

CHAPTER 20

Aldehydes, Ketones and Carboxylic Acids

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

- Formic acid when heated with conc. H_2SO_4 produces
(1983 - 1 Mark)
- 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)
- 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)
- The structure of the enol form of $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3$ with intramolecular hydrogen bonding is
(1993 - 1 Mark)
- The Cannizzaro reaction is not given by (1983 - 1 Mark)
(a) trimethylacetaldehyde (b) acetaldehyde
(c) benzaldehyde (d) formaldehyde
- 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
- Polarisation of electrons in acrolein may be written as (1988 - 1 Mark)
(a) $\delta^- \text{CH}_2 = \text{CH} - \text{CH} = \text{O} \quad \delta^+$ (b) $\delta^- \text{CH}_2 = \text{CH} - \text{CH} = \text{O} \quad \delta^+$
(c) $\delta^- \text{CH}_2 = \text{CH} - \text{CH} = \text{O} \quad \delta^+$ (d) $\delta^- \text{CH}_2 = \text{CH} - \text{CH} = \text{O} \quad \delta^-$

B True / False

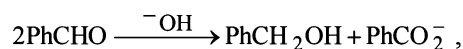
- Benzaldehyde undergoes aldol condensation in an alkaline medium.
(1982 - 1 Mark)
- Hydrolysis of an ester in presence of a dilute acid is known as saponification.
(1983 - 1 Mark)
- The yield of ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized.
(1983 - 1 Mark)
- The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol.
(1987 - 1 Mark)
- The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight.
(1991 - 1 Mark)
- 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
- 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
- Hydrogenation of benzoyl chloride in the presence of Pd on BaSO_4 gives (1992 - 1 Mark)
(a) Benzyl alcohol (b) Benzaldehyde
(c) Benzoic acid (d) Phenol

C MCQs with One Correct Answer

- 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
- When acetaldehyde is heated with Fehling's solution it gives a precipitate of (1983 - 1 Mark)
(a) Cu (b) CuO
(c) Cu_2O (d) $\text{Cu} + \text{Cu}_2\text{O} + \text{CuO}$
- The organic product formed in the reaction (1995S)
$$\text{C}_6\text{H}_5\text{COOH} \xrightarrow[\text{II } \text{H}_3\text{O}^+]{\text{I LiAlH}_4}$$

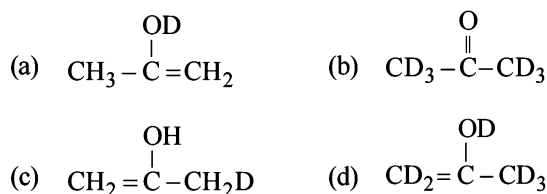
(a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{COOH} \& \text{CH}_4$
(c) $\text{C}_6\text{H}_5\text{CH}_3 \& \text{CH}_3\text{OH}$ (d) $\text{C}_6\text{H}_5\text{CH}_3 \& \text{CH}_4$
- The reaction products of $\text{C}_6\text{H}_5\text{OCH}_3 + \text{HI} \xrightarrow{\Delta}$ is : (1995S)
(a) $\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{I}$ (b) $\text{C}_6\text{H}_5\text{I} + \text{CH}_3\text{OH}$
(c) $\text{C}_6\text{H}_5\text{CH}_3 + \text{HOI}$ (d) $\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}$

11. In the Cannizzaro reaction given below, (1996 - 1 Mark)

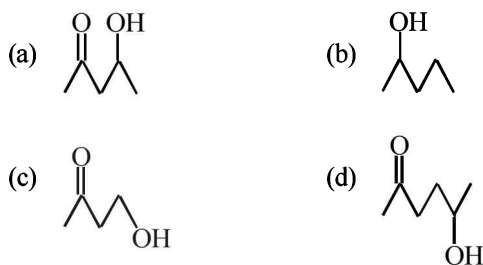


the slowest step is

- (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 .
12. 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
13. The enol form of acetone, after treatment with D_2O , gives. (1999 - 2 Marks)



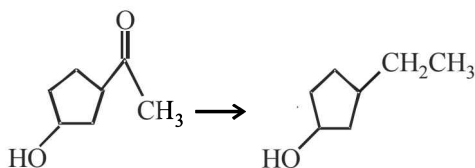
14. Which one of the following will most readily be dehydrated in acidic condition? (2000S)



15. Benzoyl chloride is prepared from benzoic acid by (2000S)

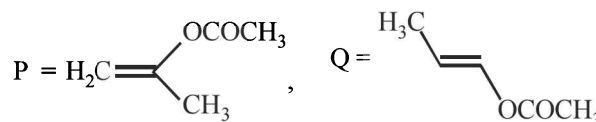


16. The appropriate reagent for the following transformation is (2000S)

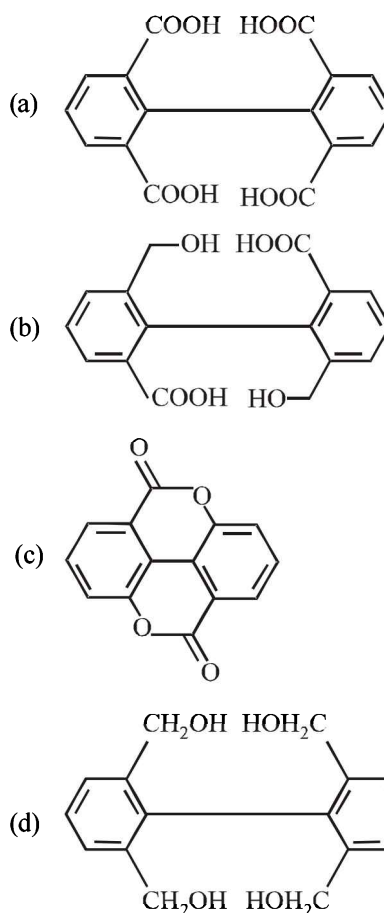
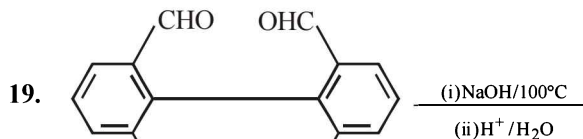


- (a) Zn(Hg), HCl (b) $\text{NH}_2\text{NH}_2, \text{OH}^-$
 (c) H_2/Ni (d) NaBH_4
17. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives (2001S)
- (a) benzyl alcohol and sodium formate
 (b) sodium benzoate and methyl alcohol
 (c) sodium benzoate and sodium formate
 (d) benzyl alcohol and methyl alcohol

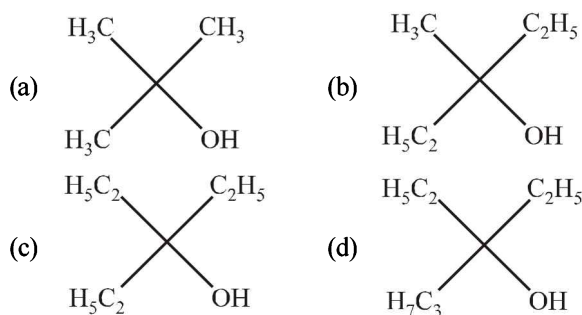
18. The product of acid hydrolysis of P and Q can be distinguished by (2003S)



- (a) Lucas Reagent (b) 2,4-DNP
 (c) Fehling's Solution (d) NaHSO_3



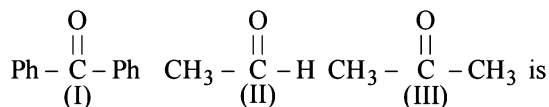
20. Ethyl ester $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P will be (2003S)



21. 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

22. The correct order of reactivity of PhMgBr with (2004S)

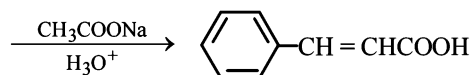
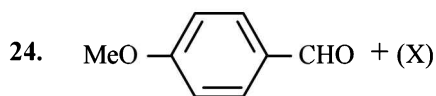


(a) (I) > (II) > (III) (b) (III) > (II) > (I)
(c) (II) > (III) > (I) (d) (I) > (III) > (II)

23. How will you convert butan-2-one to propanoic acid?

(2005S)

(a) Tollen's reagent (b) Fehling's solution
(c) NaOH/I₂/H⁺ (d) NaOH/NaI/H⁺

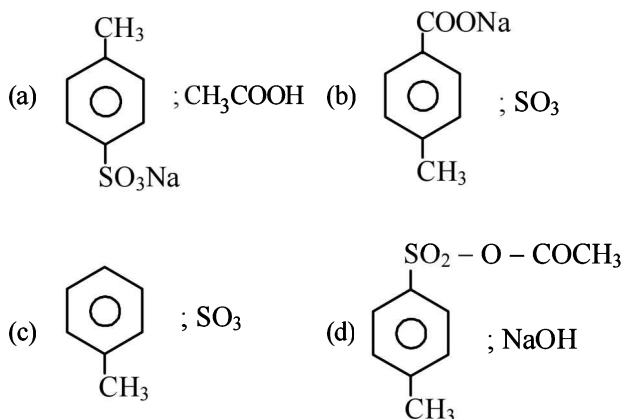


The compound (X) is

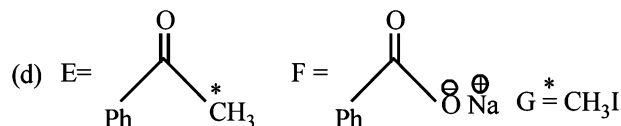
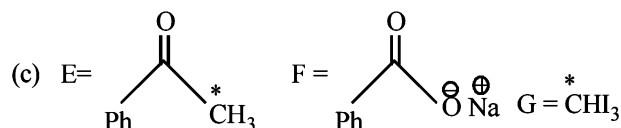
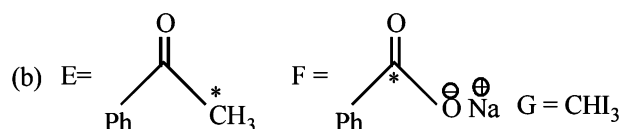
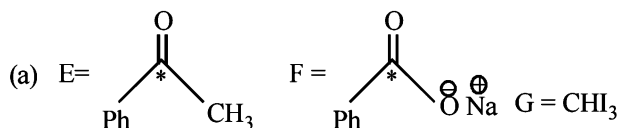
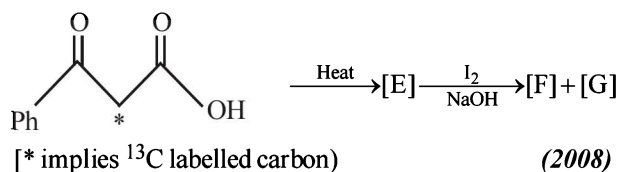
(2005S)

(a) CH₃COOH (b) BrCH₂ - COOH
(c) (CH₃CO)₂O (d) CHO - COOH

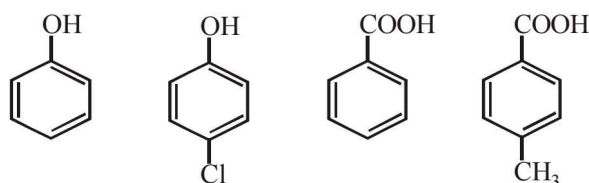
25. 4-Methylbenzenesulphonic acid reacts with sodium acetate to give (2005S)



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

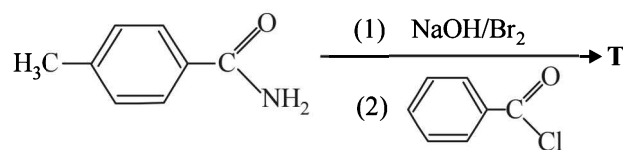


27. The correct acidity order of the following is (2009S)



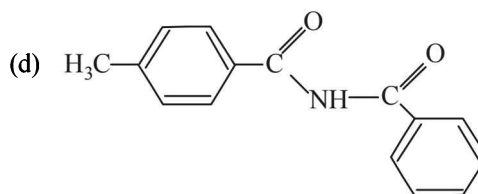
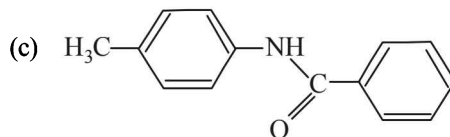
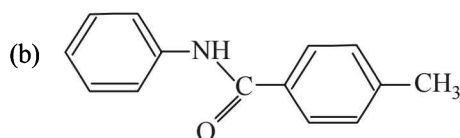
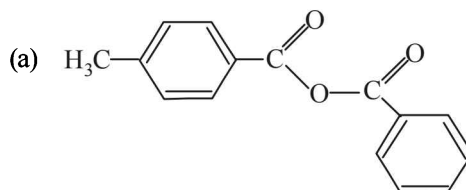
(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

28. In the reaction

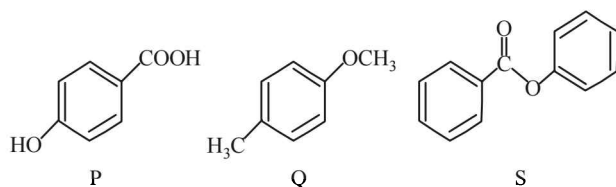


the structure of the product T is :

(2010)

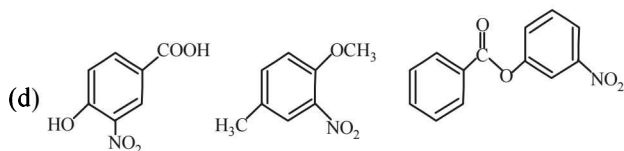
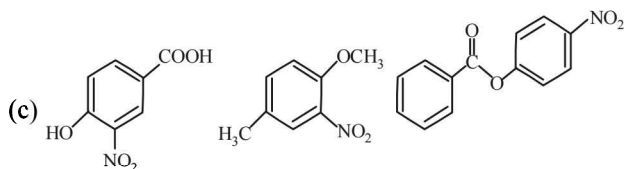
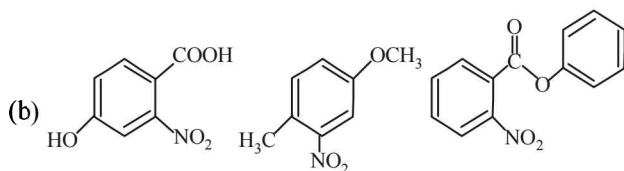
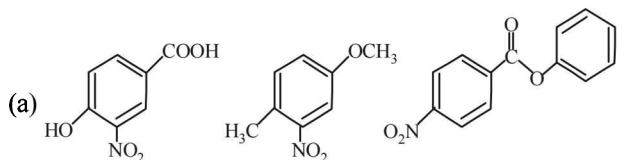


29. The compounds P, Q and S

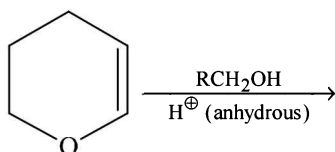


were separately subjected to nitration using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively, is :

(2010)



30. The major product of the following reaction is (2011)

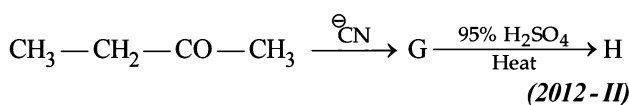


- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester

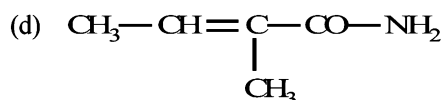
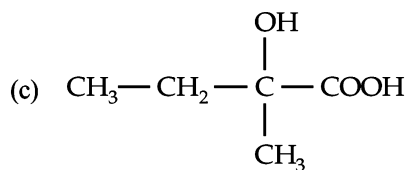
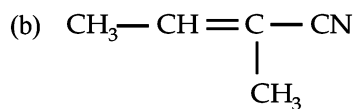
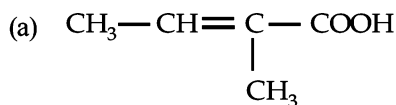
31. The carboxyl functional group ($-\text{COOH}$) is present in (2012)

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

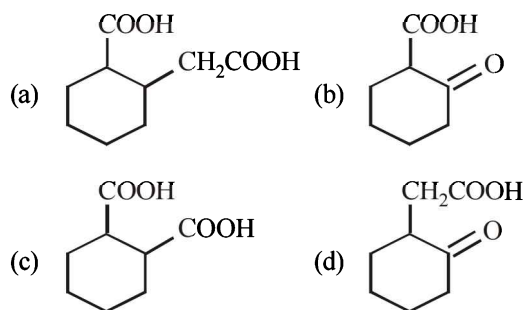
32. The major product **H** of the given reaction sequence is



(2012-II)



33. The compound that undergoes decarboxylation most readily under mild condition is (2012)

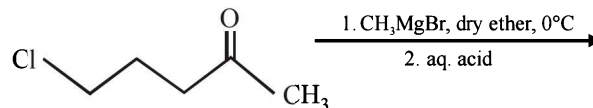


34. The compound that does NOT liberate CO_2 , on treatment with aqueous sodium bicarbonate solution, is

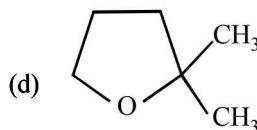
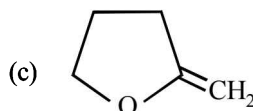
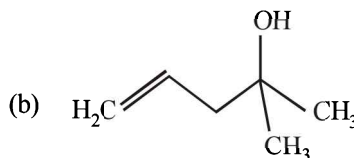
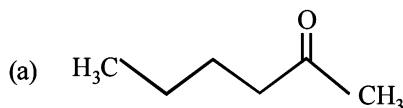
(JEE Adv. 2013)

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

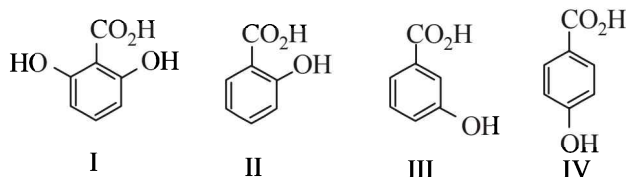
35. The major product in the following reaction is



(JEE Adv. 2014)



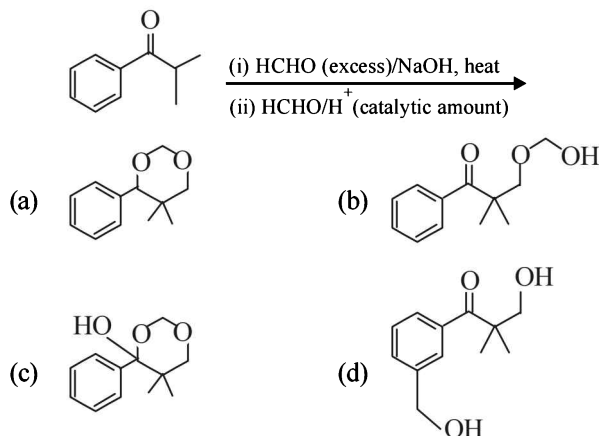
36. The correct order of acidity for the following compounds is



(JEE Adv. 2016)

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

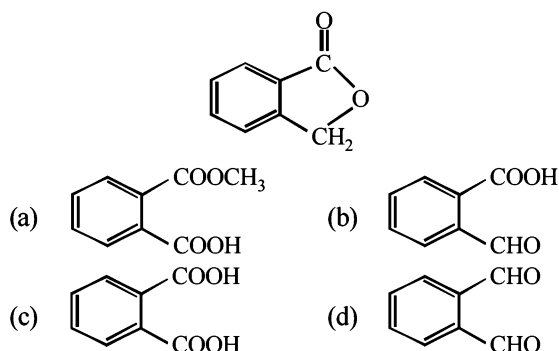
37. The major product of the following reaction sequence is
(JEE Adv. 2016)



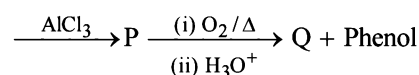
D MCQs with One or More Than One Correct

- Base catalysed aldol condensation occurs with :
(a) propionaldehyde (1984 - 1 Mark)
(b) benzaldehyde
(c) 2-methylpropionaldehyde
(d) 2,2-dimethylpropionaldehyde
- 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
- Which of the following compounds will react with ethanolic KCN? (1984 - 1 Mark)
(a) ethyl chloride (b) acetyl chloride
(c) chlorobenzene (d) benzaldehyde
- Keto-enol tautomerism is observed in (1988 - 1 Mark)
(a) $\text{H}_5\text{C}_6-\text{C}(=\text{O})-\text{H}$ (b) $\text{H}_5\text{C}_6-\text{C}(=\text{O})-\text{CH}_3$
(c) $\text{H}_5\text{C}_6-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ (d) $\text{H}_5\text{C}_6-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$
- Which of the following are examples of aldol condensation? (1989 - 1 Mark)
(a) $2\text{CH}_3\text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{CHOHCH}_2\text{CHO}$
(b) $2\text{CH}_3\text{COCH}_3 \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{COH}(\text{CH}_3)\text{CH}_2\text{COCH}_3$
(c) $2\text{HCHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{OH}$
(d) $\text{C}_6\text{H}_5\text{CHO} + \text{HCHO} \xrightarrow{\text{dil. NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$

- A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction (1998 - 2 Marks)
(b) Friedel-Craft alkylation
(c) Clemmensen reduction
(d) Reimer-Tiemann reaction
- Which of the following will react with water?
(1998 - 2 Marks)
(a) CHCl_3 (b) Cl_3CCHO
(c) CCl_4 (d) $\text{ClCH}_2\text{CH}_2\text{Cl}$
- Which of the following will undergo aldol condensation?
(1998 - 2 Marks)
(a) acetaldehyde (b) propanaldehyde
(c) benzaldehyde (d) trideuteroacetaldehyde
- Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? (2006 - 5M, -1)



10. + $\text{Cl}-\text{CH}_2\text{CH}_2\text{CH}_3$

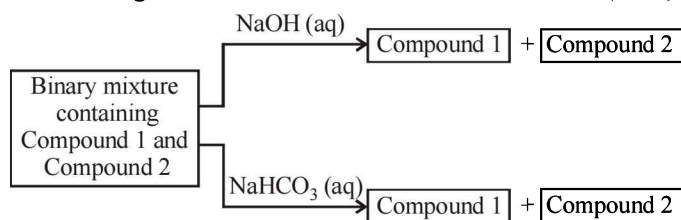


The major products P and Q are (2006 - 5M, -1)

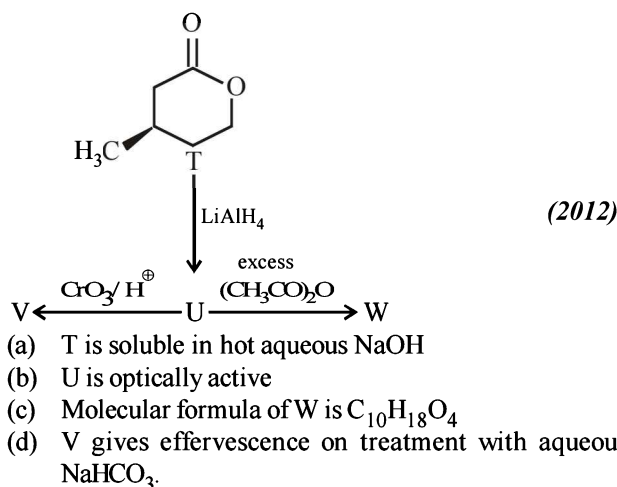
- (a) and $\text{CH}_3\text{CH}_2\text{CHO}$
(b) and CH_3COCH_3
(c) and CH_3COCH_3
(d) and $\text{CH}_3\text{CH}_2\text{CHO}$

- 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

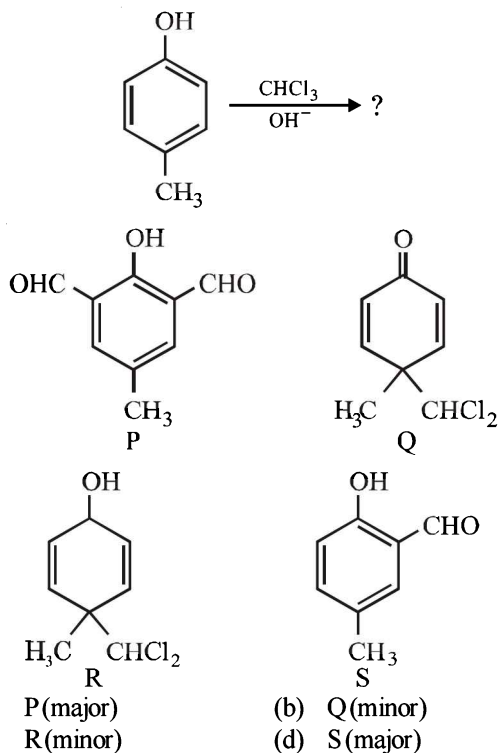
12. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction as shown in the given scheme. (2012)



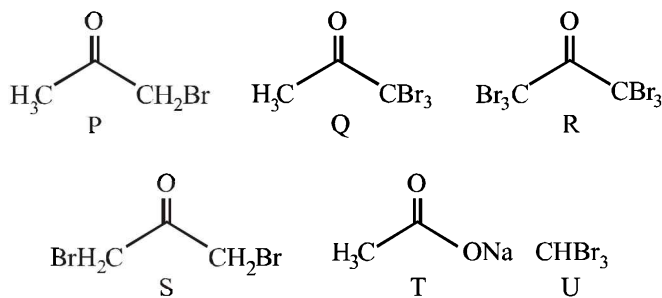
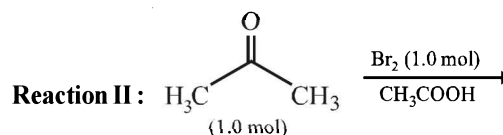
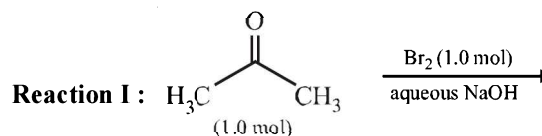
- (a) C₆H₅OH and C₆H₅COOH
 (b) C₆H₅COOH and C₆H₅CH₂OH
 (c) C₆H₅CH₂OH and C₆H₅OH
 (d) C₆H₅CH₂OH and C₆H₅CH₂COOH
13. With reference to the scheme given below, which of the given statement(s) about T, U, V and W is (are) correct ?



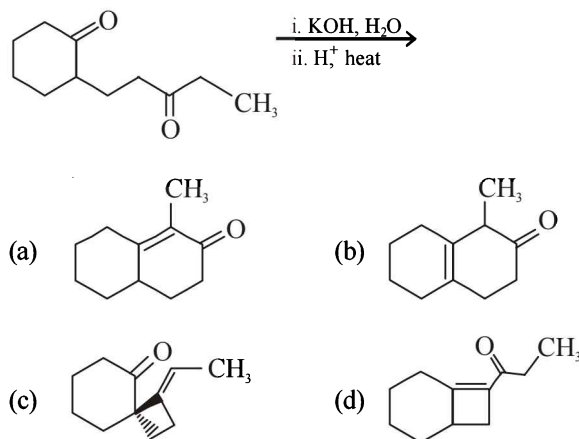
14. In the following reaction, the product(s) formed is(are) (JEE Adv. 2013)



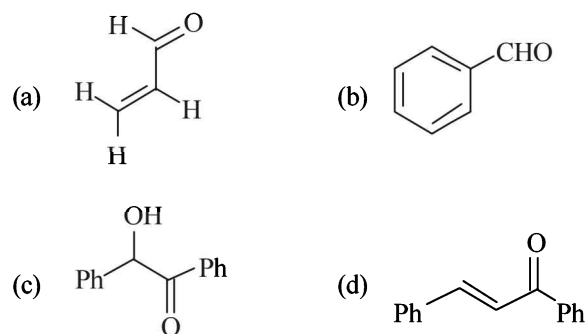
15. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are) (JEE Adv. 2013)



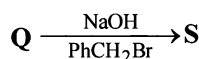
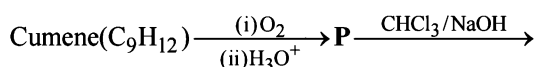
- (a) Reaction I : P and Reaction II : P
 (b) Reaction I : U, acetone and Reaction II : Q, acetone
 (c) Reaction I : T, U, acetone and Reaction II : P
 (d) Reaction I : R, acetone and Reaction II : S, acetone
16. The major product of the following reaction is (JEE Adv. 2015)



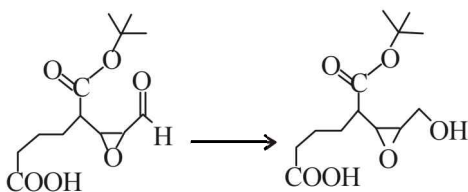
17. Positive Tollen's test is observed for (JEE Adv. 2016)



18. The correct statement(s) about the following reaction sequence is(are) (JEE Adv. 2016)



- (a) R is steam Volatile
 (b) Q gives dark violet coloration with 1% aqueous FeCl_3 solution
 (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
 (d) S gives dark violet coloration with 1% aqueous FeCl_3 solution
19. Reagent(s) which can be used to bring about the following transformation is (are) (JEE Adv. 2016)

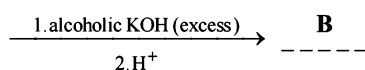
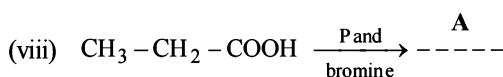


- (a) LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$ (b) BH_3 in THF
 (c) NaBH_4 in $\text{C}_2\text{H}_5\text{OH}$ (d) Raney Ni/ H_2 in THF

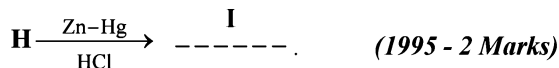
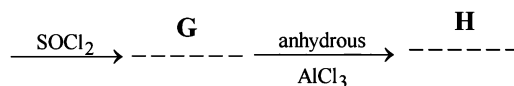
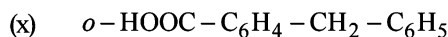
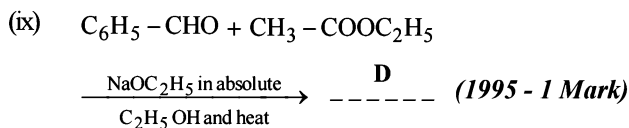
E Subjective Problems

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

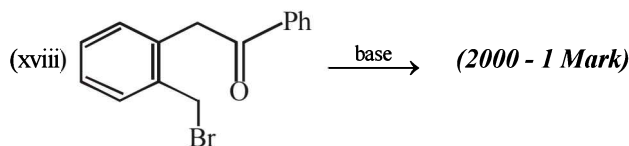
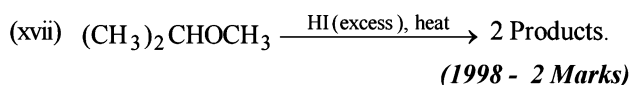
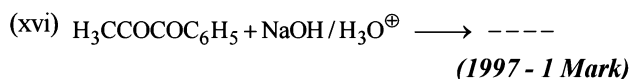
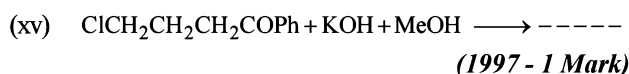
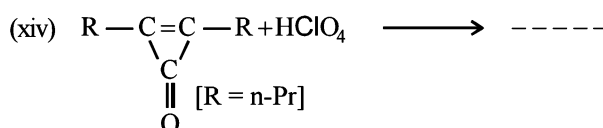
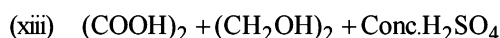
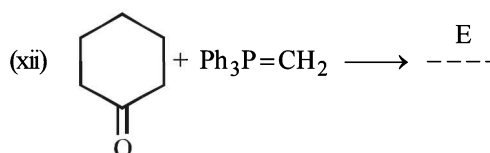
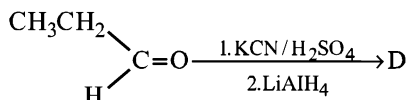
- (i) methanal reacts with ammonia (1981 - 1/2 Mark)
 (ii) ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water. (1981 - 1/2 Mark)
 (iii) benzene $\xrightarrow{\text{CH}_3\text{CH}_2\text{COCl}/\text{AlCl}_3}$ (1985 - 1 Mark)
 (iv) propanal $\xrightarrow[\text{heat}]{\text{NaOH}}$ (1985 - 1 Mark)
 (v) $\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CHO} + \text{HCHO} \xrightarrow{\text{KOH}}$ (1992 - 1 Mark)
 (vi) $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \rightarrow ? + ?$ (1993 - 2 Marks)
 (vii) $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{CH}_3 \xrightarrow[\text{(ii) H}^+]{\text{(i) CH}_3\text{MgBr (excess)}}$ (1994 - 1 Mark)



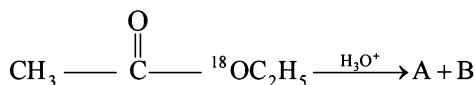
(1995 - 2 Marks)



- (xi) Complete the following reaction with appropriate structure. (1996 - 1 Mark)

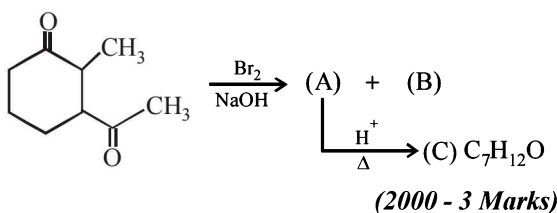


- (xix) Write the structures of the products A and B.



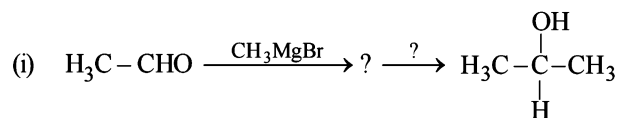
(2000 - 2 Marks)

- (xx) Identify A, B, C and give their structures.

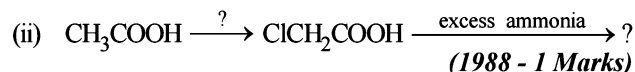


2. Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified. (1981 - 2 Marks)
3. Outline the reaction sequence for the conversion of
- methanal to ethanal (the number of steps should not be more than three). (1981 - 2 Marks)
 - acetylene to acetone (1985 - 1 Mark)
 - acetic acid to tertiary-butyl alcohol. (1989 - 1½ Marks)
 - Ethanal to 2-hydroxy-3-butenic acid. (1990 - 2 Marks)
 - Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. (1990 - 2 Marks)
 - Carry out the following transformation in not more than three steps. (1999 - 3 Marks)
- $$\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{H} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{CH}_3$$
4. Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates. (1981 - 3 Marks)
- $$\text{C}_6\text{H}_6 + \text{CH}_3 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5 - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{CH}_3 + \text{HCl}$$
5. 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)
6. Give reasons for the following :
- 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)
 - Formic acid is a stronger acid than acetic acid; (1985 - 1 Mark)
 - Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. (1985 - 2 Marks)
 - Hydrazone of aldehydes and ketones are not prepared in highly acidic medium. (1986 - 1 Mark)
 - Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion. (1991 - 1 Mark)
 - In acylium ion, the structure $\text{R} - \text{C} \equiv \text{O}^+$ is more stable than $\text{R} - \text{C}^+ = \text{O}$. (1994 - 1 Mark)
 - Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? (1997 - 2 Marks)
 - Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid. (1999 - 2 Marks)
7. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced.
- Ethanol from acetylene (1983 - 1 Mark)
 - Acetic acid from methyl iodide (1983 - 1 Mark)
8. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH. (1984 - 2 Marks)
9. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis :
- Propionic anhydride from propionaldehyde $[\text{AgNO}_3/\text{NH}_4\text{OH}, \text{P}_2\text{O}_5]$. (1984 - 2 Marks)
10. Give a chemical test/suggest a reagent to distinguish between acetaldehyde from acetone. (1987 - 1 Mark)
11. Arrange the following in increasing ease of hydrolysis $\text{CH}_3\text{COOC}_2\text{H}_5, \text{CH}_3\text{COCl}, (\text{CH}_3\text{CO})_2\text{O}, \text{CH}_3\text{CONH}_2$. (1986 - 1 Mark)
12. A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula $\text{C}_6\text{H}_{13}\text{Cl}$. Compound (A) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes (B) and (C), having formula C_6H_{12} . The mixture of (B) and (C), on ozonolysis, furnished four compounds :
- CH_3CHO ;
 - $\text{C}_2\text{H}_5\text{CHO}$;
 - CH_3COCH_3 and
 - $\text{H}_3\text{C} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CHO}$
- What are the structures of (A), (B) and (C)?
13. A liquid (X), having a molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$ 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)
14. Complete the following with appropriate structures :
- $(\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{COOH} + ?$ (1986 - 1 Mark)
 - $? \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CHO}$ (1986 - 1 Mark)
15. 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)
16. 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)

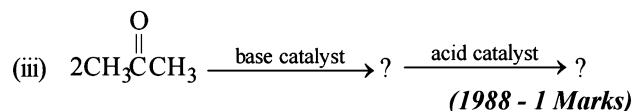
17. Complete the following reactions :



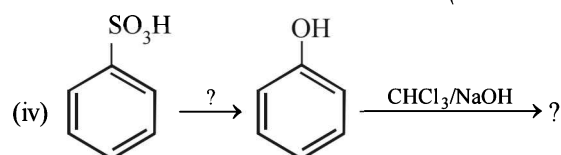
(1988 - 1 Marks)



(1988 - 1 Marks)



(1988 - 1 Marks)



(1988 - 1 Marks)

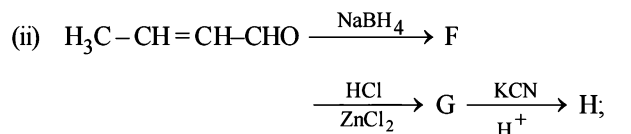
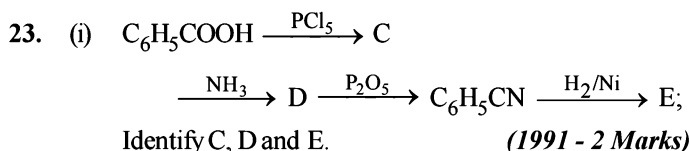
18. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markownikoff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $\text{C}_5\text{H}_{12}\text{O}$. Alcohol C on oxidation gives a ketone D. Deduce the structures of A, B, C and D and show the reactions involved. (1988 - 5 Marks)

19. A ketone 'A' which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms monoozonide D, D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. (1989 - 4 Marks)

20. 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)

21. Compound A ($\text{C}_6\text{H}_{12}\text{O}_2$) 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)

22. An organic compound containing C, H and O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O . A is insoluble in NaOH and NaHCO_3 while B is soluble in NaOH. A reacts with conc. HI to give compounds C and D. C can be separated from D by ethanolic AgNO_3 solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula, $\text{C}_7\text{H}_5\text{OBr}_3$. Identify, A, B, C, D and E with justification and give their structures. (1991 - 6 Marks)

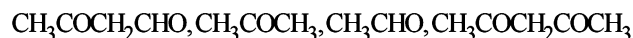


Identify F, G and H. (1991 - 2 Marks)

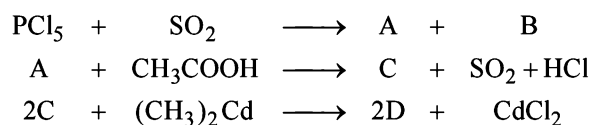
24. Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO_2 to give ethanol. Suggest structures for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

25. 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 $\text{Ca}(\text{OH})_2$ gives 'E' (molecular formula, $\text{C}_3\text{H}_6\text{O}$). 'E' does not give Tollent'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)

26. Arrange the following in increasing order of expected enol content (1992 - 1 Mark)



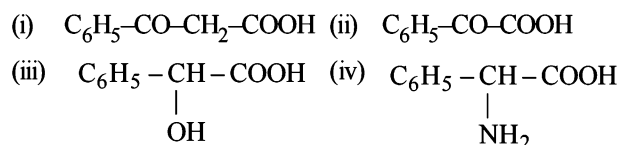
27. In the following reactions identify the compounds A, B, C and D. (1994 - $1 \times 4 = 4$ Marks)



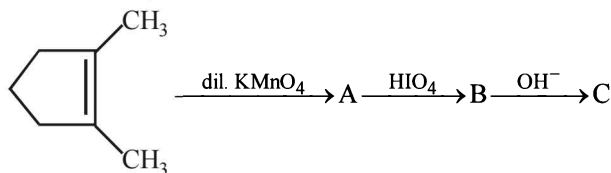
28. When gas A is passed through dry KOH at low temperature, a deep red coloured compound B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with $\text{Zn}/\text{H}_2\text{O}$ yields acetaldehyde. Identify A, B and C. (1994 - 3 Marks)

29. 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)

30. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly. (1995 - 2 Marks)

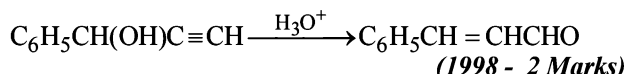


31. Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.) (1996 - 3 Marks)

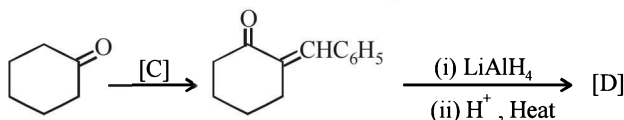


32. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved. (1998 - 6 Marks)
33. An aldehyde A ($C_{11}H_{18}O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B. (1998 - 2 Marks)

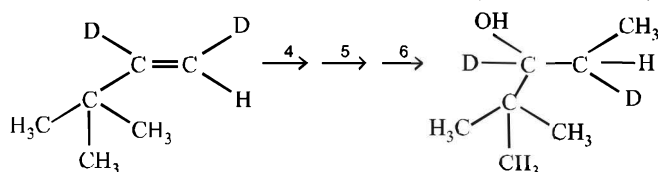
34. Write the intermediate steps for the following reaction.



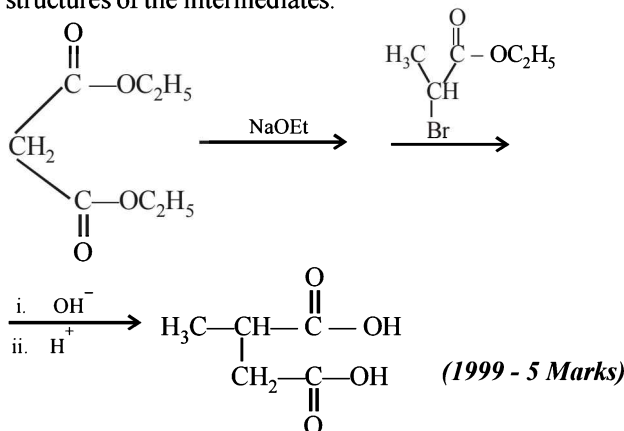
35. Complete the following reaction with appropriate structures of products/reagents : (1998 - 2 + 2 Marks)



36. Complete the following reaction with appropriate reagents : (1999 - 3 Marks)



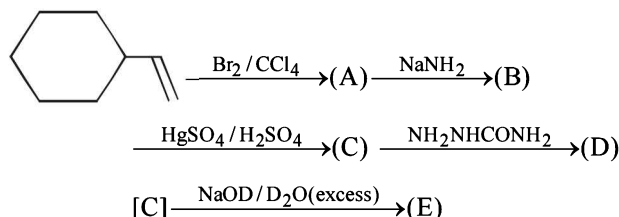
37. Explain briefly the formation of the products giving the structures of the intermediates.



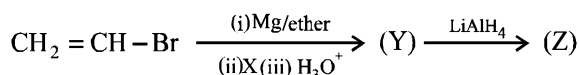
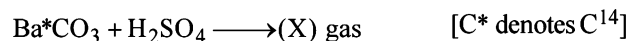
38. An organic compound A, $C_6H_{10}O$ on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetylcyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C? (2000 - 5 Marks)

39. 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)

40. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures : (2001 - 5 Marks)



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



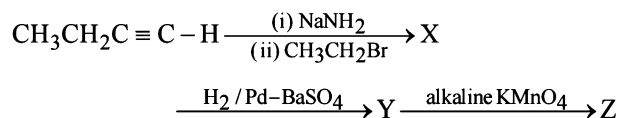
(2001 - 5 Marks)

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.

42. Five isomeric para-disubstituted aromatic compounds A to E with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds. (2002 - 5 Marks)

- Both A and B form a silver mirror with Tollen's reagent; also B gives a positive test with $FeCl_3$ solution.
- C gives positive iodoform test.
- D is readily extracted in aqueous $NaHCO_3$ solution.
- E on acid hydrolysis gives 1,4-dihydroxybenzene.

43. Identify X, Y and Z in the following synthetic scheme and write their structures.



Is the compound Z optically active? Justify your answer.

(2002 - 5 Marks)

44. A racemic mixture of (\pm) 2-phenylpropanoic acid on esterification with $(+)$ 2-butanol gives two esters. Mention the stereochemistry of the two esters produced. (2003 - 2 Marks)

45. 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)

46. 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)

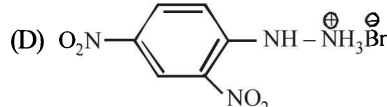
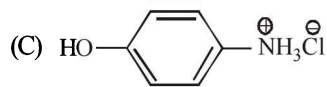
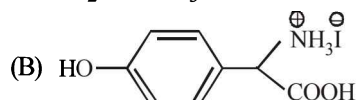
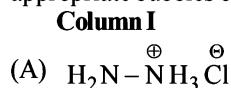
F Match the Following

DIRECTIONS (Q. No. 1) : Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
B	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
C	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>

1. 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 II

(p) sodium fusion extract of the compound gives Prussian blue colour with FeSO_4

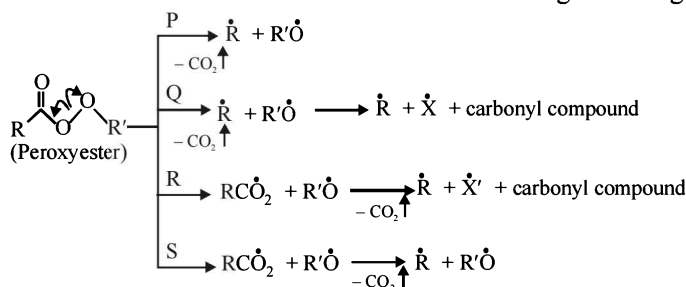
(q) gives positive FeCl_3 test

(r) gives white precipitate with AgNO_3

(s) reacts with aldehydes to form the corresponding hydrazone derivative

DIRECTIONS (Q. No. 2) : Following question has matching lists. The codes for the list have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

2. Different possible **thermal** decomposition pathways for peroxyesters 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. (JEE Adv. 2014)



List-I

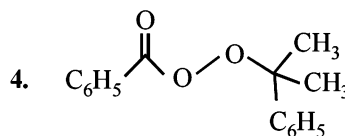
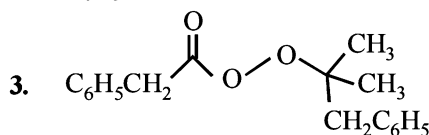
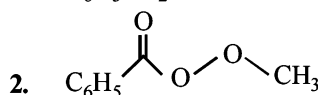
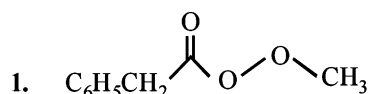
P. Pathway P

Q. Pathway Q

R. Pathway R

S. Pathway S

List-II



Code :

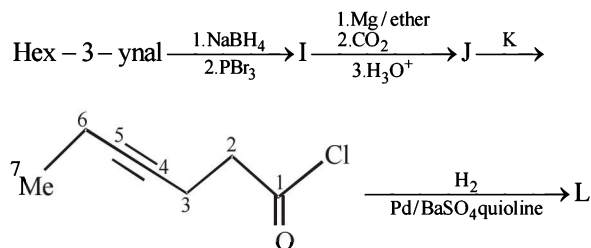
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1

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

G Comprehension Based Questions

PASSAGE-1

In the following reaction sequence, product I, J and L are formed. K represents a reagent. (2008)



1. The structure of the product I is –

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

2. The structures of compound J and K, respectively, are

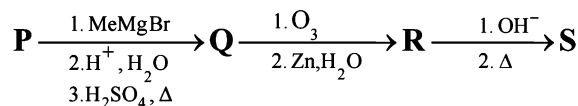
- (a)
- (b)
- (c)
- (d)

3. The structure of product L is

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

PASSAGE-2

A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly S. (2009)



4. The structure of the carbonyl compound P is

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

5. The structures of the products Q and R, respectively, are

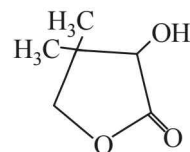
- (a)
- (b)
- (c)
- (d)

6. The structure of the product S is

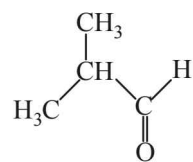
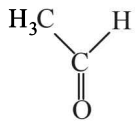
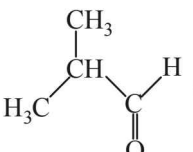
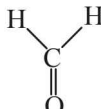
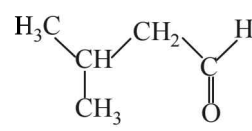
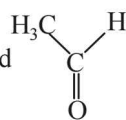
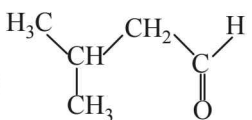
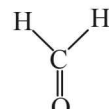
- (a)
- (b)
- (c)
- (d)

PASSAGE-3

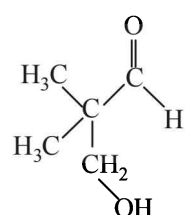
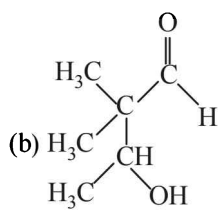
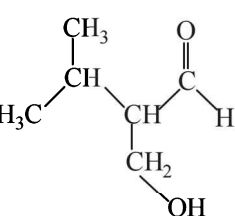
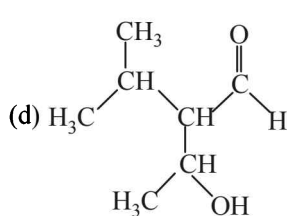
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below. (2010)



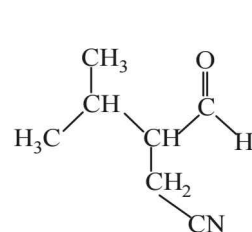
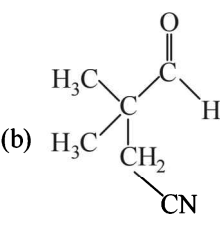
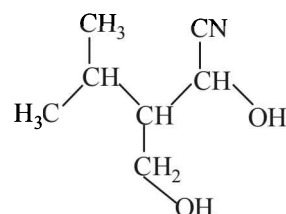
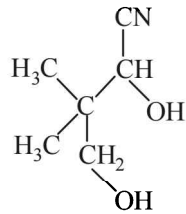
7. The compounds P and Q respectively are :

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

8. The compound R is :

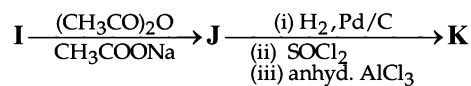
- (a)  (b) 
- (c)  (d) 

9. The compound S is :

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

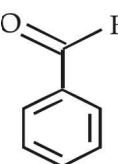
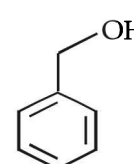
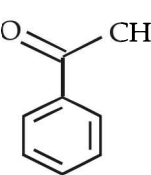
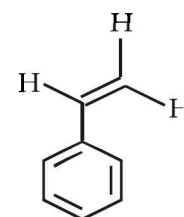
PASSAGE-4

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

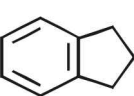
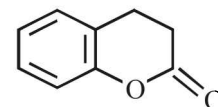
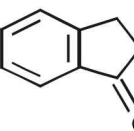
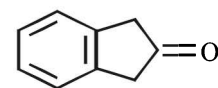


J ($\text{C}_9\text{H}_8\text{O}_2$) gives effervescence on treatment with NaHCO_3 and a positive Baeyer's test. (2012)

10. The compound I is

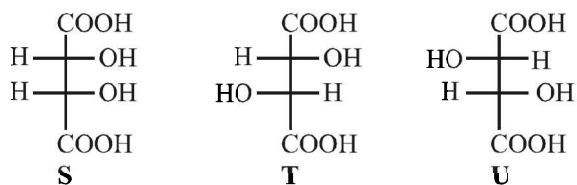
- (A)  (B) 
- (C)  (D) 

11. The compound K is

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

PASSAGE-5

P and Q are isomers of dicarboxylic acid $\text{C}_4\text{H}_4\text{O}_4$. Both decolorize $\text{Br}_2/\text{H}_2\text{O}$. 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.

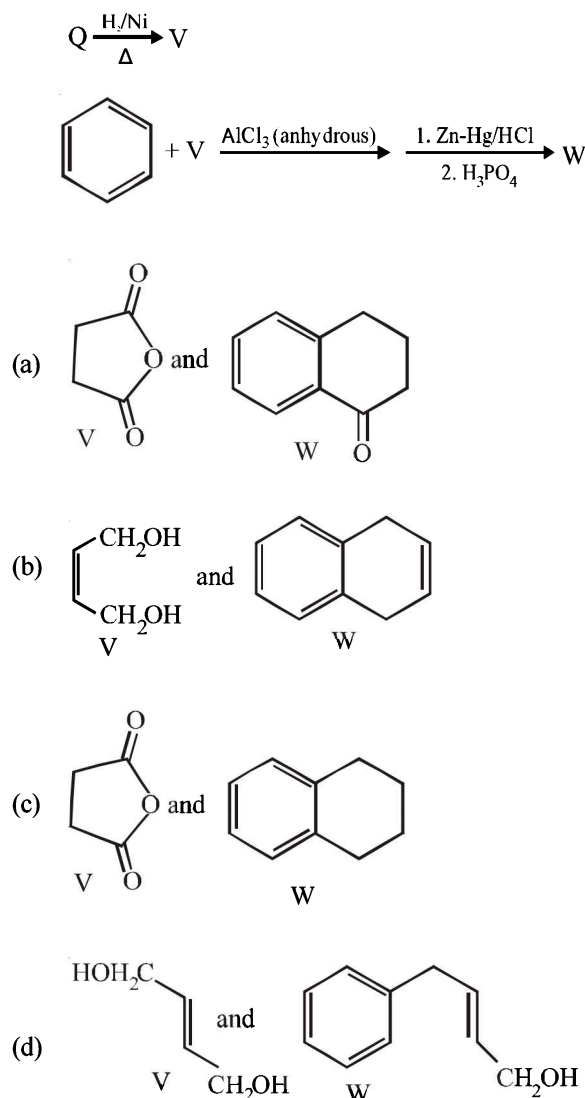


(JEE Adv. 2013)

12. Compounds formed from P and Q are, respectively

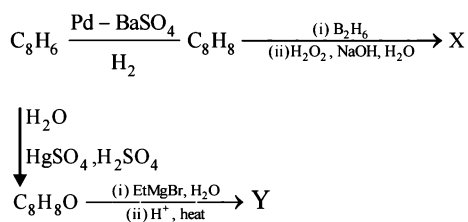
- (a) Optically active S and optically active pair (T, U)
 (b) Optically inactive S and optically inactive pair (T, U)
 (c) Optically active pair (T, U) and optically active S
 (d) Optically inactive pair (T, U) and optically inactive S

13. In the following reaction sequences V and W are respectively



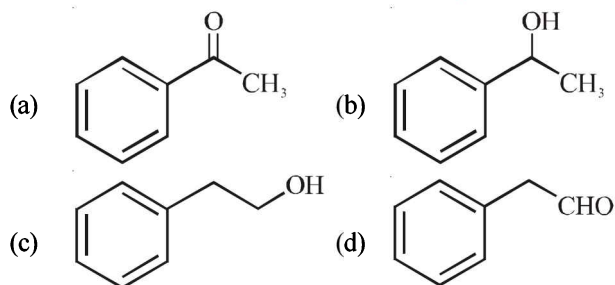
PASSAGE-6

In the following reactions



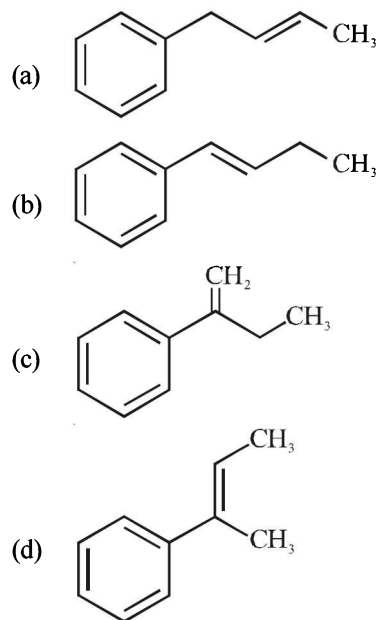
14. Compound X is

(JEE Adv. 2015)



15. The major compound Y is

(JEE Adv. 2015)



Assertion & Reason Type Questions

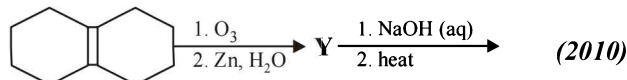
Each of this question contains STATEMENT-1 (Assertion/Statement) and STATEMENT-2 (Reason/Explanation) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (c) Statement-1 is True, Statement-2 is False
- (d) Statement-1 is False, Statement-2 is True.

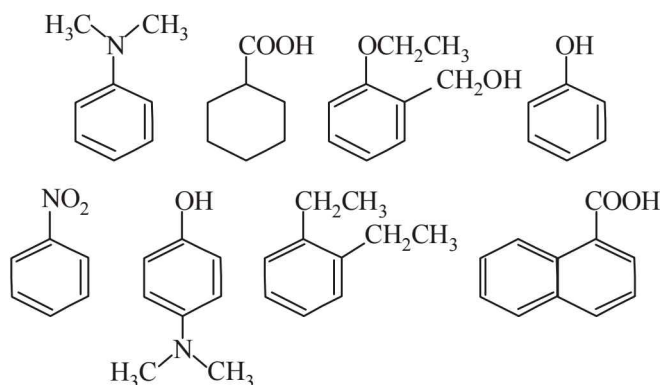
- Statement-1** : Acetate ion is more basic than the methoxide ion.
Statement-2 : The acetate ion is resonance stabilized
(1994 - 2 Marks)
- Statement-1** : Acetic acid does not undergo haloform reaction.
Statement-2 : Acetic acid has no alpha hydrogens.
(1998 - 2 Marks)
- Statement-1** : Dimethyl sulphide 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)
- Statement-1** : *p*-Hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.
Statement-2 : *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. (2007)

Integer Value Correct Type

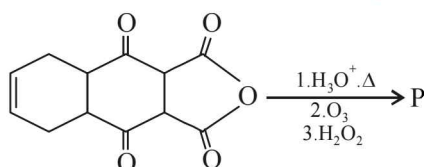
1. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



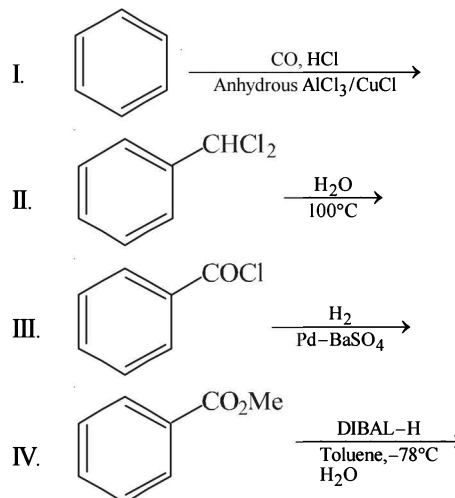
2. Amongst the following, the total number of compounds soluble in aqueous NaOH is



3. The total number of carboxylic acid groups in the product P is (JEE Adv. 2013)



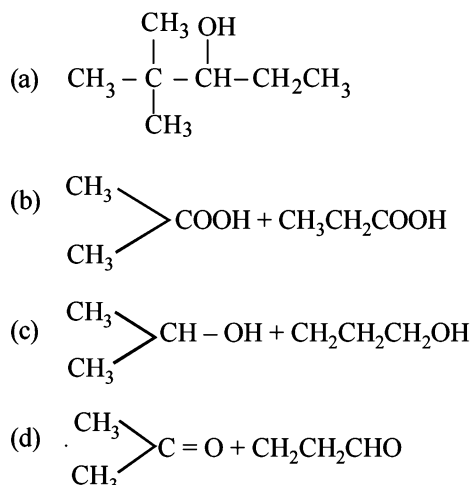
4. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with NaBH_4 (NOTE: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are (JEE Adv. 2014)
5. Among the following, the number of reaction(s) that produce(s) benzaldehyde is (JEE Adv. 2015)



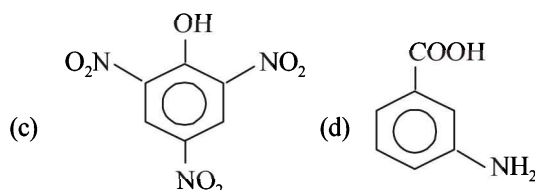
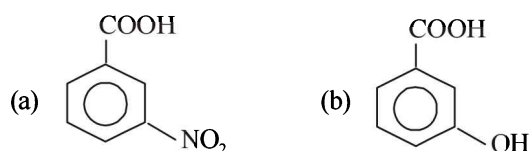
Section-B

JEE Main / AIEEE

1. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} A \xrightarrow{\text{alc. KOH}} B$. What is B?
- (a) $\text{CH}_3\text{CH}_2\text{COCl}$ (b) $\text{CH}_3\text{CH}_2\text{CHO}$ [2002]
 (c) $\text{CH}_2=\text{CHCOOH}$ (d) $\text{ClCH}_2\text{CH}_2\text{COOH}$
2. On vigorous oxidation by permanganate solution. $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CHO}$ gives [2002]



3. Picric acid is: [2002]



4. When $\text{CH}_2=\text{CH}-\text{COOH}$ is reduced with LiAlH_4 , the compound obtained will be [2003]
 (a) $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\text{CH}_2-\text{CHO}$ (d) $\text{CH}_3-\text{CH}_2-\text{COOH}$
5. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is [2004]
 (a) $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$
 (b) $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
 (c) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$
 (d) $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$
6. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives [2004]
 (a) 2-methyl-2-propanol (b) acetamide
 (c) acetone (d) acetyl iodide
7. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon? [2004]
 (a) Acetamide (b) Acetic acid
 (c) Ethyl acetate (d) Butan-2-one
8. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? [2004]
 (a) Butanal (b) Benzaldehyde
 (c) Phenol (d) Benzoic acid

9. Among the following acids which has the lowest pK_a value? [2005]

(a) $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $(\text{CH}_3)_2\text{CH}-\text{COOH}$
(c) HCOOH (d) CH_3COOH

10. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as [2005]

(a) an amine (b) an imine
(c) an anemine (d) a Schiff's base

11. The increasing order of the rate of HCN addition to compound A – D is [2006]

(A) HCHO (B) CH_3COCH_3
(C) PhCOCH_3 (D) PhCOPh
(a) $\text{D} < \text{C} < \text{B} < \text{A}$ (b) $\text{C} < \text{D} < \text{B} < \text{A}$
(c) $\text{A} < \text{B} < \text{C} < \text{D}$ (d) $\text{D} < \text{B} < \text{C} < \text{A}$

12. The correct order of increasing acid strenght of the compounds [2006]

(A) $\text{CH}_3\text{CO}_2\text{H}$ (B) $\text{MeOCH}_2\text{CO}_2\text{H}$
(C) $\text{CF}_3\text{CO}_2\text{H}$ (D) $\text{Me}_2\text{C}(\text{Me})\text{CO}_2\text{H}$

is

(a) $\text{D} < \text{A} < \text{B} < \text{C}$ (b) $\text{A} < \text{D} < \text{B} < \text{C}$
(c) $\text{B} < \text{D} < \text{A} < \text{C}$ (d) $\text{D} < \text{A} < \text{C} < \text{B}$

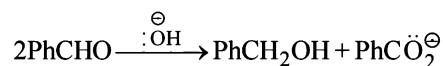
13. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : [2009]

(a) HCHO (b) CH_3COCH_3
(c) CH_3COOH (d) CH_3OH

14. Which of the following on heating with aqueous KOH, produces acetaldehyde? [2009]

(a) $\text{CH}_3\text{CH}_2\text{Cl}$ (b) $\text{CH}_2\text{ClCH}_2\text{Cl}$
(c) CH_3CHCl_2 (d) CH_3COCI

15. In Cannizzaro reaction given below



the slowest step is : [2009]

(a) the transfer of hydride to the carbonyl group
(b) the abstraction of proton from the carboxylic group
(c) the deprotonation of PhCH_2OH

(d) the attack of $:\text{OH}^-$ at the carboxyl group

16. Which of the following reagents may be used to distinguish between phenol and benzoic acid? [2011]

(a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral FeCl_3

17. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is : [2011]

(a) 2, 2, 2-Trichloroethanol
(b) Trichloromethanol
(c) 2, 2, 2-Trichloropropanol
(d) Chloroform

18. The strongest acid amongst the following compounds is :

(a) CH_3COOH [2011]
(b) HCOOH
(c) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$
(d) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$

19. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is :

(a) Diethyl ether (b) 2-Butanone [2011]
(c) Ethyl chloride (d) Ethyl ethanoate

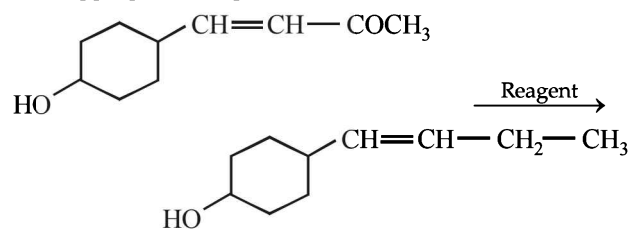
20. Silver Mirror test is given by which one of the following compounds? [2011]

(a) Acetaldehyde (b) Acetone
(c) Formaldehyde (d) Benzophenone

21. Iodoform can be prepared from all except : [2012]

(a) Ethyl methyl ketone
(b) Isopropyl alcohol
(c) 3-Methyl 2-butanone
(d) Isobutyl alcohol

22. In the given transformation, which of the following is the most appropriate reagent ? [2012]



(a) $\text{NH}_2\text{NH}_2, \text{OH}^-$ (b) $\text{Zn}-\text{Hg}/\text{HCl}$
(c) $\text{Na}, \text{Liq NH}_3$ (d) NaBH_4

23. The most suitable reagent for the conversion of $\text{R}-\text{CH}_2-\text{OH} \rightarrow \text{R}-\text{CHO}$ is: [JEE M 2014]

(a) KMnO_4
(b) $\text{K}_2\text{Cr}_2\text{O}_7$
(c) CrO_3
(d) PCC (Pyridinium Chlorochromate)

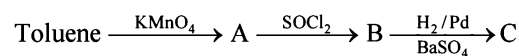
24. In the reaction,



the product C is: [JEE M 2014]

(a) Acetaldehyde (b) Acetylene
(c) Ethylene (d) Acetyl chloride

25. In the following sequence of reactions : [JEE M 2015]



the product C is :

(a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CHO}$
(c) $\text{C}_6\text{H}_5\text{COOH}$ (d) $\text{C}_6\text{H}_5\text{CH}_3$