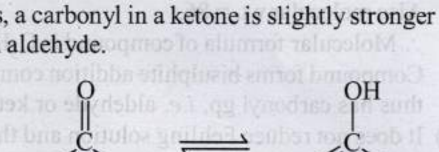
$K_{eq} = 5 \times 10^{-9}$

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

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

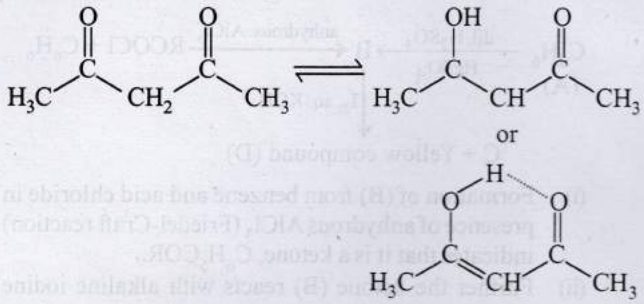
In fact, in simple carbonyl compounds, the methyl group stabilizes the carbonyl double bond much more than it stabilizes the enolic C = C bond.

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



$K_{eq} = 6 \times 10^{-7}$

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

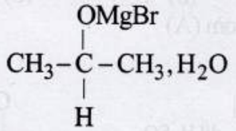


The two β-di carbonyl compounds have a much higher enol content than the two monocarbonyl compounds because of hydrogen bonding, conjugation and 6 membered cyclic form.

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

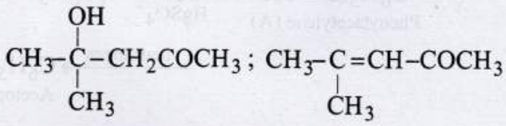
$$CH_3COCH_3 < CH_3CHO << CH_3COCH_2COCH_3 < CH_3COCH_2CHO$$

83. (*i*)



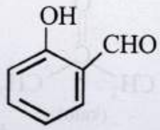
$$CH_3-\overset{OMgBr}{\underset{H}{C}}-CH_3, H_2O$$

(*ii*)



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2COCH_3\ ;\ CH_3-\underset{CH_3}{C}=CH-COCH_3$$

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



84. (*i*) Empirical formula can be calculated as

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.77	5.81	5
H	11.63	11.63	10
O	18.60	1.16	1

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

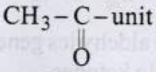
Also molecular wt. = 86.

∴ Molecular formula of compound is $C_5H_{10}O$.

(*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



$$CH_3-\underset{\underset{O}{\|}}{C}-\text{unit}$$

(*v*) Above facts reveal that the compound is

$CH_3CH_2CH_2COCH_3$ or $(CH_3)_2CHCOCH_3$

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

85. Let us summarise the given facts.

$$\text{White ppt.} \xleftarrow{AgNO_3} \underset{C_6H_{13}Cl}{(A)} \xrightarrow[KOH]{\text{hot alc.}}$$

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

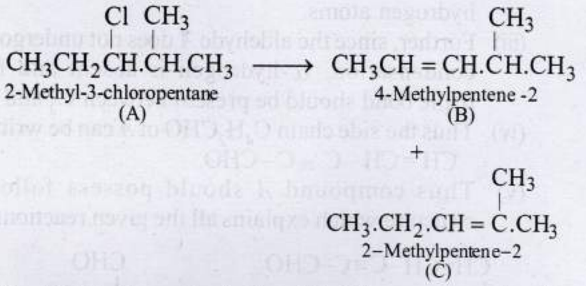
$$\underset{(i)}{CH_3CHO}+\underset{(ii)}{C_2H_5CHO}+\underset{(iii)}{CH_3COCH_3}+\underset{(iv)}{(CH_3)_2CHCHO}$$

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*)].

$$\underset{(i)}{CH_3CHO} + \underset{(iv)}{OHC.CH(CH_3)_2} \xleftarrow{O_3} \underset{\text{Olefin B }(C_6H_{12})}{CH_3CH=CH.CH(CH_3)_2}$$

$$\underset{(ii)}{C_2H_5CHO} + \underset{(iii)}{OC(CH_3)_2} \xleftarrow{O_3} \underset{\text{Olefin }(C_6H_{12})}{C_2H_5CH=C(CH_3)_2}$$

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



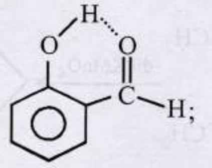
$$\underset{\underset{(A)}{\text{2-Methyl-3-chloropentane}}}{CH_3CH_2\overset{Cl}{C}H.\overset{CH_3}{C}H.CH_3} \longrightarrow \underset{\underset{(B)}{\text{4-Methylpentene -2}}}{CH_3CH=CH.\overset{CH_3}{C}H.CH_3} + \underset{\underset{(C)}{\text{2-Methylpentene-2}}}{CH_3.CH_2.CH=\overset{CH_3}{C}.CH_3}$$

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.

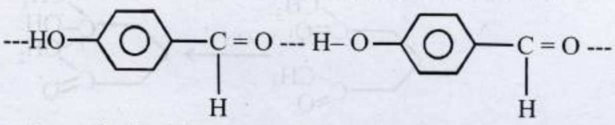
$$CH_3CHO+\underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+OH^-} \rightarrow CH_3COOH+\underset{\text{Silver mirror}}{Ag\downarrow}$$

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

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



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



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

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

$$R:C\vdots\vdots O^+: \longleftrightarrow R:C^+=\ddot{O}:$$

Acylium ion **Carbonium ion**

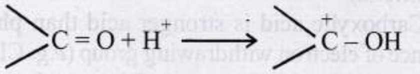
(Carbon has only six electrons)

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

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

$$CH_3.CO.CH_3 + {}^-OI \rightarrow CH_3.CO.\overline{C}H_2 + HOI$$

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



Carbon becomes more electron deficient

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.

$$H_2N-\ddot{N}H_2 \xrightarrow{H^+} H_2N+\overset{+}{N}H_3$$

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

(*v*) Alcohols show hydrogen bonding.

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

$$\begin{array}{l} C_4H_9-O-H \\ \qquad\quad\ \vdots \\ \qquad\quad\ H-O-C_4H_9 \end{array}$$

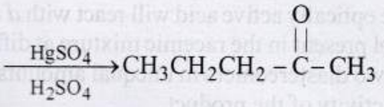
(H-bonding between two butanol molecules)

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

89. (*i*) $CH_3CH_2-C\equiv CH + Na^+\,NH_2^-$

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

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



$$\xrightarrow[H_2SO_4]{HgSO_4} CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(*ii*) $CH\equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3CHO \xrightarrow[(Oxi.)]{KMnO_4} CH_3COOH$

Acetylene

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

Acetone

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

Methanal

$$(HCOO)_2Ca \xrightarrow[heat]{(CH_3COO)_2\,Ca} 2\,CH_3CHO$$

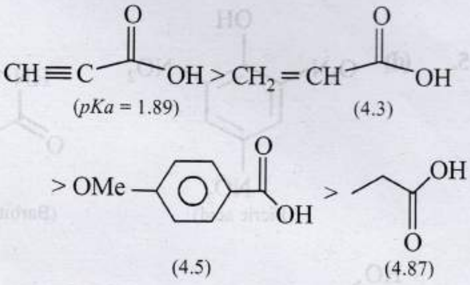
Ethanal

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

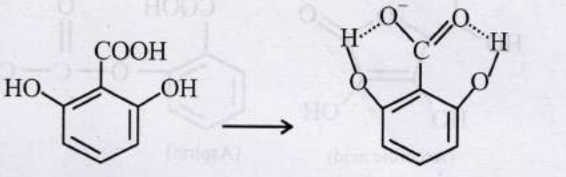
1. (a) Acidic strength depends upon the stability of anion formed higher the stability of the anion, higher will be acidic strength of the parent acid. Thus anion :

$$\underset{sp}{HC\circ\,CCOO^-} > \underset{sp^2}{H_2C=CHCOO^-} > p\text{-}C_6H_4(OMe)COO^- > \underset{sp^3}{H_3CCH_2COO^-}$$

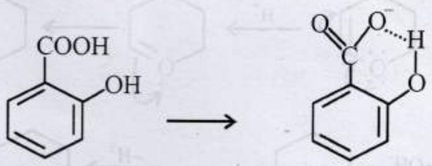
Therefore,



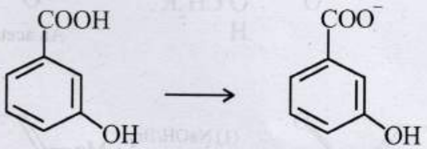
2. (a)



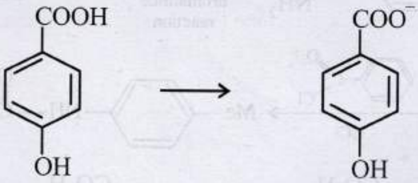
(I) (stabilizes by more H-bonding)



(II) (stabilizes by H-bonding)



(III) (stabilizes by –I effect)

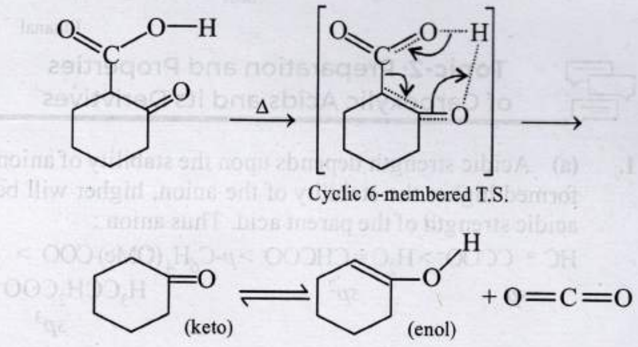


(IV) (destabilizes by +M effect)

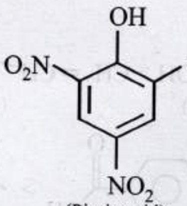
∴ Acidity order is I > II > III > IV

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

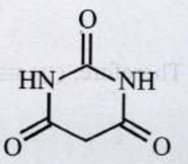
4. **(b)** β-Ketoacids undergo decarboxylation easily. It is due to the stability of transition state formed after decarboxylation of β-keto acids. This is not possible in case of other acids.



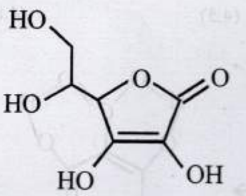
5. **(d)**



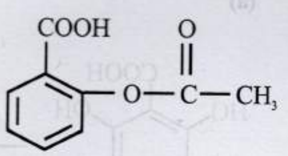
(Picric acid)



(Barbituric acid)

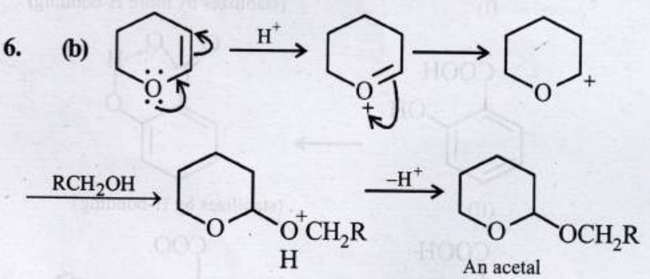


(Ascorbic acid)

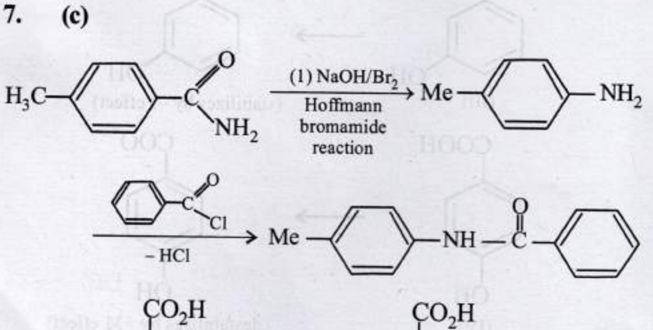


(Aspirin)

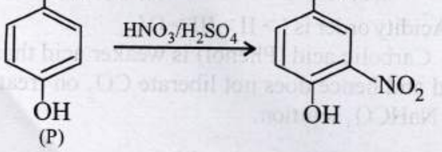
6. **(b)**



7. **(c)**

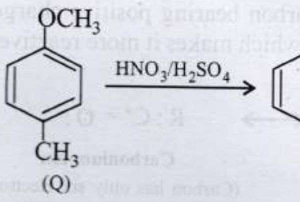


8. **(c)**



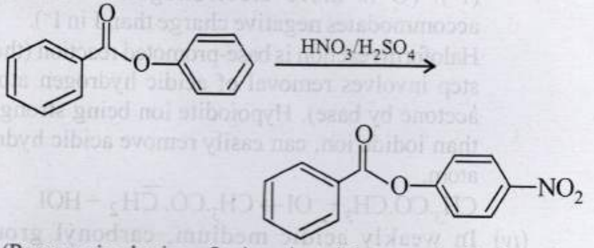
(P)

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



(Q)

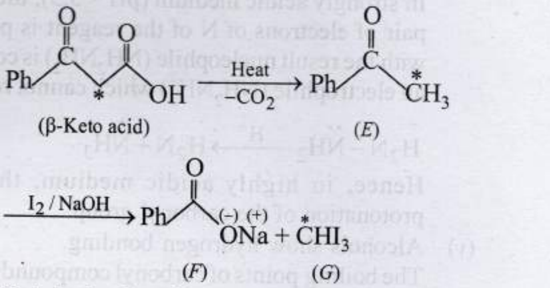
(OCH_3 group is more activating)



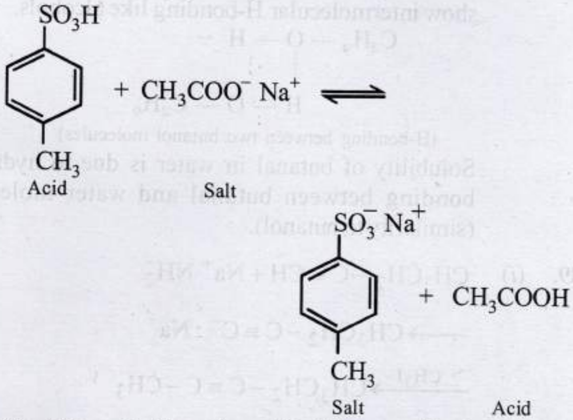
(Benzene ring having –O– is activated, benzene ring having –CO is deactivated)

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.* CH_3) decreases acidic strength.

10. **(c)**

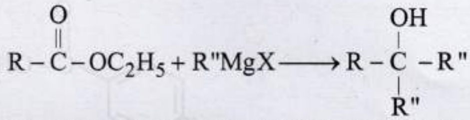


11. **(a)** This is simply a displacement reaction.



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.



$$R-\overset{\overset{O}{\|}}{C}-OC_2H_5+R''MgX\longrightarrow R-\underset{\underset{R''}{|}}{\overset{\overset{OH}{|}}{C}}-R''$$

Since, here Grignard reagent is CH_3MgBr, the 3° alcohol should have at least two methyl groups.
Hence, (a) is the correct choice.

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

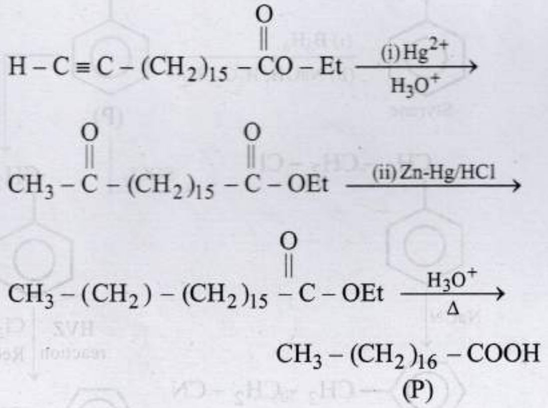
15. **(d)** $C_2H_5COOH+NaH\overset{14}{C}O_3\rightarrow$

$$C_2H_5COONa+H_2O+\overset{14}{C}O_2$$

16. **(a)** $LiAlH_4$ is a reducing agent, it reduces $-COOH$ group to $-CH_2OH$ group.

$$C_6H_5COOH\xrightarrow{LiAlH_4}C_6H_5CH_2OH$$

17. **(909)** Reactions involves are:

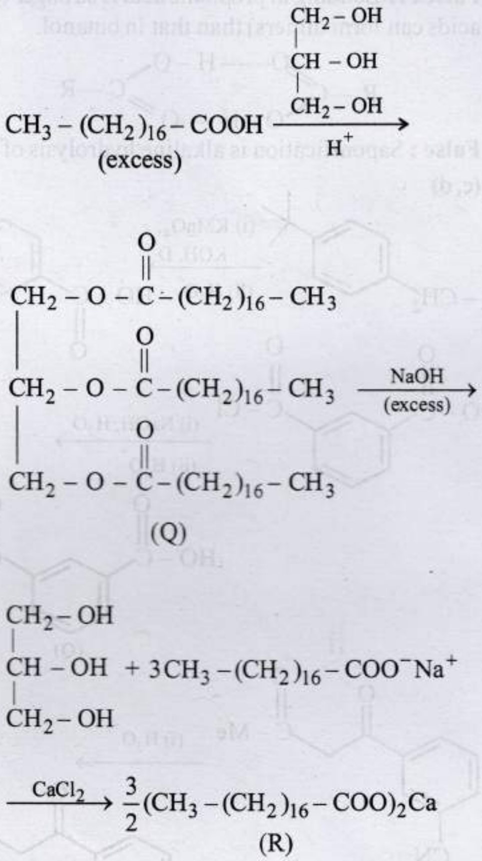


$$H-C\equiv C-(CH_2)_{15}-\overset{\overset{O}{\|}}{C}O-Et\xrightarrow[H_3O^+]{(i)\,Hg^{2+}}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_{15}-\overset{\overset{O}{\|}}{C}-OEt\xrightarrow{(ii)\,Zn\text{-}Hg/HCl}$$

$$CH_3-(CH_2)-(CH_2)_{15}-\overset{\overset{O}{\|}}{C}-OEt\xrightarrow[\Delta]{H_3O^+}$$

$$\underset{(P)}{CH_3-(CH_2)_{16}-COOH}$$



$$\underset{(excess)}{CH_3-(CH_2)_{16}-COOH}\xrightarrow[H^+]{\begin{array}{l}CH_2-OH\\ CH-OH\\ CH_2-OH\end{array}}$$

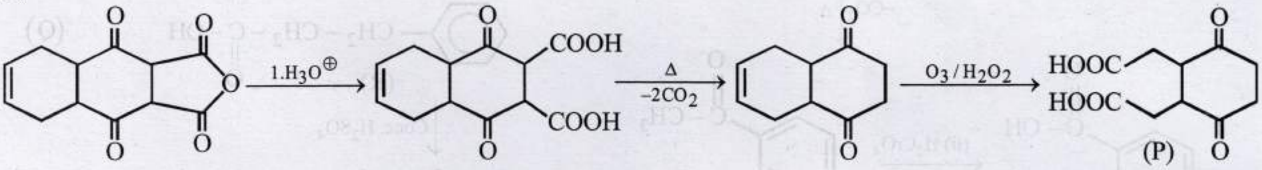
$$\underset{(Q)}{\begin{array}{l}CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{16}-CH_3\\ CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{16}-CH_3\\ CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{16}-CH_3\end{array}}\xrightarrow[(excess)]{NaOH}$$

$$\begin{array}{l}CH_2-OH\\ CH-OH\\ CH_2-OH\end{array}+3CH_3-(CH_2)_{16}-COO^-Na^+$$

$$\xrightarrow{CaCl_2}\underset{(R)}{\frac{3}{2}(CH_3-(CH_2)_{16}-COO)_2Ca}$$

1 mole of Q will 1.5 mole of R.
So, mass of R produced = 606 g × 1.5 = 909 g

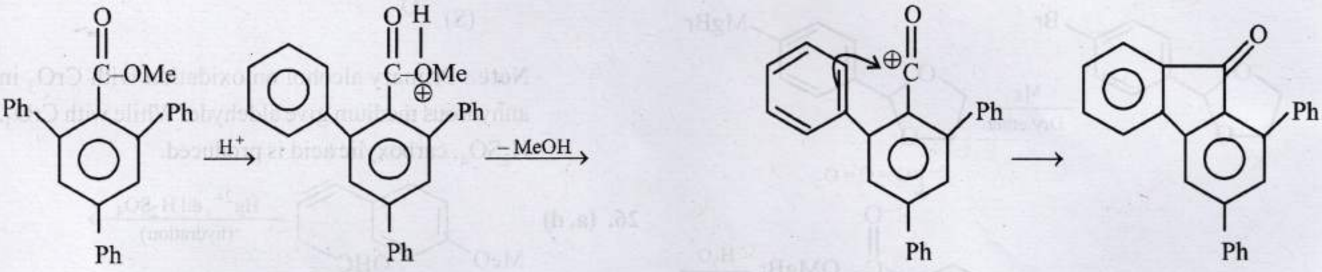
18. **(2)**



(P)
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)**

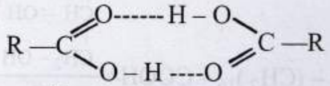


(P)

(Q)
DBE = 18

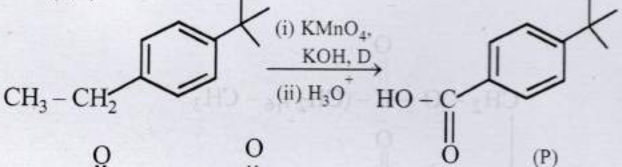
21. **CO;** $HCOOH\xrightarrow[heat]{Conc.H_2SO_4}CO+H_2O$

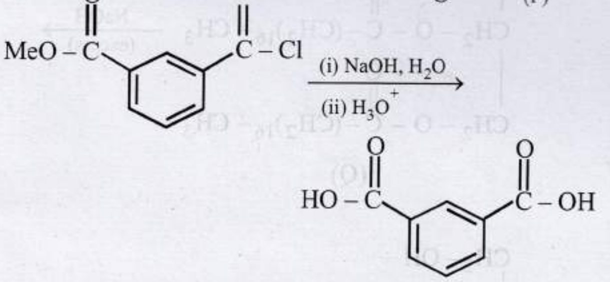
22. **False :** H-Bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.

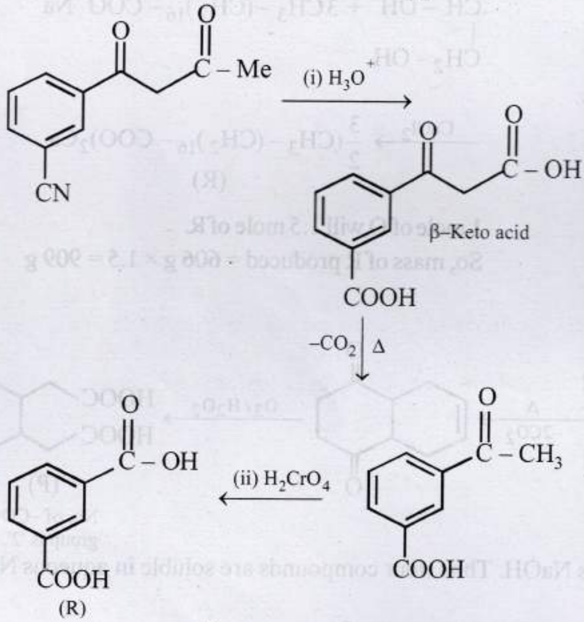


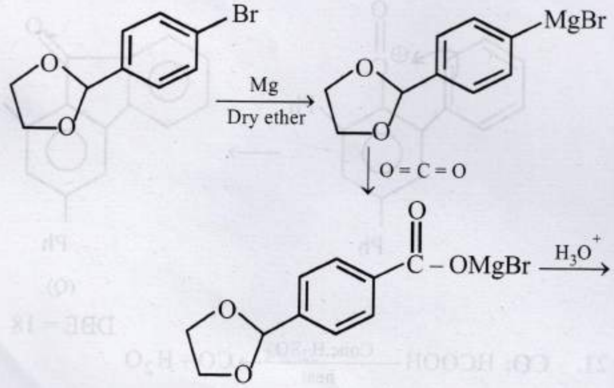
23. **False :** Saponification is alkaline hydrolysis of esters.

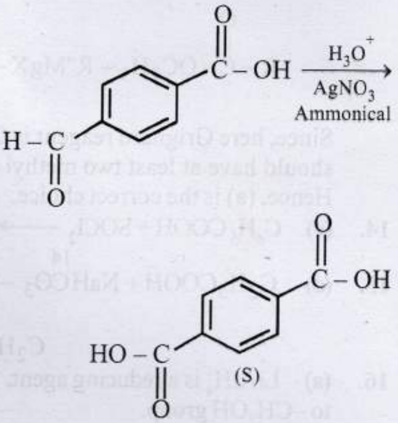
24. **(c, d)**



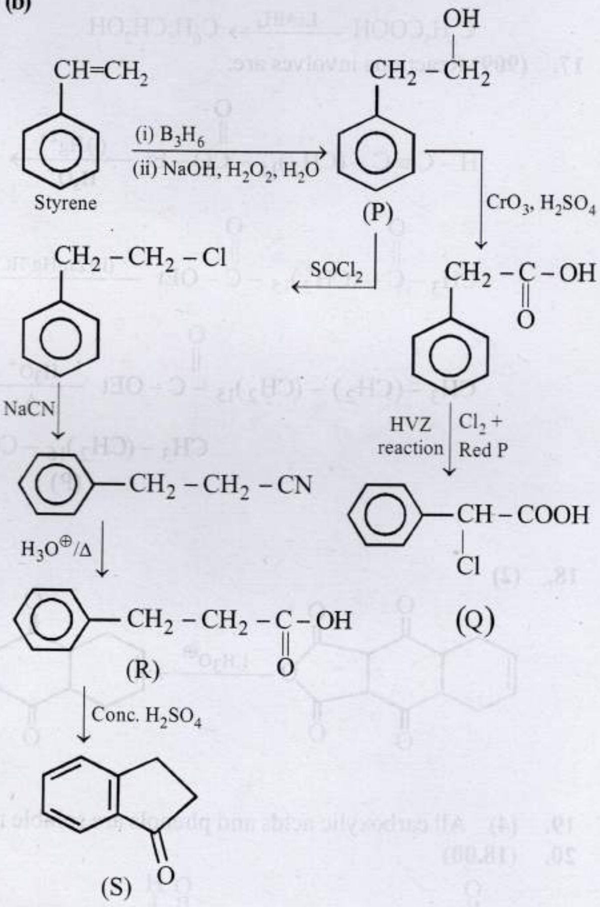






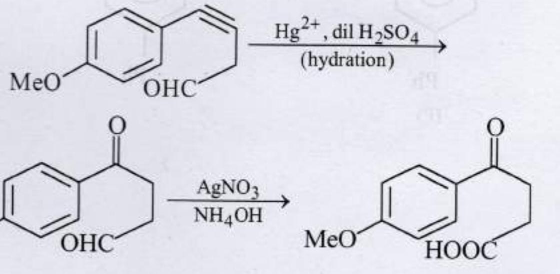


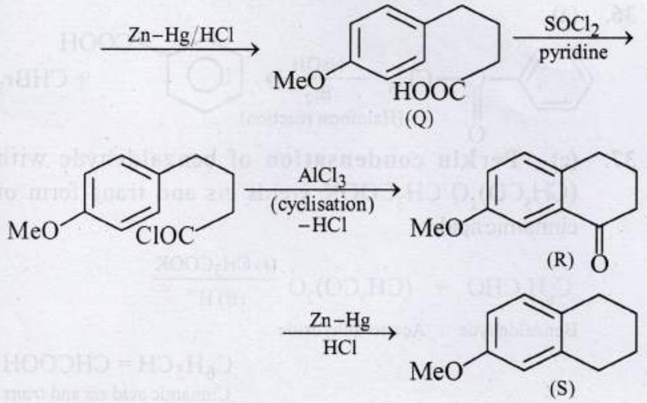
25. **(b)**



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

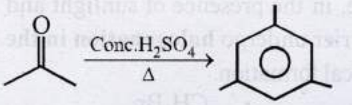
26. **(a, d)**



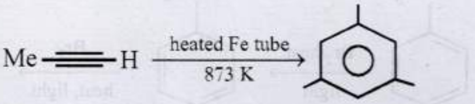


27. **(a, b, d)**

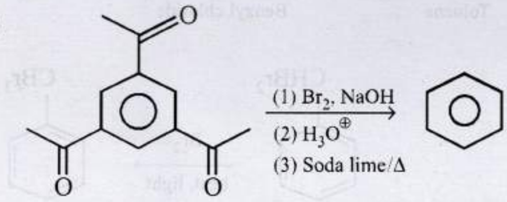
(a)



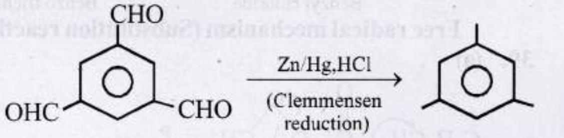
(b)



(c)



(d)



28. **(c, d)**

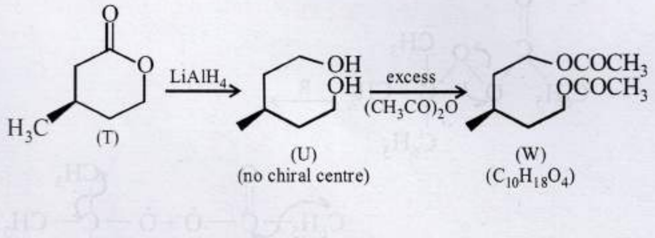
$LiAlH_4/(C_2H_5)_2O$: Reduces esters, carboxylic acids, epoxides and aldehydes and ketones.

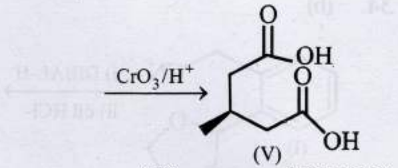
BH_3 in T.H.F : Reduces –COOH and aldehydes to alcohols but does not reduce esters and epoxides.

$NaBH_4$ in C_2H_5OH : 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)**





(Effervescence with $NaHCO_3$)

30. **(b, d)**

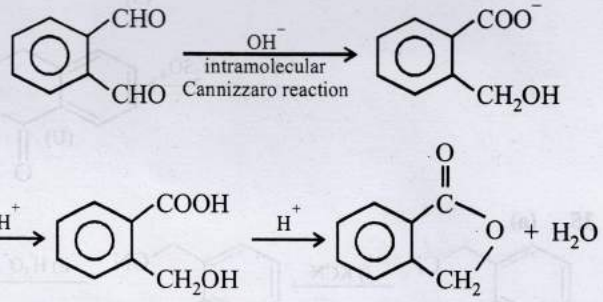
(a) Both are soluble in NaOH. Hence, **inseparable**.

(b) Only benzoic acid (C_6H_5COOH) is soluble in NaOH and $NaHCO_3$, while benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, **separable**.

(c) Although NaOH can enable separation between benzyl alcohol ($C_6H_5CH_2OH$) and phenol (C_6H_5OH) as only the latter is soluble in NaOH. However, in $NaHCO_3$, both are insoluble. Hence, **inseparable**.

(d) α-Phenylacetic acid ($C_6H_5CH_2COOH$) is soluble in NaOH and $NaHCO_3$, while benzyl alcohol ($C_6H_5CH_2OH$) 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 :

$$C_2H_5Cl \xrightarrow{KCN\,(alc.)} C_2H_5CN + KCl$$

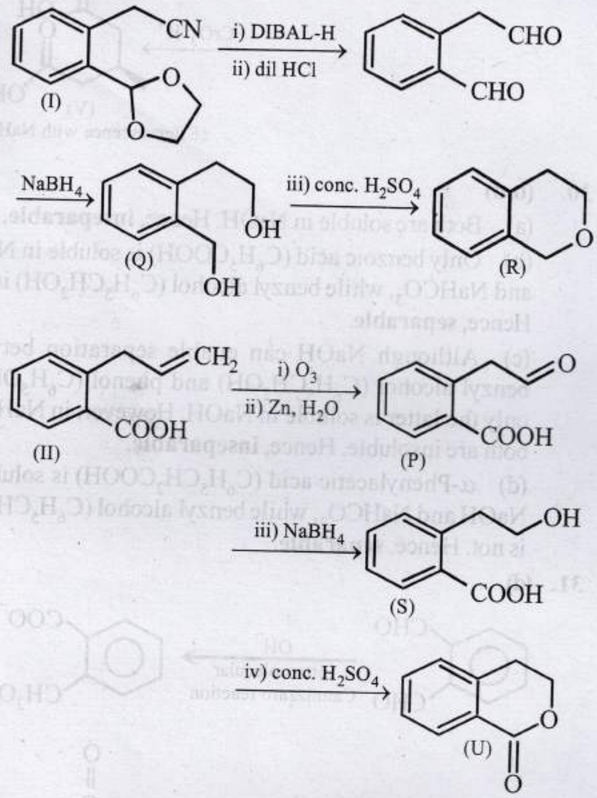
$$CH_3COCl \xrightarrow{KCN\,(alc.)} CH_3COCN + KCl$$

$$2\,C_6H_5CHO \xrightarrow{KCN\,(alc.)} C_6H_5CHOHCOC_6H_5$$

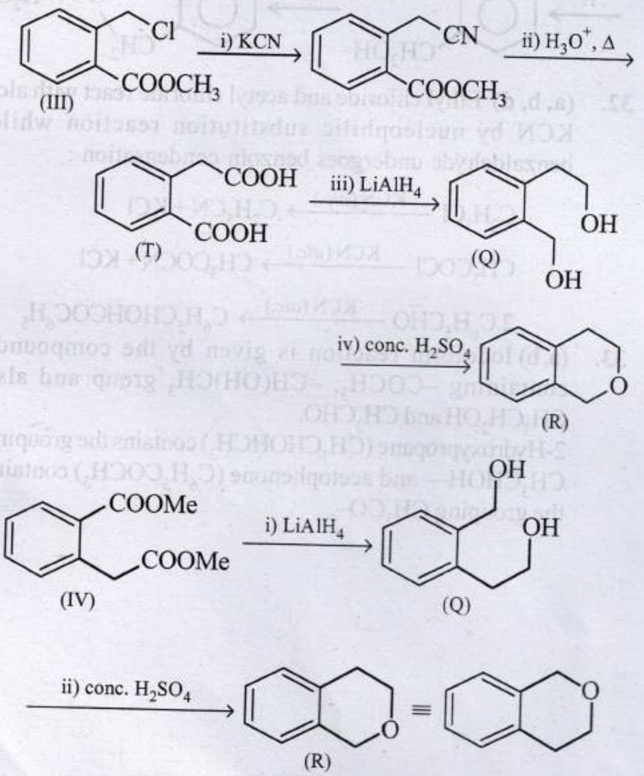
33. **(a, b)** Iodoform reaction is given by the compounds containing $-COCH_3$, $-CH(OH)CH_3$ group and also CH_3CH_2OH and CH_3CHO.

2-Hydroxypropane ($CH_3CHOHCH_3$) contains the grouping CH_3CHOH— and acetophenone ($C_6H_5COCH_3$) contains the grouping CH_3CO–.

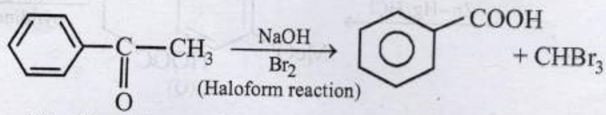
34. (b)



35. (a)



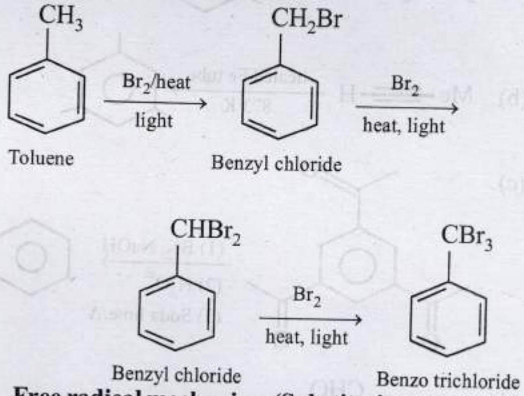
36. (a)



37. (c) **Perkin condensation** of benzaldehyde with $(CH_3CO)_2O/CH_3COOK$ yields cis and trans form of cinnamic acid.

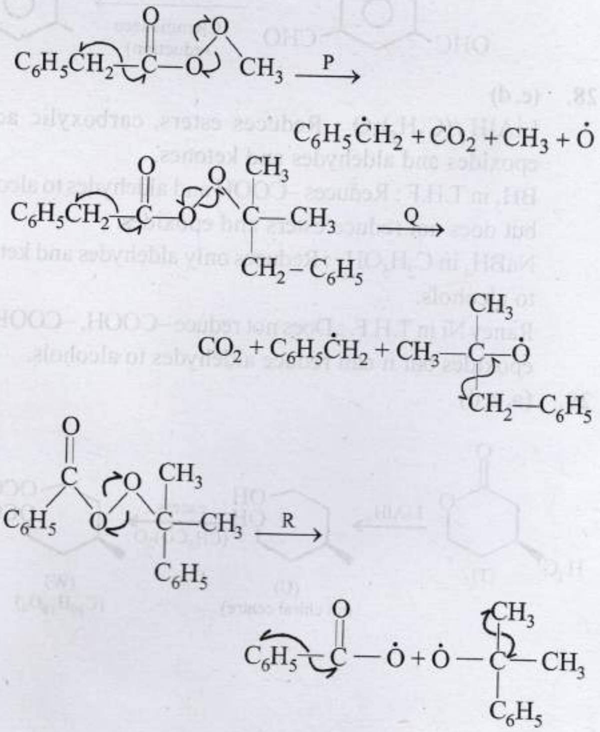
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow[(ii)\ H^+]{(i)\ CH_3COOK} \underset{\text{Cinnamic acid } cis \text{ and } trans}{C_6H_5CH = CHCOOH}$$

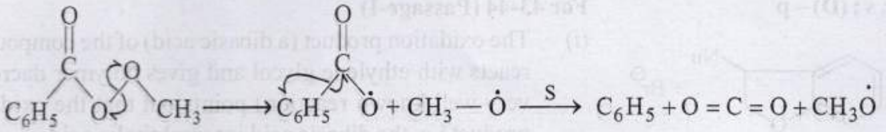
38. (d) Alkylbenzenes when treated with Br_2 at high temperature, in the presence of sunlight and absence of halogen carrier undergo **halogenation in the side chain** via free radical formation.



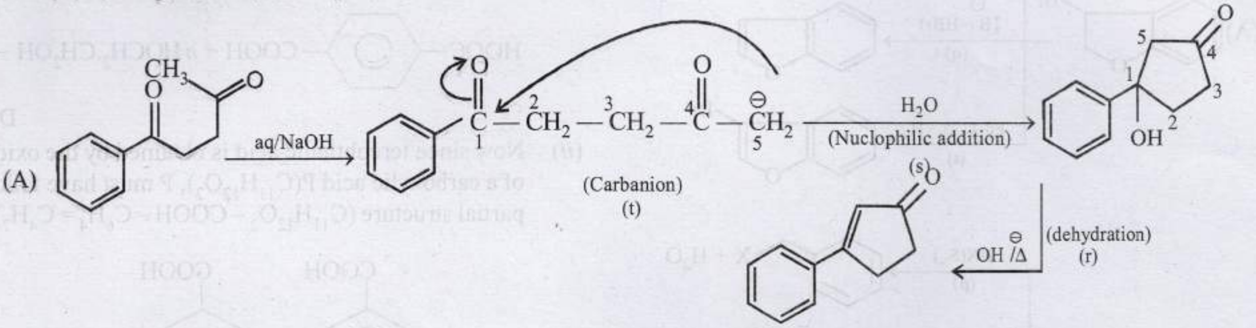
Free radical mechanism (Substitution reaction)

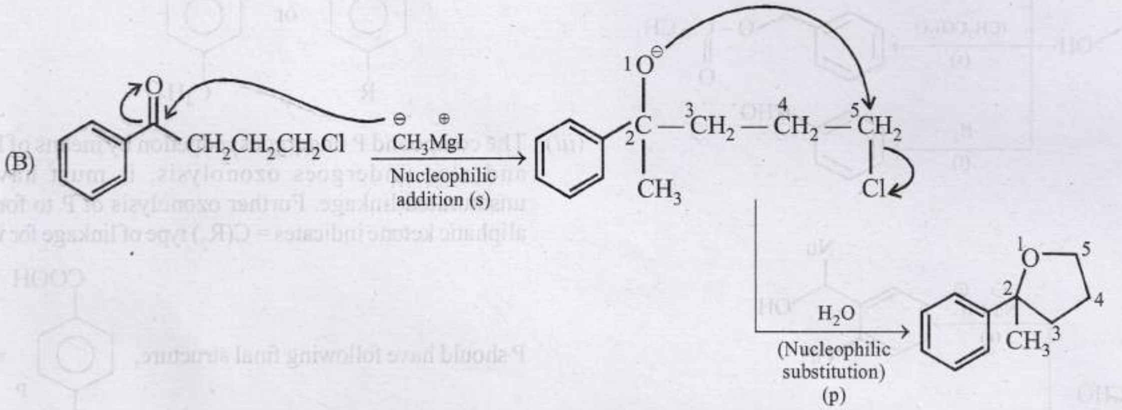
39. (a)

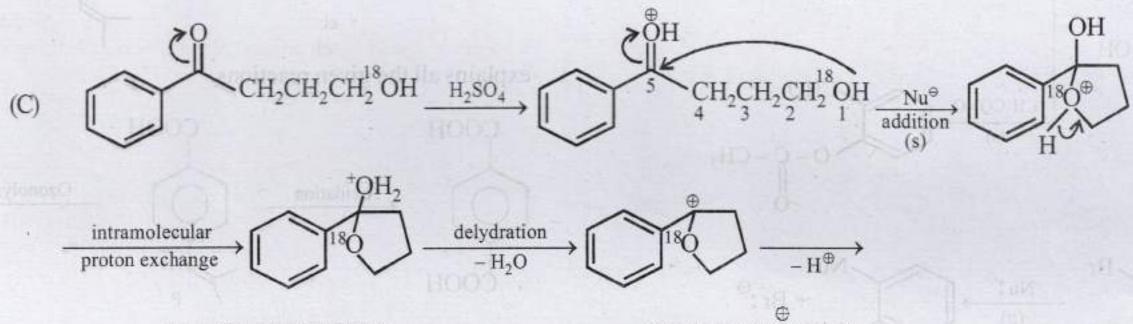


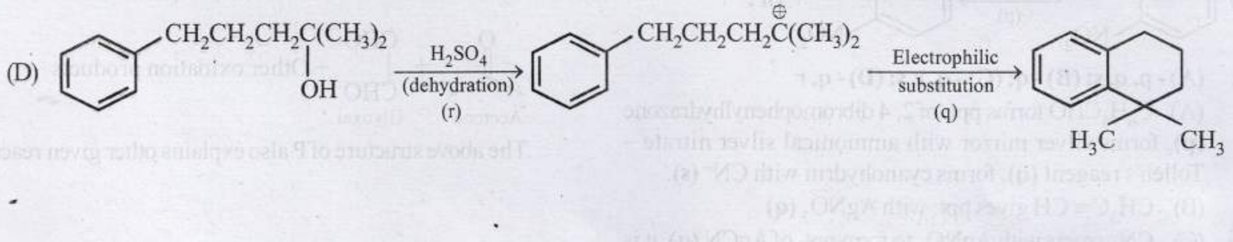


40. A – r, s, t ; B – p, s ; C - r, s; D – q, r



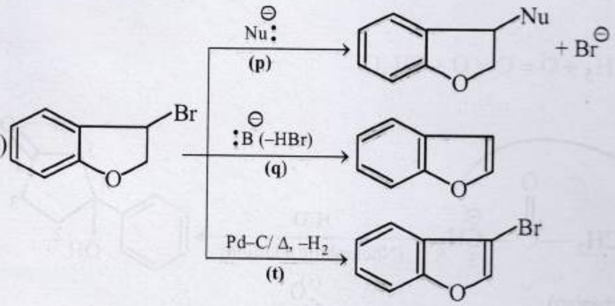




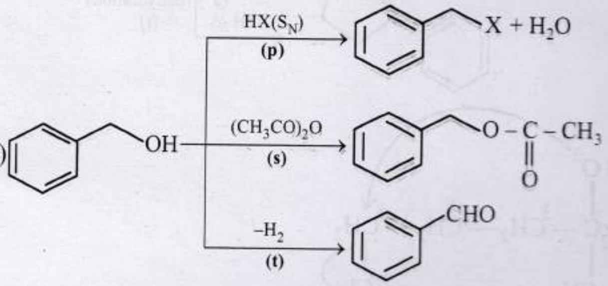


41. **(A) - p, q, t ; (B) - p, s, t ; (C) – r, s ; (D) – p**

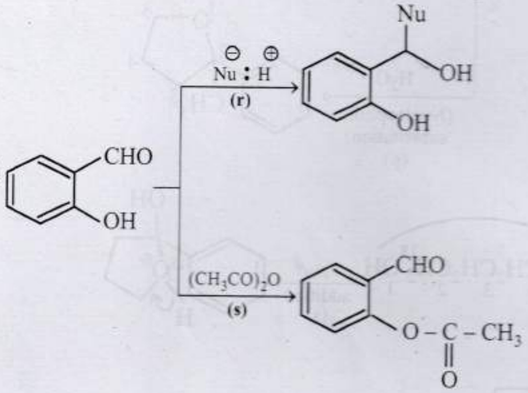
(A)



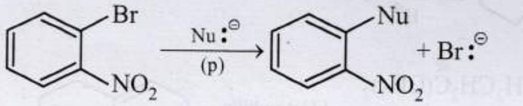
(B)



(C)



(D)



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)**.

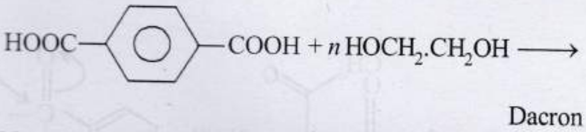
(B) $CH_3C \equiv CH$ gives ppt. with $AgNO_3$ **(q)**

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

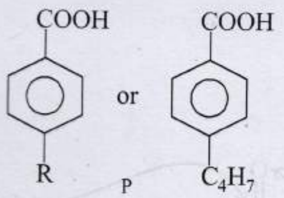
(D) I^- gives ppt. of AgI with $AgNO_3$ **(q)**, and it is a nucleophile **(r)**

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.

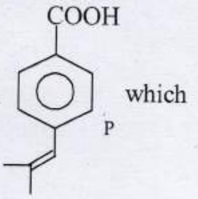


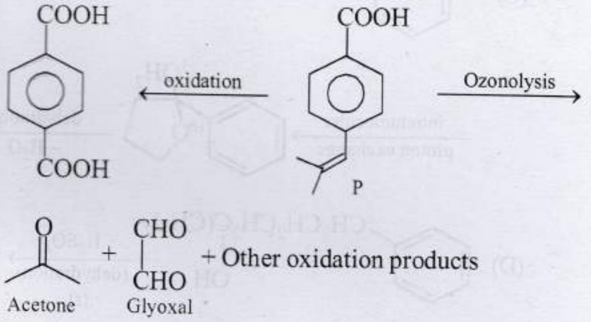
(*ii*) Now since terephthalic acid is obtained by the oxidation of a carboxylic acid $P(C_{11}H_{12}O_2)$, P must have following partial structure $(C_{11}H_{12}O_2 - COOH - C_6H_4 = C_4H_7)$



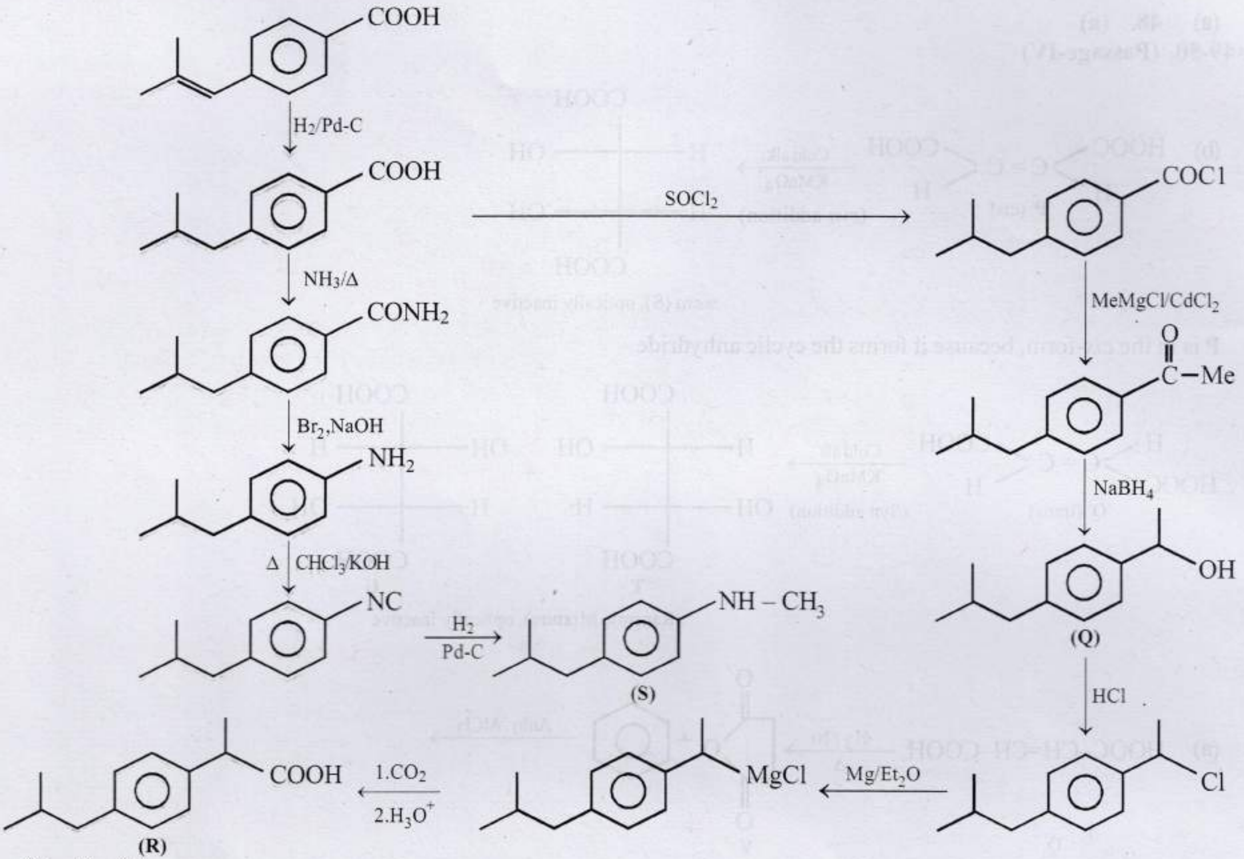
(*iii*) The compound P undergoes reduction by means of H_2/Pd and also undergoes ozonolysis, it must have an unsaturated linkage. Further ozonolysis of P to form an aliphatic ketone indicates $= C(R_2)$ type of linkage for which

P should have following final structure, which explains all the given reactions.



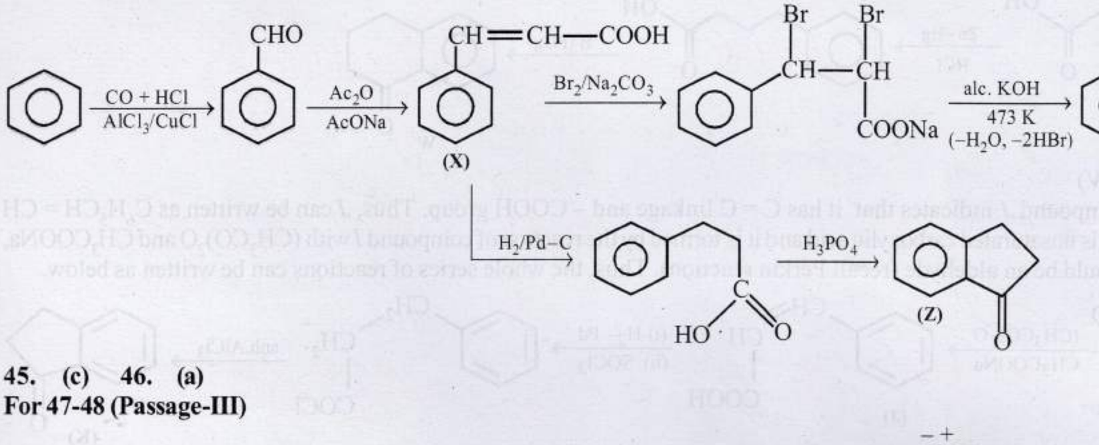


The above structure of P also explains other given reactions.



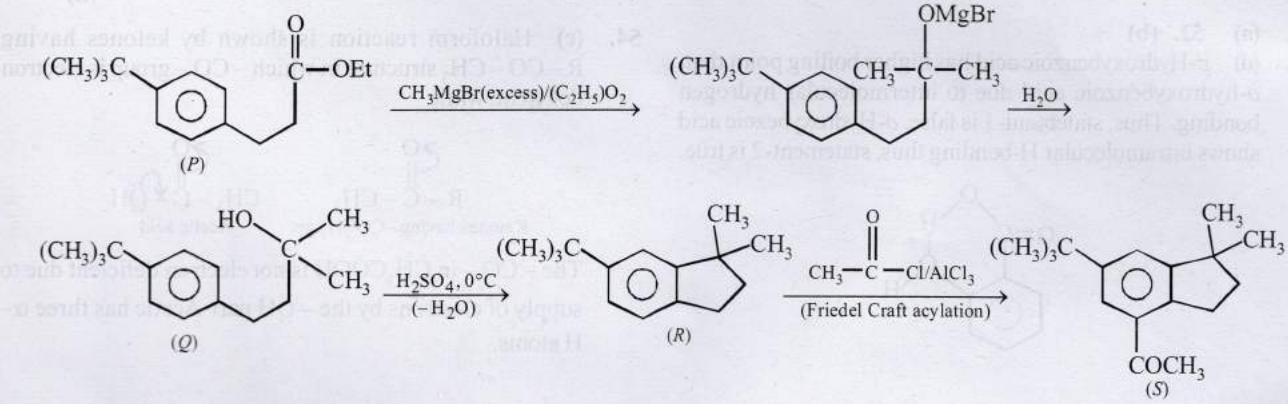
43. (a) 44. (b)

For 45-46 (Passage-II)



45. (c) 46. (a)

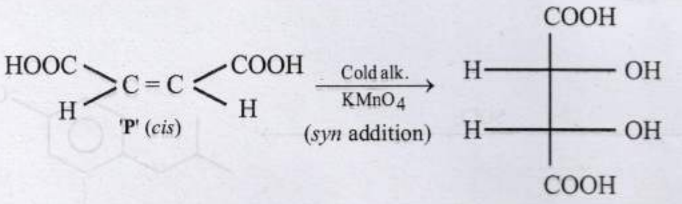
For 47-48 (Passage-III)



47. (a) 48. (a)

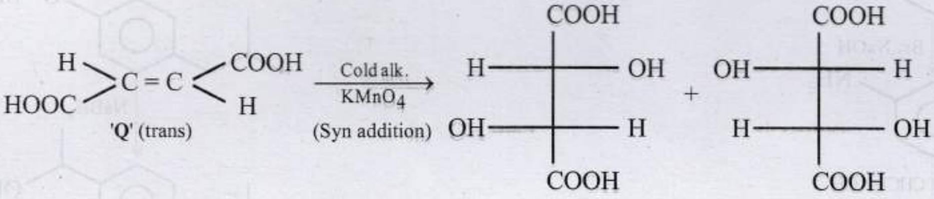
For 49-50. (Passage-IV)

49. (b)



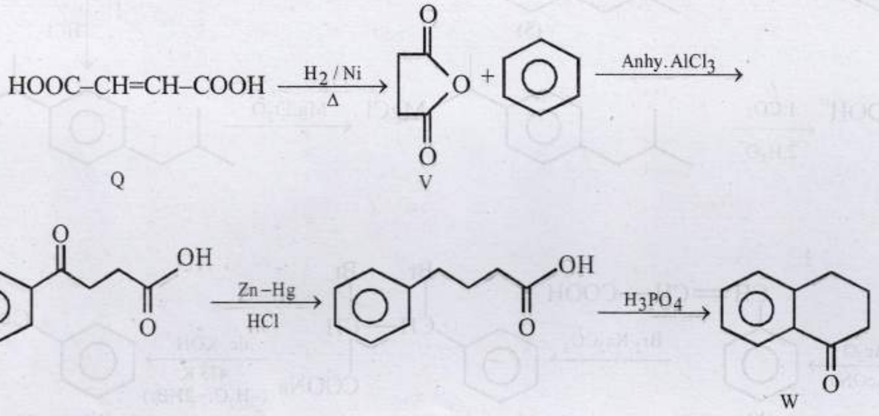
meso (**S**), optically inactive

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



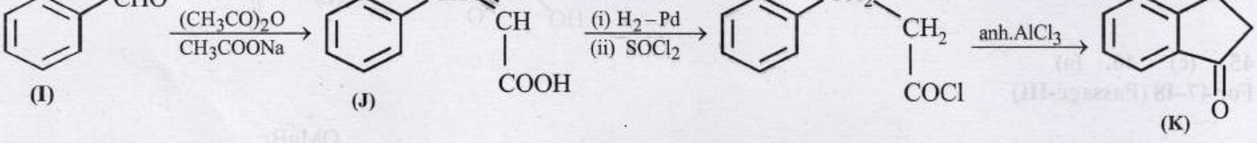
(Racemic Mixture), optically inactive

50. (a)



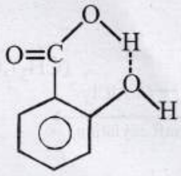
For 51- 52 (Passage-V)

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

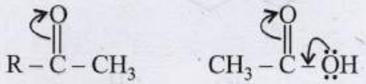


51. (a) 52. (b)

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



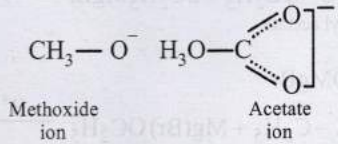
54. (c) Haloform reaction is shown by ketones having $R - CO - CH_3$ structure in which – CO – group is electron deficient, while



Ketones having $-COCH_3$ gp. Acetic acid

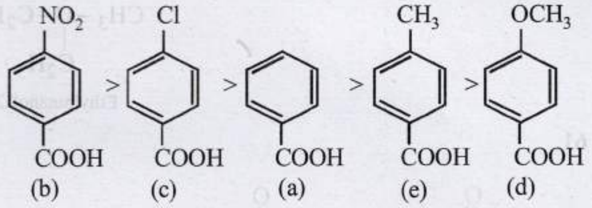
The – CO – in CH_3COOH is not electron deficient due to supply of electrons by the – ÖH part-Acetic has three α– H atoms.

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



Hence, acetate ion is less basic than methoxide ion.

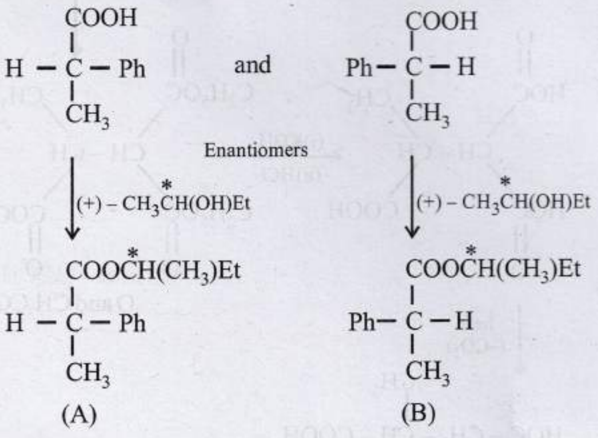
56. Higher the K_a value, more stronger is the acid.
Correct order of acidic strength of the given acids is



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

	(b)	(c)	(a)	(e)	(d)
K_a value	30.6×10^{-5}	10.2×10^{-5}	6.4×10^{-5}	4.2×10^{-5}	3.3×10^{-5}

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



(A) and (B) are diasteromers.

The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction. (+) – Acid reacts with (+) –alcohol to give an (+)-(+)-ester, while (–) acid reacts with (+) alcohol to give (–)-(+)-ester. These two esters are diastereoisomers.

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

IV < II < V < III < I

58. $Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow \underset{(X)}{\overset{*}{C}O_2} \uparrow$

$$CH_2=CHBr \xrightarrow[\text{ether}]{\text{(i)Mg}} CH_2=CHMgBr \xrightarrow[\text{(ii)}H_3O^+]{\text{(ii)}\overset{*}{C}O_2(X)}$$

$$\underset{(Y)}{CH_2=CH\overset{*}{C}OOH} \xrightarrow{LiAlH_4} \underset{(Z)}{CH_2=CH.\overset{*}{C}H_2OH}$$

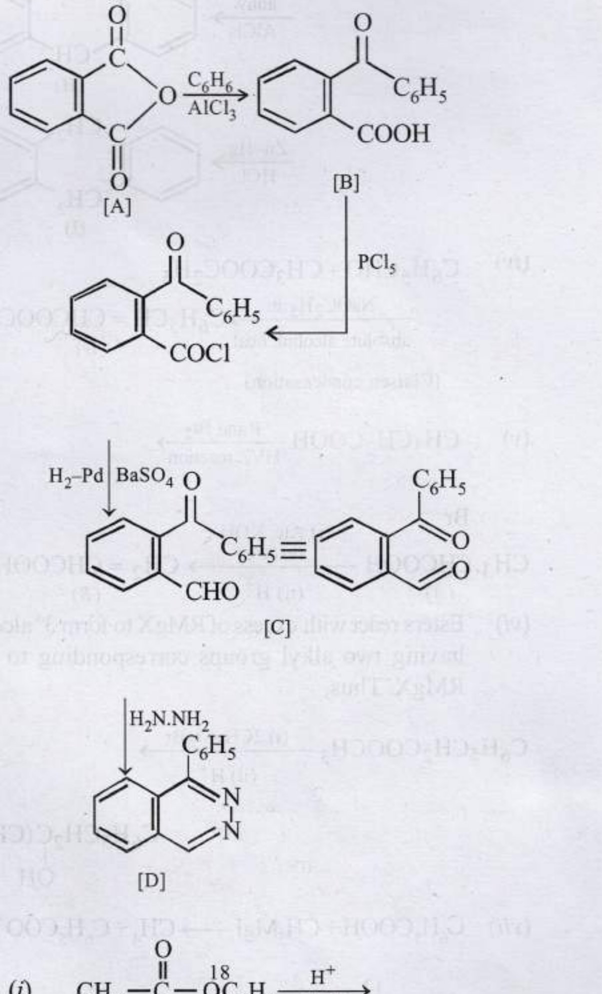
Formation of $\overset{*}{C}H_2O$ from (Z)

$$CH_2=CH.\overset{*}{C}H_2OH \xrightarrow{H^+}$$

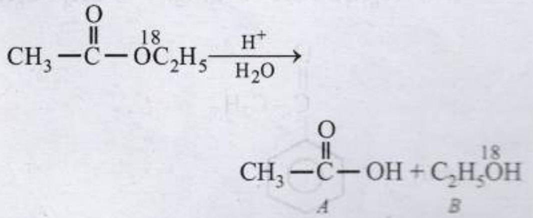
$$[CH_2=CH.\underset{\oplus}{\overset{*}{C}}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=\overset{*}{C}H_2]$$

$$\xrightarrow{Br^-} BrCH_2.CH=\overset{*}{C}H_2 \xrightarrow{O_3} \overset{*}{C}H_2=O$$

59.



60. (*i*)

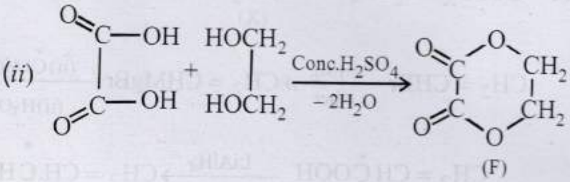


$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{18}{O}C_2H_5 \xrightarrow[H_2O]{H^+}$$

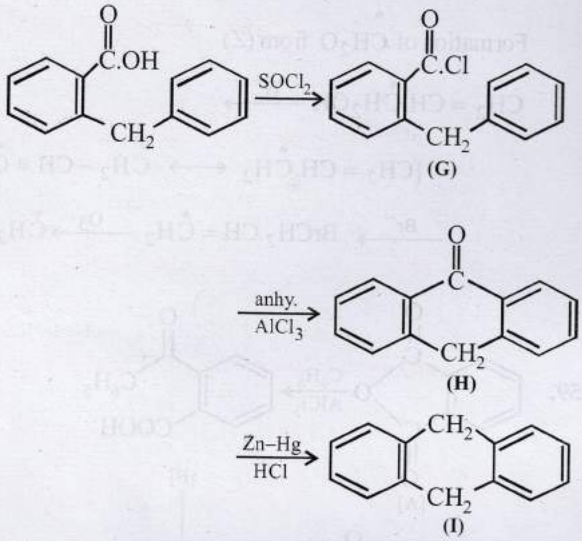
$$\underset{A}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{B}{C_2H_5\overset{18}{O}H}$$

(Ester hydrolysis involves acyl-oxygen fission)

(ii)



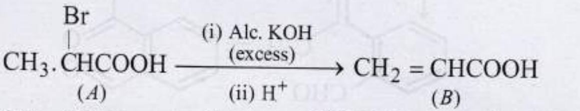
(iii)



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

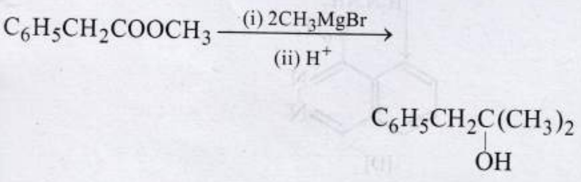
(Claisen condensation)

(v) $CH_3CH_2COOH \xrightarrow[\text{HVZ reaction}]{\text{P and }Br_2}$



$$\underset{(A)}{CH_3.\overset{Br}{\overset{|}{C}}HCOOH} \xrightarrow[\text{(ii) }H^+]{\text{(i) Alc. KOH (excess)}} \underset{(B)}{CH_2=CHCOOH}$$

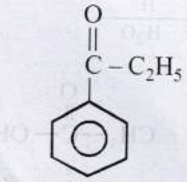
(vi) Esters react with excess of RMgX to form 3° alcohols having two alkyl groups corresponding to R of RMgX. Thus,



$$C_6H_5CH_2COOCH_3 \xrightarrow[\text{(ii) }H^+]{\text{(i) }2CH_3MgBr} C_6H_5CH_2\underset{OH}{\underset{|}{C}}(CH_3)_2$$

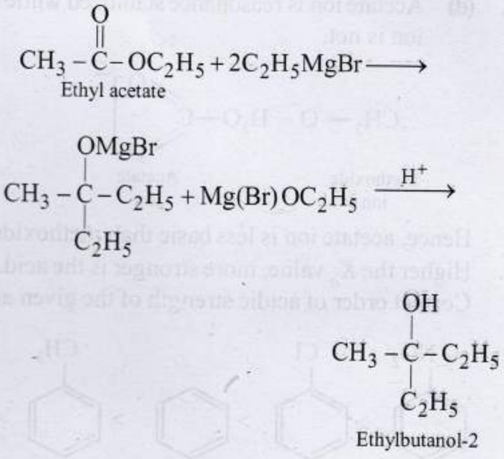
(vii) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COOMgI$

(viii)



Phenyl ethyl ketone

(ix)



$$CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5 + 2C_2H_5MgBr \longrightarrow$$

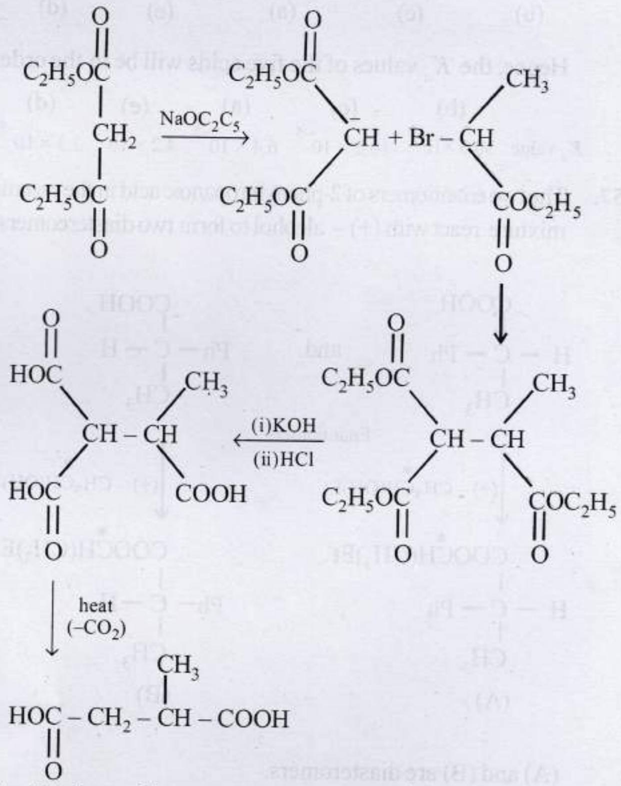
Ethyl acetate

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

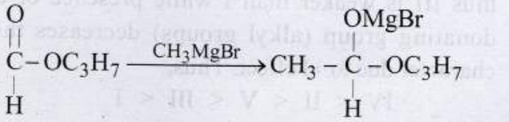
$$CH_3-\underset{C_2H_5}{\overset{OH}{C}}-C_2H_5$$

Ethylbutanol-2

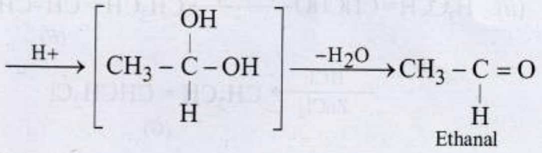
61.



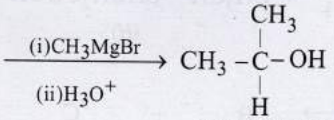
62. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formates) or tertiary alcohols (from esters other than formates). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence, ester A ($C_4H_8O_2$) should be $HCOOC_3H_7$. Thus the various reactions and nature of compound B can be established as below.



$$\underset{H}{\overset{O}{\overset{||}{C}}}-OC_3H_7 \xrightarrow{CH_3MgBr} CH_3-\underset{H}{\overset{OMgBr}{C}}OC_3H_7$$

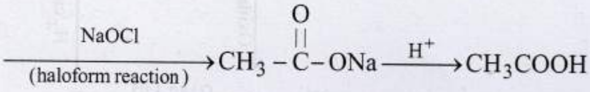


$\xrightarrow{H+} \left[CH_3-\overset{OH}{\underset{H}{C}}-OH\right] \xrightarrow{-H_2O} CH_3-\underset{H}{C}=O$ Ethanal



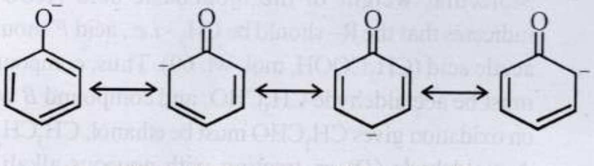
$\xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr} CH_3-\overset{CH_3}{\underset{H}{C}}-OH$

Isopropanol [B]

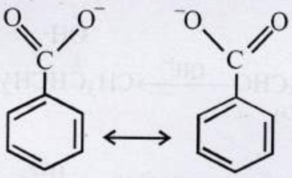


$\xrightarrow[\text{(haloform reaction)}]{NaOCl} CH_3-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow{H^+} CH_3COOH$

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



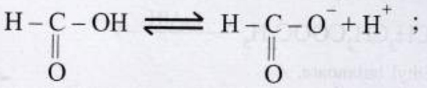
Resonating structures of phenoxide ion



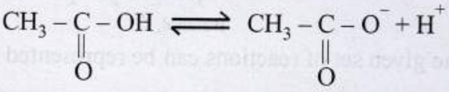
Resonating structures of benzoate ion

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

(ii)



$H-\underset{O}{\underset{\|}{C}}-OH \rightleftharpoons H-\underset{O}{\underset{\|}{C}}-O^- + H^+$;



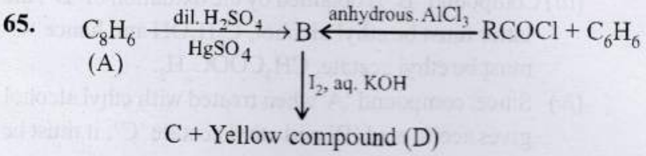
$CH_3-\underset{O}{\underset{\|}{C}}-OH \rightleftharpoons CH_3-\underset{O}{\underset{\|}{C}}-O^- + H^+$

(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.

65.



$\underset{(A)}{C_8H_6} \xrightarrow[HgSO_4]{dil.\,H_2SO_4} B \xleftarrow{anhydrous.\,AlCl_3} RCOCl + C_6H_6$

$B \xrightarrow{I_2,\ aq.\ KOH} C + \text{Yellow compound (D)}$

(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.

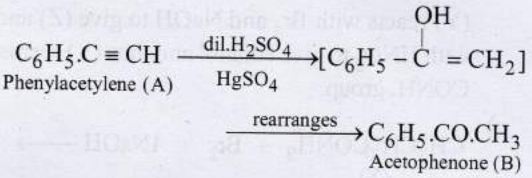
(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone (B) is $-CH_3$. Hence, (B) should be $C_6H_5.CO.CH_3$.

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

Thus, compounds (A) to (D) are

$\underset{(A)}{C_6H_5.C\equiv CH}$ $\underset{(B)}{C_6H_5.CO.CH_3}$ $\underset{(C)}{C_6H_5COOH}$ $\underset{(D)}{CHI_3}$

Formation of (B) from (A)



$\underset{\text{Phenylacetylene (A)}}{C_6H_5.C\equiv CH} \xrightarrow[HgSO_4]{dil.H_2SO_4} [C_6H_5-\overset{OH}{C}=CH_2]$

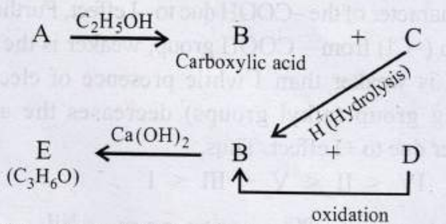
$\xrightarrow{\text{rearranges}} \underset{\text{Acetophenone (B)}}{C_6H_5.CO.CH_3}$

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

$\underset{(A)}{SOCl_2} + CH_3COOH \longrightarrow \underset{(C)}{CH_3COCl} + SO_2 + HCl$

$\underset{(C)}{2CH_3COCl} + (CH_3)_2Cd \longrightarrow \underset{(D)}{2CH_3-CO-CH_3} + CdCl_2$

67.



$A \xrightarrow{C_2H_5OH} \underset{\text{Carboxylic acid}}{B} + C$

$C \xrightarrow{H^+\ \text{(Hydrolysis)}} B + D$

$D \xrightarrow{\text{oxidation}} B$

$B \xrightarrow{Ca(OH)_2} \underset{(C_3H_6O)}{E}$

(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 CH_3COOH.

(*iii*) Compound 'B' is obtained by the oxidation of 'D', the latter must be ethyl alcohol, C_2H_5OH and hence 'C' must be ethyl acetate, $CH_3COOC_2H_5$.

(*iv*) Since, compound 'A' when treated with ethyl alcohol gives acetic acid 'B' and ethyl acetate 'C', it must be acetic anhydride.

$$\begin{tikzcd}
\underset{(A)}{CH_3CO.O.COCH_3} + C_2H_5OH \arrow[r] & \underset{(B)}{CH_3COOH} + & \underset{(C)}{CH_3COOC_2H_5} \arrow[d, "H^+"] \\
\underset{(E)}{CH_3COCH_3} & \underset{(B)}{CH_3COOH} + \arrow[l, "Ca(OH)_2", "heat"'] & \underset{(D)}{C_2H_5OH} \arrow[l, bend left, "oxidation"]
\end{tikzcd}$$

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 C_3H_7NO.

(Y) reacts with Br_2 and NaOH to give (Z) and (Z) reacts with HNO_2 to give ethanol and thus (Y) seems to have —$CONH_2$ group.

$$\underset{(Y)}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \longrightarrow$$

$$\underset{\text{(Z) basic}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(Y) is formed from (X) having Cl on treatment with NH_3 and So, (X) is CH_3CH_2COCl *i.e.*, propanoyl chloride.

$$\underset{(X)}{CH_3CH_2COCl} + NH_3 \rightarrow \underset{(Y)}{CH_3CH_2CONH_2}$$

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,

$$IV < II < V < III < I$$

70. (*i*) $C_6H_5COOH \xrightarrow{PCl_5} \underset{(C)}{C_6H_5COCl} \xrightarrow{NH_3}$

$$\underset{(D)}{C_6H_5CONH_2} \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} \underset{(E)}{C_6H_5CH_2NH_2}$$

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

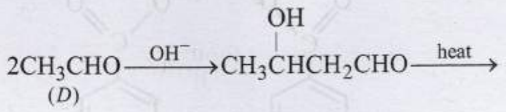
$$\xrightarrow[ZnCl_2]{HCl} \underset{(G)}{CH_3CH = CHCH_2Cl}$$

$$\xrightarrow[H^+]{KCN} \underset{(H)}{CH_3CH = CHCH_2COOH}$$

71.

$$\begin{tikzcd}
\underset{C_6H_{12}O_2}{A} \arrow[r, "Reduction", "by\ LiAlH_4"'] & B \arrow[d, "Oxidation"] & + & C \\
\underset{\substack{\text{Monobasic acid}\\ \text{(Mol. wt. = 60)}}}{F} & D \arrow[l, "oxi."'] \arrow[rr, "(i)\ aq.\ OH^-", "(ii)\ heat"'] & & E \arrow[u, "H_2/catalyst"']
\end{tikzcd}$$

Molecular weight of the monobasic acid (RCOOH) indicates that the R– should be CH_3– *i.e.*, acid *F* should be acetic acid (CH_3COOH, mol. wt. 60). Thus, compound *D* must be acetaldehyde CH_3CHO, and compound *B* which on oxidation gives CH_3CHO must be ethanol, CH_3CH_2OH. Acetaldehyde (*D*) on treating with aqueous alkali will undergo aldol condensation.



$$\underset{(D)}{2CH_3CHO} \xrightarrow{OH^-} CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO \xrightarrow{heat}$$

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

Nature of A. Thus it is evident that reduction of *A* with $LiAlH_4$ gives two alcohols; *B* (ethanol) and *C* (butanol). Hence, *A* must be an ester *i.e.*, ethyl butanoate ($CH_3CH_2CH_2COOC_2H_5$).

$$\underset{\text{Ethyl butanoate, }A}{CH_3CH_2CH_2COOC_2H_5} \xrightarrow{LiAlH_4}$$

$$\underset{\text{Butanol, }C}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Ethanol, }B}{C_2H_5OH}$$

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

$$\text{Aq. NaOH} \xrightarrow[\text{High temp., pressure}]{\text{Gas B}} \text{Sod. salt of acid } A$$

$$\xrightarrow[\text{(ii) } H_2SO_4]{\text{(i) NaOH (heat)}} \text{Dibasic acid, } C$$

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 $C = CHO_2$

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

Mol. wt. of acid $C = 45 \times 2 = 90$
∴ Mol. formula of $C = C_2H_2O_4$

Since it is dicarboxylic acid, it must have two –COOH groups. Hence C is $\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}}$

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

$$2NaOH(aq.) \xrightarrow{2CO_2(B)} \underset{(A)}{\begin{array}{c}HCOONa\\+\\HCOONa\end{array}}$$

$$\xrightarrow[\text{heat}]{NaOH} \begin{array}{c}COONa\\|\\COONa\end{array} \xrightarrow{H_2SO_4} \underset{(C)}{\begin{array}{c}COOH\\|\\COOH\end{array}}$$

73. (*i*) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{PCl_5} CH_3COCl$

$$\xrightarrow{C_6H_5MgBr} C_6H_5COCH_3$$

$$\xrightarrow{C_6H_5MgBr} CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-OMgBr$$

$$\xrightarrow{HOH} (C_6H_5)_2\underset{\underset{OH}{|}}{C}CH_3 \xrightarrow[-H_2O]{\text{heat}}$$

$$(C_6H_5)_2C=CH_2$$

$$\xrightarrow{CrO_3} C_6H_5COC_6H_5 + \underset{\text{Methanoic acid}}{HCOOH}$$

(*ii*) $\underset{\text{Ethanal}}{CH_3.CHO} \xrightarrow[\text{(cross aldol condens)}]{HCHO/NaOH} \underset{\underset{OH}{|}}{CH_2}CH_2CHO$

$$\xrightarrow[\text{(heat)}]{\text{Dehydration}} \underset{\text{propenal}}{CH_2=CHCHO}$$

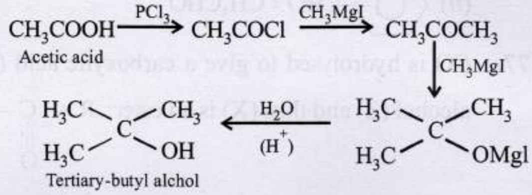
$$\xrightarrow{HCN} CH_2=CH-\underset{\underset{OH}{|}}{CH}-CN$$

Propenal cyanohydrn

$$\xrightarrow[H^+]{\text{hydrolysis}} CH_2=CH-\underset{\underset{OH}{|}}{CH}-COOH$$

2-Hydroxy-3-butenoic acid

(*iii*)



74. $P/Cl_2, NH_2CH_2COONH_4$

75.

$$\begin{tikzcd}
A \arrow[r, "\text{mild}", "\text{oxi}"'] \arrow[d, "CH_3COOH,\ H_2SO_4"] & C \arrow[r, "\text{(i) 50\% KOH}", "\text{(ii) HCl}"'] & A + D \arrow[d, "\text{(i) }PCl_5\ \text{(ii) }NH_3"] \\
\text{Ester, B} & HCN & E \arrow[l, "(-H_2O)"']
\end{tikzcd}$$

The above reactions lead to following conclusions.

(i) Reaction of (A) with CH_3COOH in presence of H_2SO_4 to form ester (B) indicates that (A) is an alcohol.

(ii) Reaction of (C) with 50% KOH followed by acidification to give alcohol (A) and the compound (D) seems to be the Cannizzaro reaction. Hence, (C) must be an aldehyde and (D) must be an acid. The nature of (C) as aldehyde is again in consistent with the fact that it is obtained by the mild oxidation of (A) which has been established as an alcohol.

(iii) Structure of acid (D) is established by its given facts.

$$\underset{(D)}{-COOH} \xrightarrow{PCl_5} -COCl \xrightarrow{NH_3} \underset{(E)}{-CONH_2}$$

$$\xrightarrow{-H_2O} HCN$$

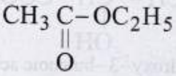
Formation of HCN by the dehydration of (E) establishes that (E) is $HCONH_2$ and hence (D) is HCOOH.

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

Thus, the various compounds are as below :

(A)	(B)	(C)	(D)	(E)
CH_3OH	CH_3COOCH_3	HCHO	HCOOH	$HCONH_2$
Methyl alcohol	Methyl acetate	Formaldehyde	Formic acid	Formamide

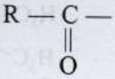
76. (*i*)

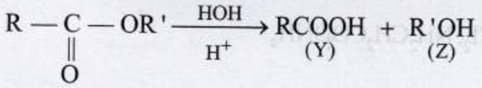


$CH_3\underset{\underset{O}{\|}}{C}-OC_2H_5$

(*ii*)  $-CHO + CH_3CHO$

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





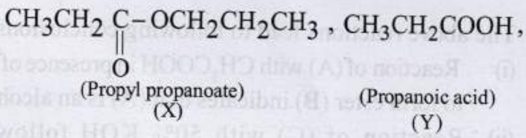
$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[H^+]{HOH} \underset{(Y)}{RCOOH} + \underset{(Z)}{R'OH}$

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

$\underset{(Z)}{R'OH} \xrightarrow{\text{Oxidation}} RCOOH$

or $RCH_2OH \longrightarrow RCOOH$ $(\therefore R' \text{ is } R—CH_2)$

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



$\underset{\substack{\text{(Propyl propanoate)}\\(X)}}{CH_3CH_2\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_3}$, $\underset{\substack{\text{(Propanoic acid)}\\(Y)}}{CH_3CH_2COOH}$,

$CH_3CH_2CH_2OH$

(Propan–1–ol)
(Z)

78. The weaker a base better is its leavability.

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:

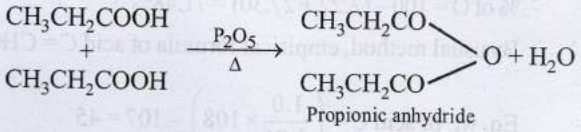
$NH_2^- > OR^- > OCOR^- > Cl^-$

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:

$CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$.

79. $CH_3CH_2CHO + [O] \xrightarrow[\text{(Tollen's reagent)}]{AgNO_3/NH_4OH} CH_3CH_2COOH + 2Ag$



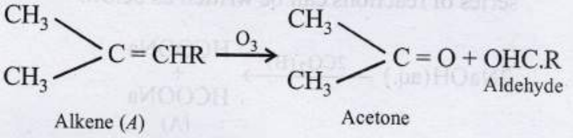
Propionic anhydride

80. (*i*) $C_2H_2 \xrightarrow[Hg^{2+}]{H_2SO_4\text{(dil.)}} CH_3CHO \xrightarrow[\text{reduction}]{H_2/\text{cat.}} CH_3CH_2OH$

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

$\xrightarrow{H^+/H_2O} \underset{\text{Acetic acid}}{CH_3COOH}$

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

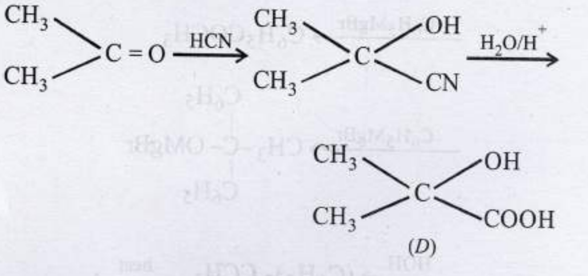


As per problem :

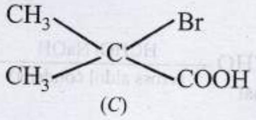
$RCHO \xrightarrow{[O]} RCOOH\,[B] \xrightarrow{P/Br_2}$

Bromo compound $[C] \xrightarrow{H_2O}$ Hydroxy acid $[D]$

Structure of (*D*) is determined by the reaction :

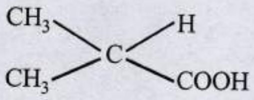


The compound (*D*) is obtained by hydrolysis of (*C*) with aqueous alkali. Since (*C*) is a bromo compound, therefore it has a bromo group whereas the compound (*D*) has a hydroxyl group. Therefore, structure of *C* is

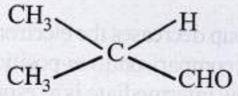


(*C*)

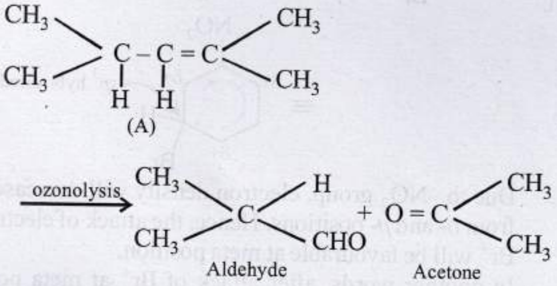
The compound (*C*) is formed by bromination of compound (*B*), therefore, the compound (*B*) is



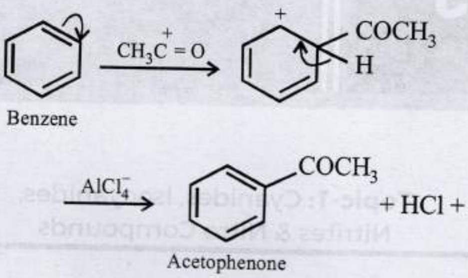
The compound (*B*) is formed by oxidation of an aldehyde therefore, the structure of the aldehyde is



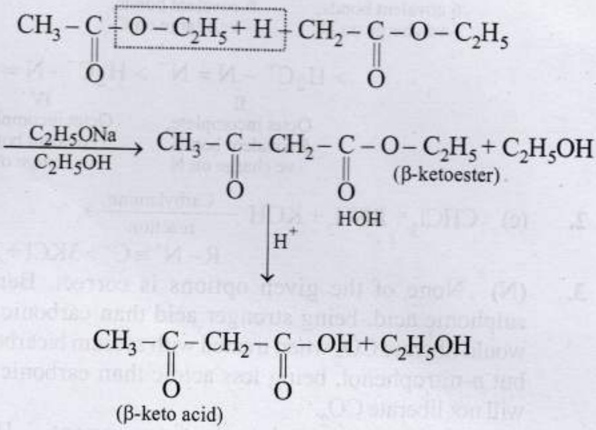
The aldehyde and acetone are formed by ozonolysis of alkene. Therefore, the double bond in alkene should be between the carbon atoms of the two carbonyl compounds (the aldehyde and acetone). Therefore, the compounds and the reactions are identified as



82. $CH_3COCl + AlCl_3 \rightarrow CH_3C^+=O + AlCl_4^-$



83. First step is Claisen condensation.



$$CH_3-\underset{\underset{O}{\|}}{C}-\boxed{O-C_2H_5+H}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5$$

$$\xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5+C_2H_5OH$$

(β-ketoester)

$$\Big\downarrow{\scriptstyle H^+}^{HOH}$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OH+C_2H_5OH$$

(β-keto acid)