

Aldehydes, Ketones and Carboxylic acids

SUBJECTIVE PROBLEMS:

Q1.

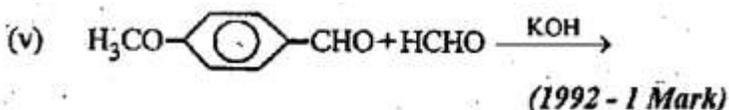
Write the structural formula of the main organic product formed when:

(i) Methanol reacts with ammonia (IIT JEE 1981 - ½ Mark)

(ii) Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water. (IIT JEE 1981 – ½ Mark)

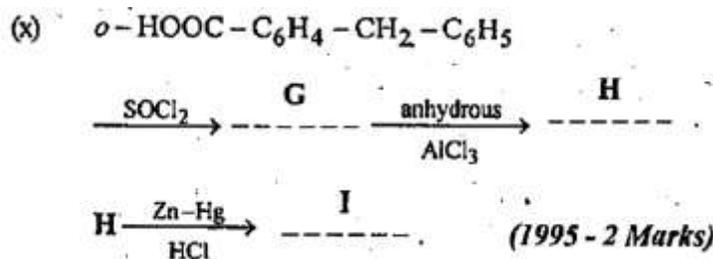
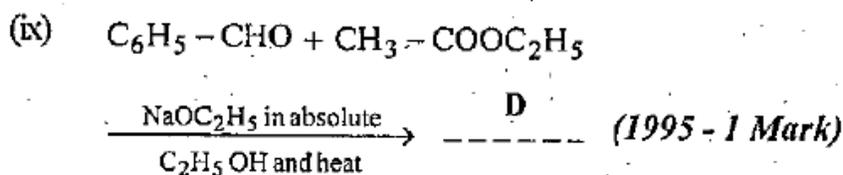
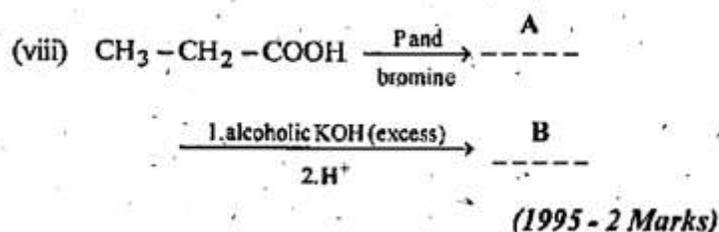
(iii) Benzene $\xrightarrow{CH_3CH_2COCl / AlCl_3}$ (IIT JEE 1985 – 1 Mark)

(iv) Propanol $\xrightarrow[heat]{NaOH}$ (IIT JEE 1985 – 1 Mark)

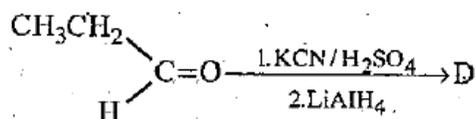


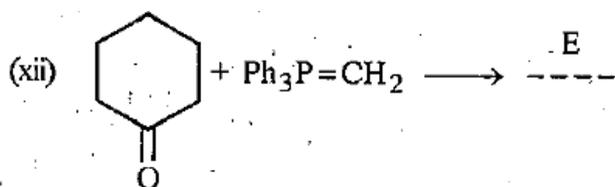
(vi) $C_6H_5COOH + CH_3MgI \rightarrow ? + ?$ (IIT JEE 1993 – 2 Marks)

(vii) $C_6H_5CH_2CO_2CH_3 \xrightarrow[(ii) H^+]{(i) CH_3MgBr(excess)}$ (IIT JEE 1994 – 1 Mark)

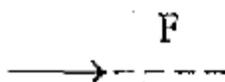
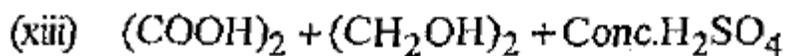


(xi) Complete the following reaction with appropriate structure (IIT JEE 1996 – 1 Marks)

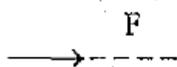
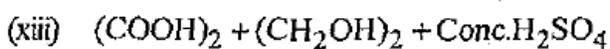




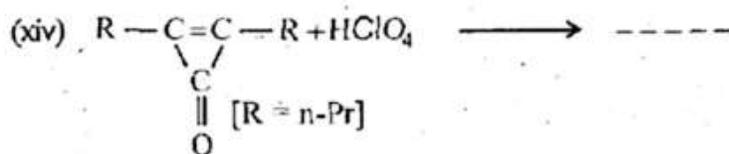
(1997 - 1 Mark)



(1997 - 1 Mark)



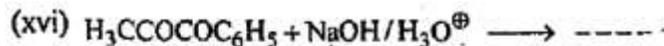
(1997 - 1 Mark)



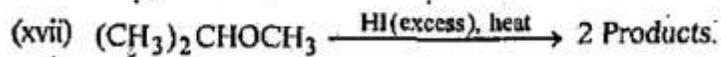
(1997 - 1 Mark)



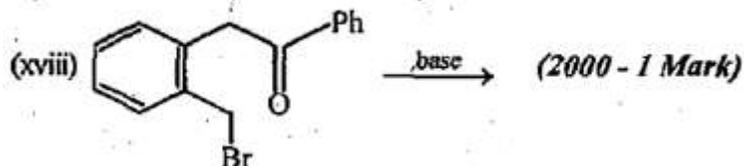
(IIT JEE 1997 - 1 Mark)



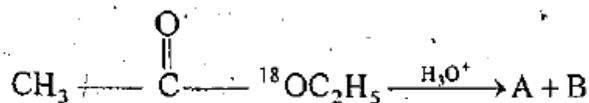
(1997 - 1 Mark)



(1998 - 2 Marks)

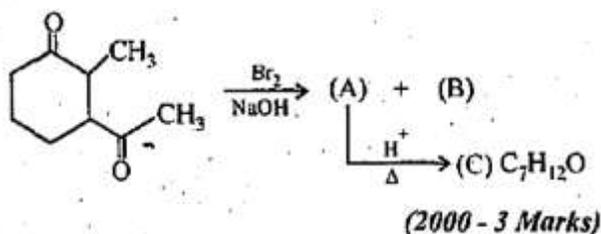


(xix) Write the structures of the products A and B.



(2000 - 2 Marks)

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



Q2.

Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified. (IIT JEE 1981 - 2 Marks)

Q3.

Outline the reaction sequence for the conversion of

(i) Methanol to ethanol (the number of steps should not be more than three).

(IIT JEE 1981 - 2 Marks)

(ii) Acetylene to acetone

(1985 - 1 Mark)

(iii) Acetic acid to tertiary-butyl alcohol.

(1989 - 1 ½ Mark)

(iv) Ethanol to 2-hydroxy-3-butenic acid.

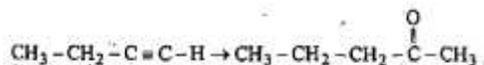
(IIT JEE 1990 - 2 Marks)

(v) Ethanoic acid to a mixture of methanoic acid and biphenyl ketone.

(IIT JEE 1990 - 2 Marks)

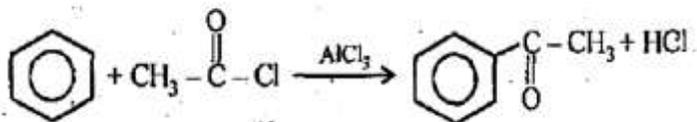
(vi) Carry out the following transformation in not more than three steps.

(IIT JEE 1999 - 3 Marks)



Q4.

Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates. (IIT JEE 1981 - 3 Marks)



Q5.

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 hydroxyl 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.

(IIT JEE 1982 - 2 Mark)

Q6.

Give reasons for the following:

(i) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. **(IIT JEE 1983 – 1 Mark)**

(ii) Formic acid is a stronger acid than acetic acid; **(IIT JEE 1985 – 1 Mark)**

(iii) Suggest a reason for the larger difference between the boiling points of butanol and butan-2-ol, although they have almost the same solubility in water. **(IIT JEE 1985 – 2 Mark)**

(iv) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. **(IIT JEE 1986 – 1 Mark)**

(v) Iodoform is obtained by the reaction of acetone with hypiodite but not with iodide ion. **(IIT JEE 1991 – 1 Mark)**

(vi) In acylium ion, the structure $\text{R} - \text{C} \equiv \text{O}^+$ is more stable than $\text{R} - \text{C}^+ = \text{O}$. **(IIT JEE 1994 – 1 Mark)**

(vii) Although peroxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? **(IIT JEE 1997 – 2 Mark)**

(viii) Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid. **(IIT JEE 1999 – 2 Mark)**

Q7.

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

(i) Ethanol from acetylene **(IIT JEE 1983 – 1 Mark)**

(ii) Acetic acid from methyl iodide **(IIT JEE 1983 – 1 Mark)**

Q8.

What happens when p-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH? **(IIT JEE 1984 – 2 Mark)**

Q9.

Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis:

Propionic anhydride from propionaldehyde

$[\text{AgNO}_3/\text{NH}_4\text{OH}, \text{P}_2\text{O}_5]$. **(IIT JEE 1984 – 2 Mark)**

Q10.

Give a chemical test/suggest a reagent to distinguish between acetaldehyde from acetone. **(IIT JEE 1987 – 1 Mark)**

Q11.

Arrange the following in increasing ease of hydrolysis

$\text{CH}_3\text{COOC}_2\text{H}_5$, CH_3COCl , $(\text{CH}_3\text{CO})_2\text{O}$, CH_3CONH_2 . **(IIT JEE 1986 – 1 Mark)**

Q12.

A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes (B) and (C), having formula C_6H_{12} . The mixture of (B) and (C), on ozonolysis, furnished four compounds: (IIT JEE 1986 – 4 Marks)

- (i) CH_3CHO ;
 (ii) C_2H_5CHO ;
 (ii) CH_3COCH_3 and
 (iv) $\begin{array}{c} H_3C-CH-CHO \\ | \\ CH_3 \end{array}$

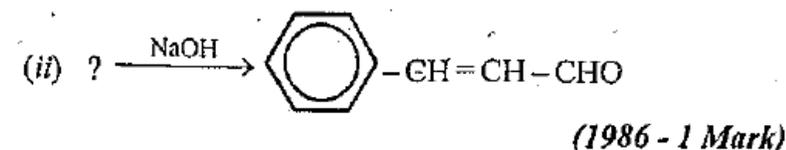
What are the structures of (A), (B) and (C)?

Q13.

A liquid (X), having a molecular formula $C_6H_{12}O_2$ is hydrolyses 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)? (IIT JEE 1986 - 3 Marks)

Q14.

Complete the following with appropriate structures:

**Q15.**

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? (IIT JEE 1987 - 5 Marks)

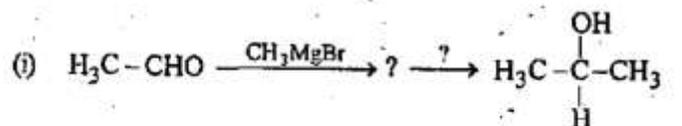
Q16.

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 pent chloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

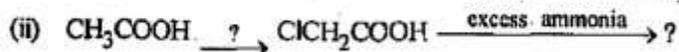
(IIT JEE 1987 – 5 Marks)

Q17.

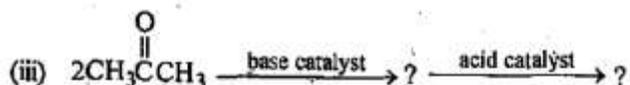
Complete the following reaction:



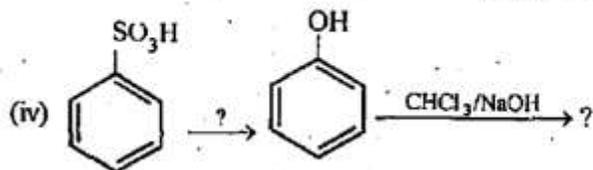
(1988 - 1 Marks)



(1988 - 1 Marks)



(1988 - 1 Marks)



(1988 - 1 Marks)

Q18.

A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methyl butane 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 acetone D. Deduce the structures of A, B, C and D and show the reactions involved.

(IIT JEE 1988 - 5 Marks)

Q19.

A ketone 'A' which undergoes halo form 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.

(IIT JEE 1989 - 4 Marks)

Q20.

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.

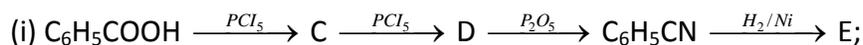
(IIT JEE 1990 - 5 Marks)

Q21.

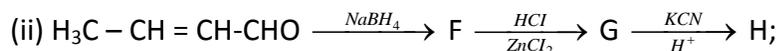
Compound A (C₆H₁₂O₂) on reduction with LiAlH₄ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave C. The compound D was oxidized further to give F which was found to be a monobasic acid (molecular weight = 60.0). Deduce the structures of A, B, C, D and E. **(IIT JEE 1990- 4 Marks)**

Q22.

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 CO₂ and 0.072 g of H₂O. A is insoluble in NaOH and NaHCO₃ 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 AgNO₃ solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula, C₈H₈OBr₃. Identify, A, B, C, D and E with justification and give their structures. **(IIT JEE 1991 - 6 Marks)**

Q23.

Identify C, D and E. **(IIT JEE 1991 – 2 Marks)**



Identify F, G and H. **(IIT JEE 1991 – 2 Marks)**

Q24.

Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analyses as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br₂ and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO₂ to give ethanol. Suggest structures for 'X', 'Y' and 'Z'. **(IIT JEE 1992 – 1 Marks)**

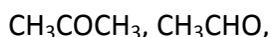
Q25.

An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with KMnO₄ also gives 'B'. 'B' on heating with Ca(OH)₂ gives 'E' (molecular formula, C₃H₆O) 'E' does not give Tollent's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenylhydrazone. Identify 'A', 'B', 'C', 'D' and 'E'. **(IIT JEE 1992 - 3 Marks)**

Q26.

Arrange the following in increasing order of expected enol content

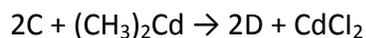
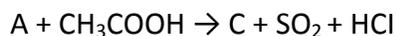
(IIT JEE 1992 - 1 Mark)



Q27.

In the following reactions identify the compounds A, B, C and D.

(IIT JEE 1994 - 1 x 4 = 4 Marks)

**Q28.**

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 Zn/H₂O yields acetaldehyde. Identify A, B and C.

(IIT JEE 1994 - 3 Marks)

Q29.

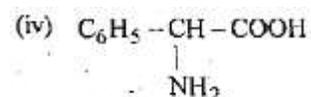
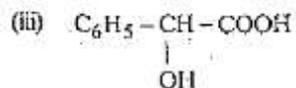
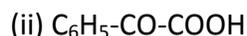
An organic compound A, C₈H₆, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields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

(IIT JEE 1994 - 3 Marks)

Q30.

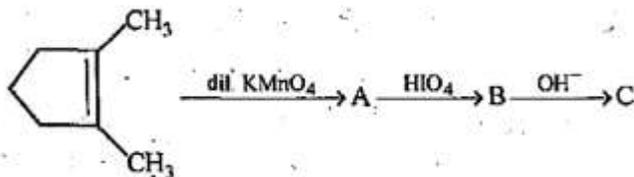
Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly.

(IIT JEE 1995 - 2 Marks)

**Q31.**

Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.)

(IIT JEE 1996 - 3 Marks)

**Q32.**

A hydrocarbon A of the formula C₇H₁₂ on ozonolysis gives a compound B which undergoes aldol condensation giving 1-acetylcyclopentene. Identify A and B.

(IIT JEE 1997C - 2 Marks)

Q33.

How many asymmetric carbon atoms are created during the complete reduction of benzoin in (PhCO-COPh) with LiAlH_4 ? also write the number of possible Stereoisomers in the product

(IIT JEE 1997C – 2 Marks)

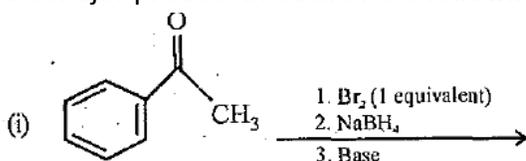
Q34.

A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved.

(IIT JEE 1997C-3 Marks)

Q35.

Predict the major product in each of the following reactions

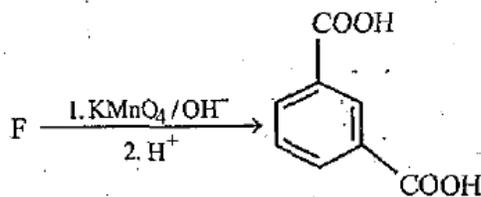
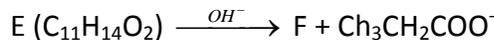


(IIT JEE 1997C-1 Marks)

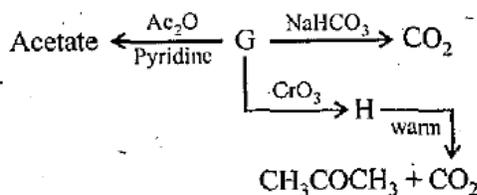
Q36.

(i) Write down the structure of E and F.

(IIT JEE 1997C-2 Marks)



(ii) Write down the structure of G and H where G is $\text{C}_4\text{H}_8\text{O}_3$.

**Q37.**

An ester A ($\text{C}_4\text{H}_8\text{O}_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved.

(IIT JEE 1998 - 6 Marks)

Q38.

An aldehyde A ($C_{11}H_8O$), which does not undergo self aldol condensation, gives Benz aldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B. (IIT JEE 1998 – 2 Marks)

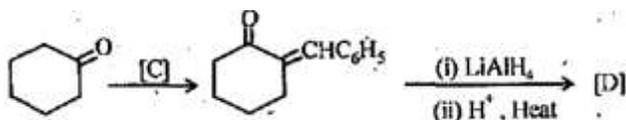
Q39.

Write the intermediate steps for the following reaction.

**Q40.**

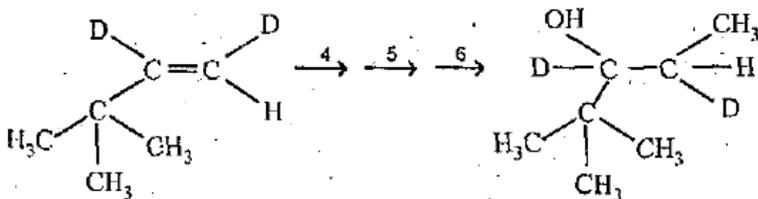
Complete the following reaction with appropriate structures of products/reagents:

(IIT JEE 1998 – 2 + 2 Marks)

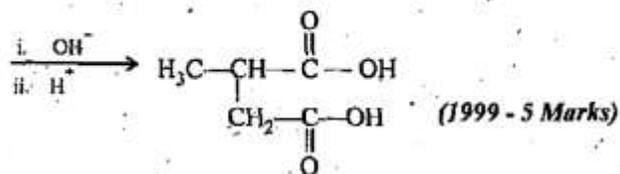
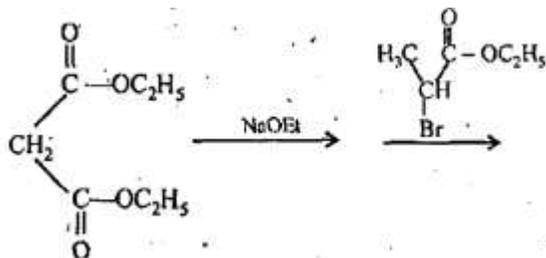
**Q41.**

Complete the following reaction with appropriate reagents:

(IIT JEE 1999 – 3 Marks)

**Q42.**

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



(IIT JEE 1999 – 5 Marks)

Q43.

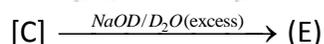
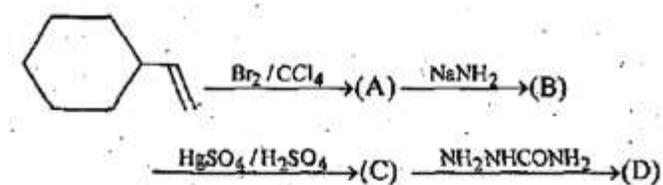
An organic compound **A**, C_6H_{10} on reaction with CH_3MgBr followed by acid treatment gives compound **B**. The compound **B** on ozonolysis gives compound **C**, which in presence of a base gives 1-acetylcyclopentene **D**. The compound **B** on reaction with HBr gives compound **E**. Write the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

Q44.

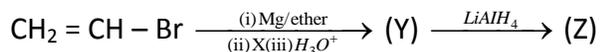
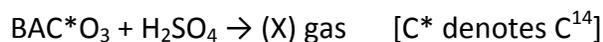
An organic compound **A**, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound **B**. The compound **B** on treatment with PCl_5 , followed by reaction with H_2/Pd ($BaSO_4$) gives compound **C**, which on reaction with hydrazine gives a cyclic compound **D** ($C_4H_{10}N_2$). Identify **A**, **B**, **C** and **D**. Explain the formation of **D** from **C**. **(IIT JEE 2000 - 5 Marks)**

Q45.

Identify (**A**), (**B**), (**C**), (**D**) and (**E**) in the following schemes and write their structures :

(IIT JEE 2001 – 65 Marks)**Q46.**

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

**(IIT JEE 2001 – 5 Marks)**

Explain the formation of labeled 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.

Q47.

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. **(IIT JEE 2002 - 5 Marks)**

(i) Both **A** and **B** form a silver mirror with Tollen's reagent; also **B** gives a positive test with $FeCl_3$ solution.

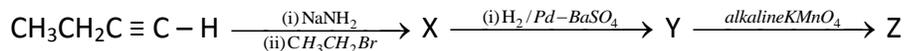
(ii) **C** gives positive iodoform test.

(iii) **D** is readily extracted in aqueous $NaHCO_3$ solution.

(iv) **E** on acid hydrolysis gives 1, 4-dihydroxybenzene.

Q48.

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



Is the compound Z optically active? Justify your answer.

(IIT JEE 2002 – 5 Marks)

Q49.

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

(IIT JEE 2003 - 2 Marks)

Q50.

Compound A of molecular formula $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$ exists in keto form and predominantly in enolic form 'B'. On oxidation with KMnO_4 , 'A' gives m-chlorobenzoic acid. Identify 'A' and 'B'.

(IIT JEE 2003 - 2 Marks)

Q51.

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.

(IIT JEE 2005 - 2 Marks)