



CHEMISTRY

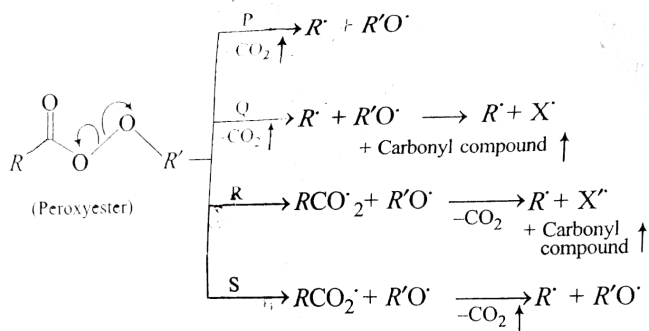
BOOKS - IIT-JEE PREVIOUS YEAR (CHEMISTRY)

CARBOXYLIC ACID AND THEIR DERIVATIVES

Topic I Objective Question

1. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from peroxyesters are shown below. Match each pathway from column I with an appropriate structure from Column II and select the correct answer using the code given below

the lists.



- A.

P	Q	R	S
1	3	4	2
- B.

P	Q	R	S
2	4	3	1
- C.

P	Q	R	S
4	1	2	3
- D.

P	Q	R	S
3	2	1	4

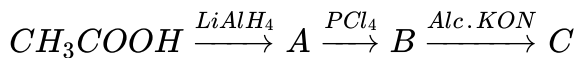
Answer: A



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Jee Main And Advanced

1. In the reaction



The product C is

- A. acetaldehyded
- B. acety lene
- C. ethylene
- D. acetly chloride

Answer: C



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2. The compound that does not liberate CO_2 , on treatment with aqueous sodium bicarbonate is

- A. benzoic acid
- B. benzenesulphonic acid

C. salicylic acid

D. carbolic acid (Phenol)

Answer: D



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3. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to yield $CH_3CH_2NH_2$. A is .

A. CH_3COOH

B. $CH_3CH_2CH_2COOH$

C. $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - COOH$

D. CH_3CH_2COOH

Answer: D



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4. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecule of the former compound is .

A. 2

B. 5

C. 4

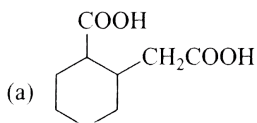
D. 6

Answer: B

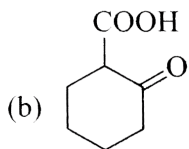


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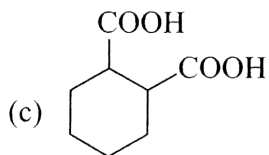
5. The compound that undergoes decarboxylation most readily under mild condition is



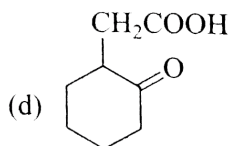
A.



B.



C.



D.

Answer: B



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6. The carboxyl functional group ($-COOH$) is present in :

A. picric acid

B. barbituric acid

C. ascorbic acid

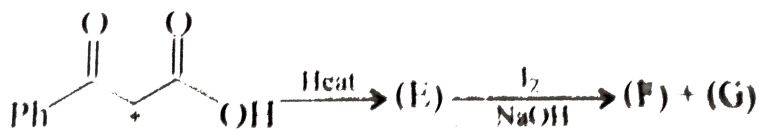
D. aspirin

Answer: D

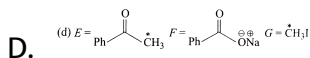
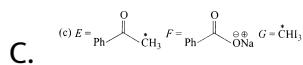
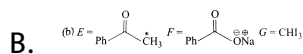
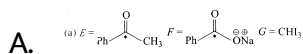


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7. In the following reaction sequence, the correct structures of (E), (F) and (G) are:



(*implies ^{13}C -labelled carbon)

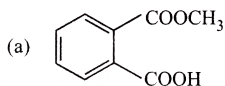
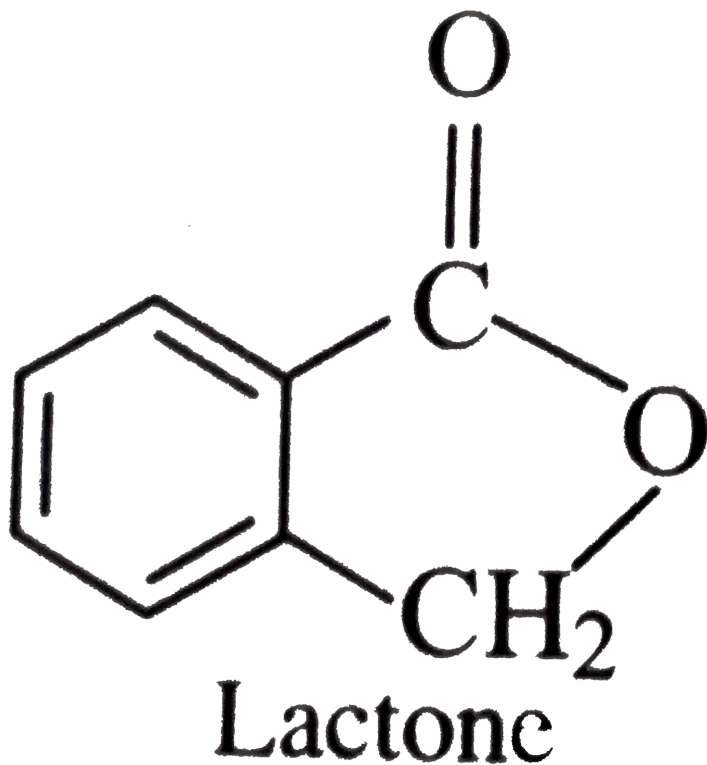


Answer: C

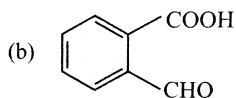


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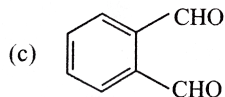
8. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the main product ?



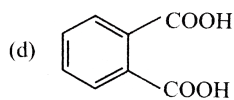
A.



B.



C.



D.

Answer: C



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9. When benzene sulphonic acid and P-nitrophenol are treated with $NaHCO_3$, the gases released, respectively, are :

A. SO_2 , NO_2

B. SO_2 , NO

C. SO_2 , CO_2

D. CO_2 , CO_2

Answer: D



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10. Benzamide on treatment with $POCl_3$ gives :

- A. aniline
- B. benzonitrile
- C. chlorobenzene
- D. benzyl amine

Answer: B



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11. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be :

- A. optically active mixture
- B. pure enantiomer

C. meso compound

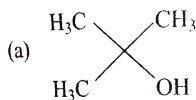
D. racemic mixture

Answer: D

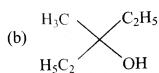


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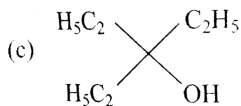
12. Ethylester $\xrightarrow[\text{excess}]{\text{CH}_3\text{CH}_2\text{MgBr}}$ P. The product P will be



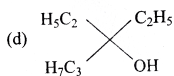
A.



B.



C.

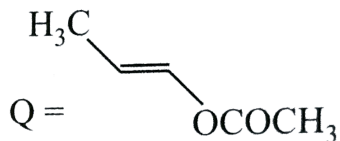
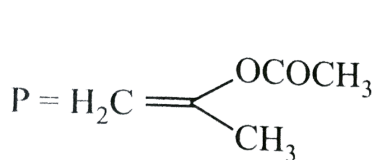


D.

Answer: A

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13. The product of acidic hydrolysis of *P* and *Q* can be distinguished by



- A. Lucas reagent
- B. 2,4-DNP
- C. fehling's solution
- D. NaHSO_3

Answer: A

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14. Benzoyl chloride is prepared from benzoic acid by :

- A. $\text{Cl}_2, h\nu$

B. SO_2Cl_2

C. SO_2

D. Cl_2, H_2O

Answer: A



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15. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The carbon of CO_2 comes from

A. methyl group

B. carboxylic acid group

C. methylene group

D. bicarbonate group

Answer: D



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16. Hydrogenation of benzoyl chloride in the presence of $Pd/BaSO_4$ gives :

- A. benzyl alcohol
- B. benzaldehyde
- C. benzoic acid
- D. phenol

Answer: B



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17. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine ?

- A. PCl_5
- B. $NaOH + Br_2$

C. Sodalime

D. Hot conc. H_2SO_4

Answer: B



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18. Which of the following is basic ?

A. CH_3CH_2OH

B. H_2O_2

C. $HOCH_2CH_2OH$

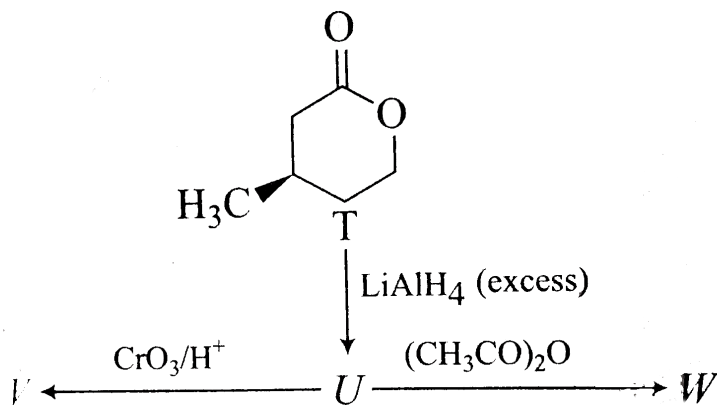
D. CH_3COOH

Answer: A



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



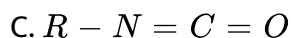
- A. T is soluble in hot aqueous NaOH
- B. U is optically active
- C. Molecular formula of W is $\text{C}_{10}\text{H}_{18}\text{O}_4$
- D. V gives effervescence on treatment with aqueous NaHCO_3

Answer: A::C::D



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20. The reaction of $RCONH_2$ with a mixture of Br_2 and aqueous KOH gives RNH_2 as the main product. The intermediate (s) involved in this reaction is (are) .



Answer: A::C



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21. p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

- A. Statement I is true, Statement II is true, Statement I is a correct explanation of Statement II.
- B. Statement I is true, Statement II is true, Statement II is not the correct explanation of Statement I.
- C. Statement I is true, Statement II is false.
- D. Statement I is false, Statement II is true.

Answer: D



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22. Acetic acid does not undergo haloform reaction.

Acetic acid has no α -hydrogen.

- A. Statement I is true, Statement II is true, Statement I is a correct explanation of Statement II.

B. Statement I is true, Statement II is true, Statement II is not the correct explanation of Statement I.

C. Statement I is true, Statement II is false.

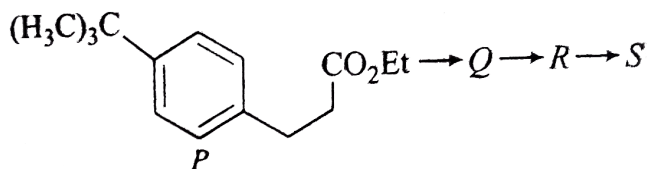
D. Statement I is false, Statement II is true.

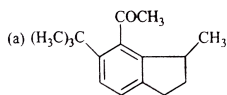
Answer: C



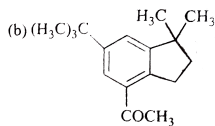
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23. The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O give Q the compound Q on treatment with H_2SO_4 at $0^\circ C$ gives R. the reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2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

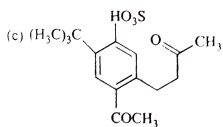




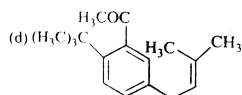
A.



B.



C.



D.

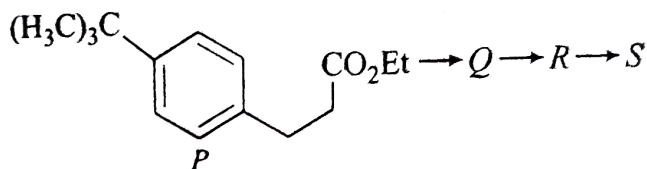
Answer: A



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

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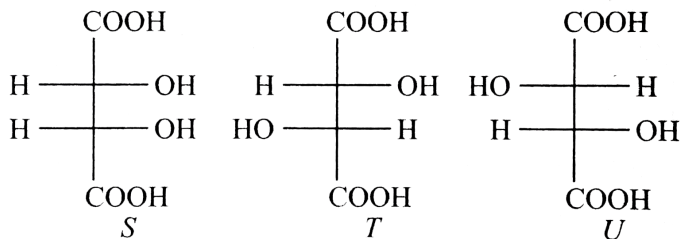
- A. Aromatic sulfonation and friedel- Crafts acylation
- B. Friedel-Crafts alkylation and Firedel-Crafts acylation
- C. Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
- D. Dehydration and Friedel-Crafts acylation

Answer: C



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25. P and Q are isomer of dicarboxylic acid $C_4H_4O_4$ Both decolourise 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.



Compounds formed P and Q are, respectively

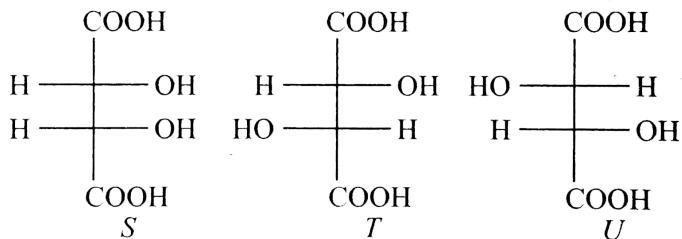
- A. Optically active S and optically active pair (T,U)
- B. Optically inactive S and optically inactive pair (T,U)
- C. Optically active pair (Y,U) and optically active S
- D. Optically inactive pair (T,U) and optically inactive S

Answer: B

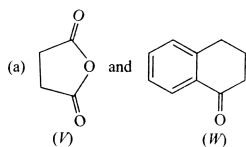
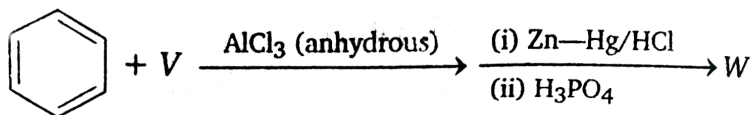
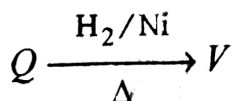
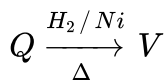


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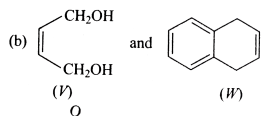
26. P and Q are isomer of dicarboxylic acid $C_4H_4O_4$. Both decolourise Br_2/H_2O . On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U.



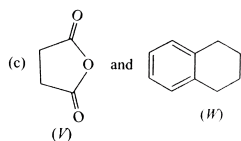
In the following reaction sequences V and W are respectively



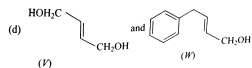
A.



B.



C.

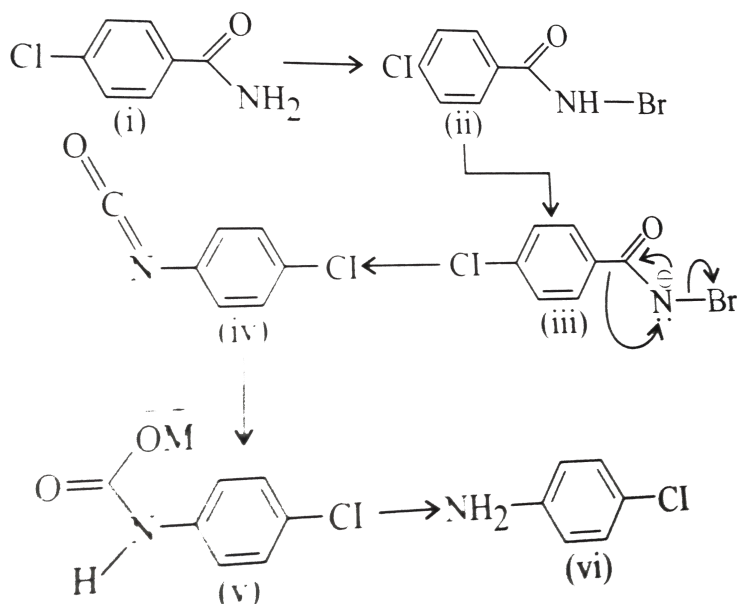


D.

Answer: A

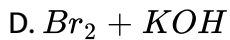
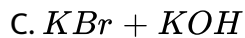
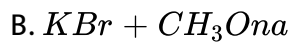
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27. $RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this $RCONHBr$ is formed from which this reaction has derived its name. Electron-donating group at phenyl activities the reaction. Hofmann degradation reaction is an intramolecular reaction.

How can the conversion of (i) \rightarrow (ii) be brought about ?

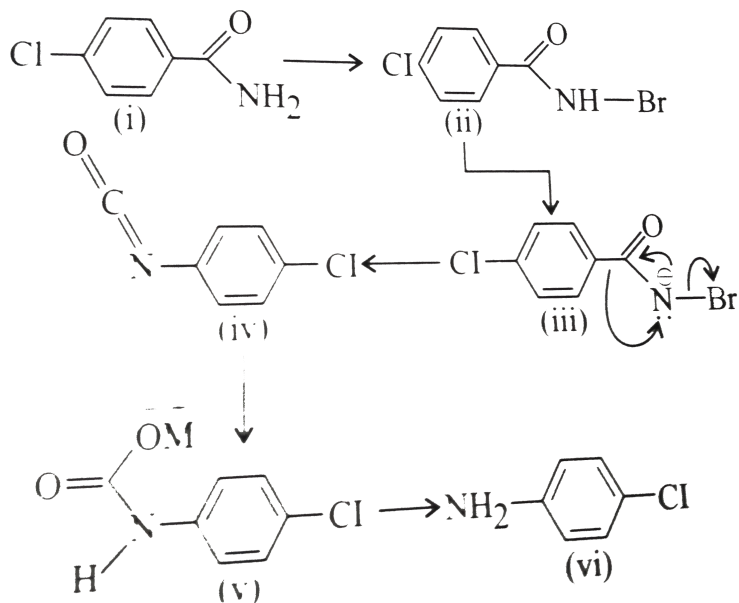


Answer: D



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28. $RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this $RCONHBr$ is formed from which this reaction has derived its name. Electron-donating group at phenyl activities the reaction. Hofmann degradation reaction is an intramolecular reaction.

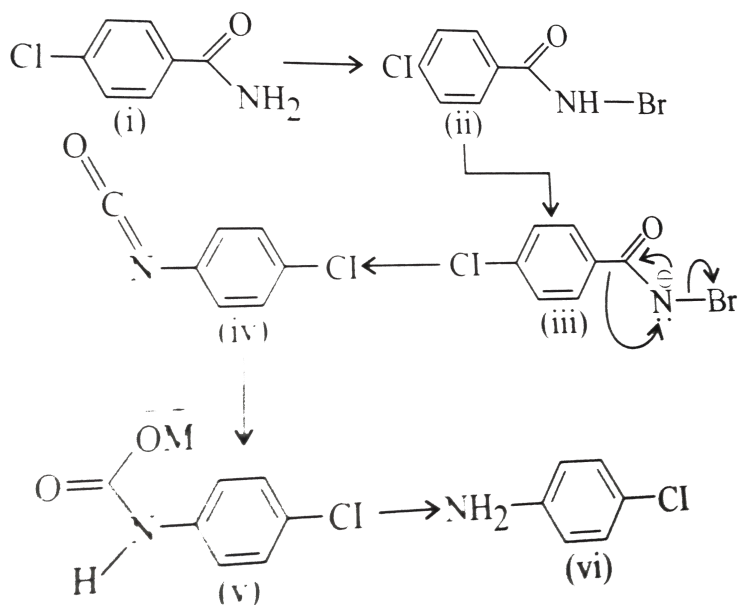
Which is the rate-determining step in Hofmann bromamide degradation ?

- A. Formation of (I)
- B. Formation (II)
- C. Formation of (III)
- D. Formation of (IV)

Answer: D

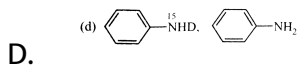
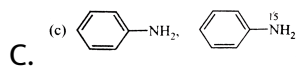
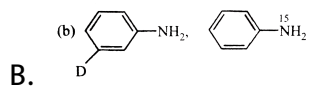
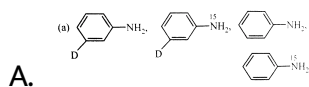
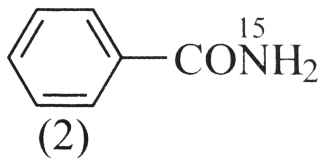
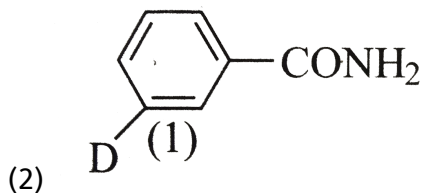
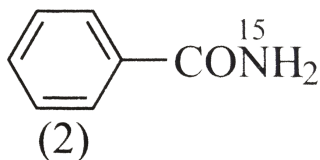
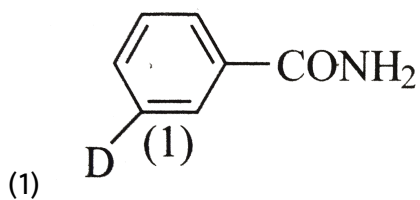


29. $RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this $RCONHBr$ is formed from which this reaction has derived its name. Electron-donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

What are the constituent amines formed when the mixture of (1) and (2) undergoes Hofmann bromamide degradation ?



Answer: B



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30. Formic acid when heated with *conc.* H_2SO_4 produces



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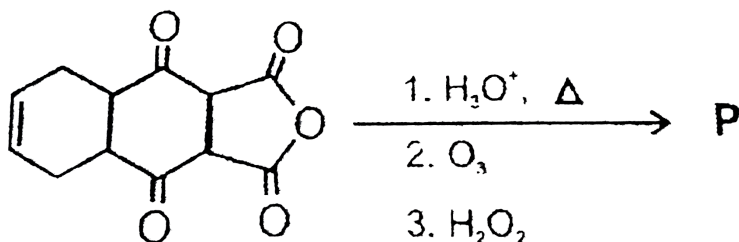
31. The boiling point of propionic acid is more than that of n-butyl alcohol, an alcohol of comparable molecular weight.

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32. Hydrolysis of an ester in the presence of a dilute acid is known as

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33. The total number of carboxylic acid groups in the product P is:



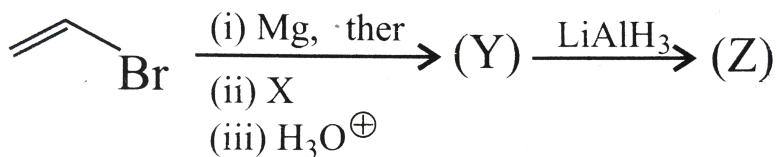
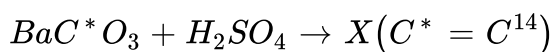
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34. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form B. On oxidation with $KMnO_4$, A gives m-chlorobenzoic acid. Identify A and B



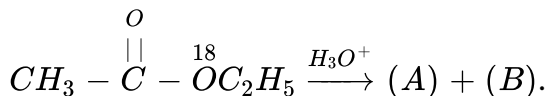
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35. Identify $Z + Y$ in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Take C^* as carbon in the entire scheme.



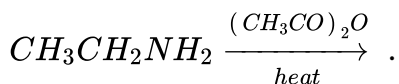
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36. Write the structures of products (A) and (B)



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37. The products (A) and (B) of the reaction



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38. An ester $A(C_4H_8O_2)$, on treatment with excess of methyl magnesium bromide 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.



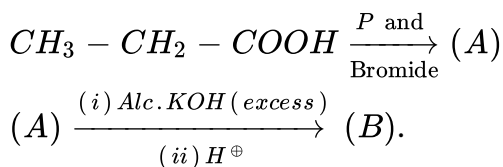
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39. A hydrocarbon A of the molecular formula C_8H_{10} . On ozonolysis gives only the compound $B(C_4H_6O_2)$. The compound B can also be obtained from the alkyl bromide $C(C_3H_5Br)$ upon treatment with Mg in dry ether followed by the addition of CO_2 and acidification. Identify A , B and C and also give equations for the reactions.



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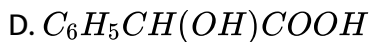
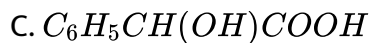
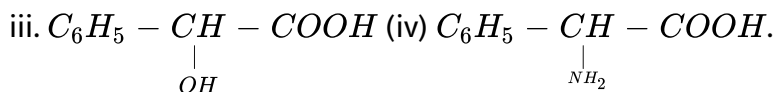
40. Complete the following sequence of reactions with appropriate structures.



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41. Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly.



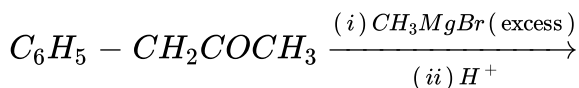


Answer: N/A



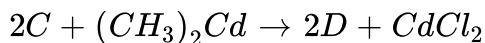
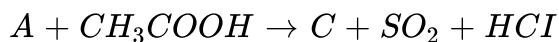
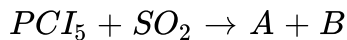
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42. Predict the major product in the following reaction :



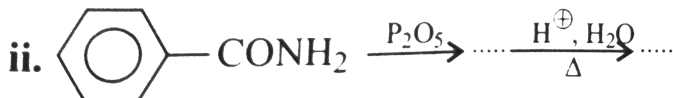
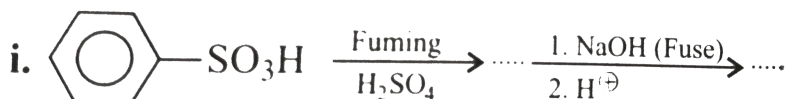
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43. In the following reactions. Identify the compounds A, b, c and D



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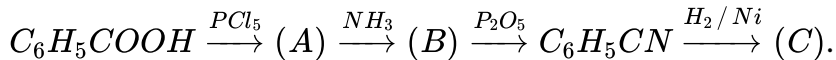
44. Complete the following sequence of the reactions with appropriate structures.



(i)

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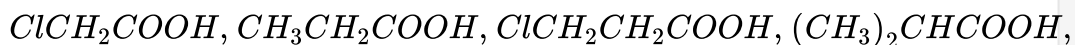
45. In the following identify the compounds/reaction conditions represented by the alphabets (A), (B), and (C) :



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46. Arrange the following as stated :

'Increasing order of acidic strength'.



.



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47. How will you bring about the following conversion ?

'Ethanoic acid to a mixture of methanoic acid and diphenyl ketone'.



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48. Give reasons for the following :

'Carbon-oxygen bond lengths in formic acid are 1.23Å and 1.36Å and

both carbon-oxygen bonds in sodium formate have the same value, i.e., 1.27\AA .



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49. Write the balanced equations for the following reaction :

'Acetamide is reacted with bromine in the presence of potassium hydroxide'.



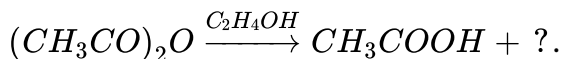
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50. A liquid (X) having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chrome acid gives (Y) . What are the structures of (X), (Y), and (Z) ?



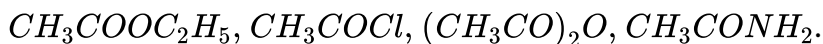
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51. Complete the following with appropriate structures :



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52. Arrange the following in order of their increasing ease of hydrolysis :



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53. Give reason in one or two sentences for the following : 'Formic acid is a stronger acid than acetic acid'.



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54. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis.

'Propionic anhydride from propionaldehyde'.

$[AgNO_3, NH_4OH, P_2O_5]$.



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55. Give reasons for the following in one or two sentences.

'Acetic acid can be halogenated in the presence of P and Cl_2 , but formic acid cannot be halogenated in the same way'.



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56. State with balanced equation what happens when 'Acetic anhydride reacts with phenol in the presence of a base'.



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57. Write the structural formula of the main organic product formed when ethyl acetate is treated with double the molar quantity of

$MeMgBr$ and the reaction mixture is poured into H_2O .



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58. Write the chemical equation to show what happens when 'Ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified'.



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59. Fischer esterification of phenylacetic acid with 1- propanol gave a mixture of 93 % of the ester, propyl phenylacetate, contaminated with 7 % unreacted acid. Which of the following treatments would be best used to purify the ester?

A. Reduce the unwanted acid with $LiAlH_4$ in ether

B. Wash an ether solution of the crude product with concentrated brine (aq.NaCl)

C. Wash an ether solution of the crude product with 5 % aqueous sulphuric acid

D. Wash an ether solution of the crude product with 5 % aqueous sodium carbonate

Answer: A



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60. The $C - NH_2$ bond in acetamide is 0.1 Å shorter than the $C - NH_2$ bond in ethylamine. Why?

A. $N : H$ repulsion in ethylamine

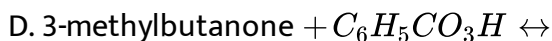
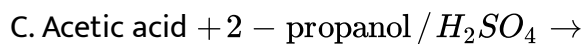
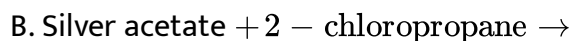
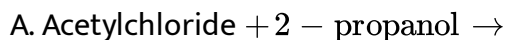
B. Hyperconjugation in ethylamine

C. Dipole interactions in acetamide

D. $p\pi$ resonance in acetamide

Answer: D

61. Which of the following reaction will produce isopropyl acetate in the best yield?



Answer: A

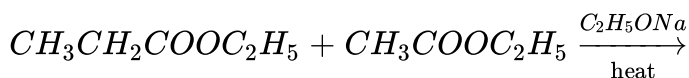
62. An organic acid (X) has molecular formula $C_8H_{16}O_2$. X on heating with NH_3 forms Y which on treatment with alkaline Br_2 from Z. Z on treatment with HNO_2 followed by with H_2SO_4 gives 2,4- dimethyl 1-2

pentene. How many different acids (X) can give the indicated final product?



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63. In the following Cross-Claisen condensation reaction, how many different β -ketone esters would be formed?



A. 4

B. 2


C. 3

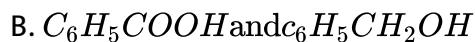
D. 1

Answer: A



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



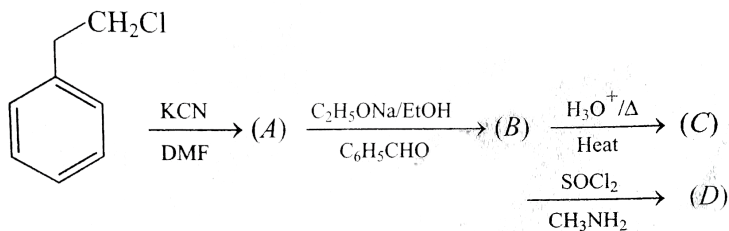
Answer: B::D



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Subjective Questions

1. Find the final product A,B,C and D of the reaction



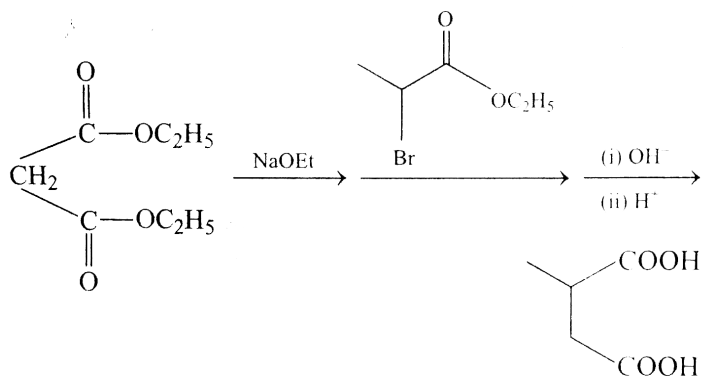
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2. (\pm) 2-Phenylpropanoic acid on treatment with (+) 2-butanol gives (A) and (B). Deduce their structures and also establish stereochemical relation between them.



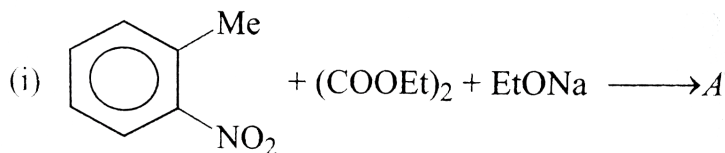
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3. Explain briefly the formation of the products giving the structures of the intermediates

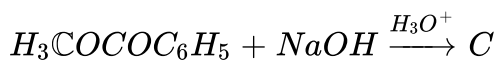
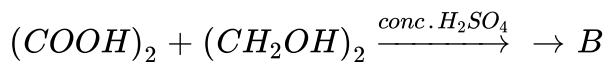


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4. Complete the following. Giving the structures of the principle organic



product



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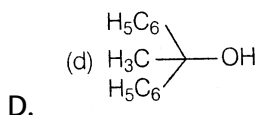
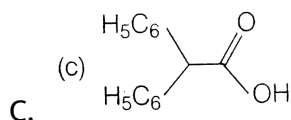
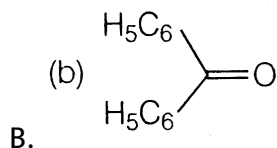
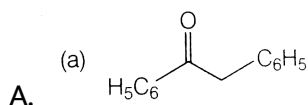
1. Ethyl acetate undergoes the following sequence of reactions

treatment with excess phenylmagnesium bromide in ether

heating with conc. H_3PO_4

treatment B_2H_6 in ether, followed by alkaline H_2O_2

treatment with Jones' reagent (CrO_3 in aqueous acid + acetone)

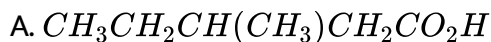


Answer: A



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2. A carboxylic acid X is treated with bromine(1 mole) in the presence of a little phosphorous. The isolated product is heated with a strong base and then oxidized with $O_3 / Zn - H_2O$. one of the two oxidation products is a natural compound which reacts with hydroxylamine to give an oxime, X can be



Answer: A



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3. Match the reaction from Column I with the expected products from column II :

Column I		Column II	
(A)	$\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{C}_2\text{H}_5\text{ONa}} \xrightarrow[\text{Heat}]{\text{HO}^-, \text{H}_2\text{O}}$	(p)	
(B)	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{C}_2\text{H}_5\text{ONa}} \xrightarrow[\text{Heat}]{\text{HO}^-, \text{H}_2\text{O}}$	(q)	
(C)	$\text{CH}_3\text{COOH} + \text{CH}_3\text{Li}(\text{excess}) \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{HO}^-, \text{H}_2\text{O}}$	(r)	butanone
(D)	$\text{Propanone} + \text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{C}_2\text{H}_5\text{ONa}}$	(s)	3-pentanone
		(t)	
		(u)	propanone



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