(6 pages)

OCTOBER 2011 **P/ID 40121/PCHA**

Time : Three hours Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

1. Write down the Newmann projection formula of α – phenylpropionaldehyde.

2. Name cis-2-butene and trans-2-butene under E, Z system.

3. Draw the Sawhorse representation of the different conformations of ethane.

4. Cis-decalin shows one proton peak whereas trans-decalin shows two proton peak. Explain.

5. Cis-cyclohexane-1,3-dicarboxylic acid forms a cyclic anhydride whereas the trans isomer does not. Explain.

6. The reaction of substituted dimethylanilines with methyliodide (in aqueous acetone) gives the trimethylanilinium iodide with $\rho = -3.30$. Explain.

7. With a suitable example explain anchimeric assistance.

8. Using Kekule structure prove that the arenium ion is a hybrid of threo allylic type resonance structures.

9. Direct nitration of aniline is not a satisfactory reaction. How can it be carried out?

10. How can formyl group be introduced into the benzene ring?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

All questions carry equal marks.

11. (a) (i) Discuss the disymmetry in biphenyl derivatives with four examples. (10)

(ii) Cis-2-butene adds to bromine to give racemic product only and no meso product is obtained. Give reason. (5)

(iii) With a suitable example discuss prochirality. (5)

Or

(b) (i) Discuss the disymmetry in allenes. (10)

(ii) Explain the structures of the five stereoisomeric forms of truxillic acid.(5)

(iii) Describe any one method for the diastereoselective synthesis of alkenes. (5)

12. (a) (i) Draw the Newmann projections of all possible conformers of n-butane. Comment on their relative stabilities with the aid of a potential energy diagram. (10)

(ii) The proton nmr spectrum of cyclohexane at –100° C is a doublet whereas at room temperature it is a singlet. Explain. (5)

(iii) Draw the two forms of cis-9-methyldecalin and explain. (5)

Or

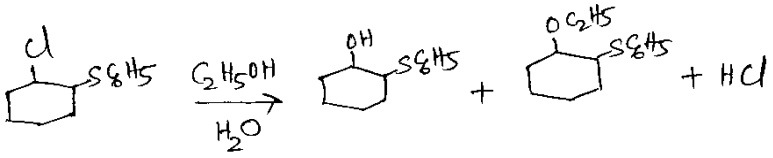
(b) (i) Discuss a chemical method for the determination of configuration of 2-decalol. (10)

(ii) Draw chair conformations of cis-1,3 cyclohexane and trans-1,3 cyclohexane and explain. (5)

(iii) What is torsional strain? With a suitable example how torsional strain influences the stability of conformers. (5)

13. (a) (i) With a suitable example explain nucleophilic substitution at a bridgehead. (10)

(ii) Consider the following reaction. (5)



Explain why the rate of the reaction is 70,000 times faster when the thiosubstituent is trans to the chloro substituent.

(iii) How is ethyl acetoacetate converted to dimethyl acetone? (5)

Or

(b) (i) Discuss the factors that influence rate of nucleophilic substitution reactions. (10)

(ii) The reaction between RNH_2 and RX is a nucleophilic substitution reaction. Explain. (5)

(iii) With one example for each prove that acetoacetic ester is a promising starting material for the synthesis of methyl ketones and carboxylic acids. (5)

14. (a) (i) Discuss any two methods for the generation of benzyne intermediate. (10)

(ii) What is diazonium coupling? Explain the mechanism. (5)

(iii) How does pyrrole react with maleic anhydride? (5)

Or

(b) (i) Prove that nitration of pyridine occurs mainly at C_3. (5)

(ii) How can one synthesise 4-nitro pyridine from pyridine? (5)

(iii) How are the following compounds prepared?

(1) 1, 2, 3-trimethyl benzene

(2) 3, 4-dibromonitrobenzene (5)

(iv) Write notes on Zeigler alkylation. (5)

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