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D 1096

Reg. No. : .....

Q.P. Code : [D 07 PCH 01]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

First Year

Chemistry

ORGANIC CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Explain the use of Hammett equation in analysing the mechanism of reactions involving aromatic intermediates.
- (b) Describe the utility of isotope labeling and crossover experiments in studying the mechanism of organic transformations.
- (c) Explain why
  - (i) Azulene has a permanent dipole moment
  - (ii) Cyclooctatetraene is tub shaped

(iii) Benzyl cation easily rearranges to tropylium cation and

(iv) Cyclopentadienyl anion is aromatic.

(6+6+8)

2. (a) Discuss the effect of different groups in mono and disubstituted aromatic systems in orienting the electrophile during substitution.

(b) Discuss the mechanisms of Friedel-Crafts acylation, Jacobson reaction and Gattermann-Koch reaction.

(c) Explain why

(i) Polyalkylation is possible during Friedel-Crafts reaction but not polyacylation and

(ii) The nitration of aniline by nitrating mixture yields m-nitroaniline rather than o-nitroaniline or p-nitroaniline.

(6+9+5)

3. (a) Comment on the ease or otherwise of effecting nucleophilic substitution reactions at

(i) Vinyl carbon

(ii) Allylic carbon and

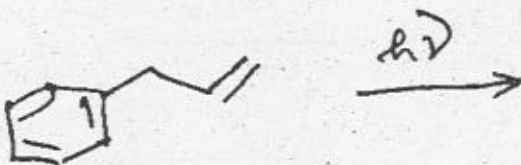
(iii) Bridge head carbon

Explain with examples.

- (b) What are ambident nucleophiles? Give examples. Explain how they attack an electron deficient system governed by the conditions of the reactions.
- (c) Explain why
- (i) An alcohol may be converted to its tosylate before effecting  $SN^2$  displacement and
- (ii) Iodide is a good nucleophile compared to other halides. (9+6+5)
4. (a) What are nitrenes? How are they generated? Compare the structural features and stability of nitrenes with that of carbenes.
- (b) Give a brief account of E1-E2-E1CB spectrum.
- (c) Write briefly on the pyrolytic is elimination reactions.
- (d) Describe the factors that influence the substitution is elimination ratio during the reaction of a base/nucleophile with aliphatic halides. (5+5+5+5)
5. (a) Comment on the stability and geometry of free radicals.
- (b) Describe the mechanism, scope and applications of the following reactions:
- (i) Hunsdiecker reaction
- (ii) Gomberg reaction
- (iii) Pechmann reaction
- (iv) Ullmann reaction. (4+16)

6. (a) What are mannich bases? How are they prepared? Explain the mechanism of their formation.
- (b) Illustrate the methods of preparing *cis* and *trans*-1,2-diols.
- (c) Discuss the mechanism of benzoin condensation which type of aldehydes are reluctant to undergo this reaction?
- (d) Compare the case of electrophilic addition across a double bond and a triple bond.  
(5+5+5+5)
7. (a) Draw the orbital correlation diagrams for
- (i) Disrotatory ring closure of 1,3-butadiene and
- (ii) Conrotatory ring closure of 1,3,5-hexatriene. Prove that both are thermally forbidden.

- (b) Explain how cope and claisen rearrangements involve [3, 3]-sigmatropic rearrangement.
- (c) State the generalised woodward Hoffmann rules for periajelic transformations.
- (d) Write the product in the following reaction with mechanism.



(10+4+4+2)

8. (a) Give an account of the optical isomerism exhibited by nitrogen containing compounds.
- (b) Discuss the conformational features of trans-decalin.

- (c) Describe cahn-Ingold - prelog way of assigning the R/S configuration to a chiral centre.
- (d) Explain why the chair form of cyclohexane is more stable than other forms.

Draw

- (i) The chair form of cyclohexane and indicate the  $\beta$ -axial bonds and
- (ii) The boat form cyclohexane and indicate the flag pole and torsional bonds. (5+5+5+5)
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M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

First Year

Chemistry

**INORGANIC CHEMISTRY - I**

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Discuss the preparation and explain the structure of any one hexanuclear cluster. (10)
- (b) Write short notes on organometallic clusters. (10)
  
2. (a) How are phosphazines prepared? Explain the structure and bonding in them. (10)
- (b) How is  $S_4N_4$  prepared? Explain the structure and properties of SN ring compounds? (10)

3. (a) Discuss ferro and antiferromagnetism of solids. (10)
- (b) What is meissener effect? Explain 1-2-3 superconductors? (10)
4. (a) Explain in detail shell model (10)
- (b) Explain the following :
- (i) Binding energy
- (ii) N - P ratio. (10)
5. (a) What is Q value? Calculate the Q value for the reaction?
- $${}^{14}_7\text{N} + {}^4_2\text{He} \longrightarrow {}^{17}_8\text{O} + {}^1_1\text{H} + \text{Q}. \quad (10)$$
- (b) Write a note on spallation reaction with examples. (10)
6. (a) What is the source of stellar energy? Write the equation for the relevant nuclear reactions? (10)
- (b) Explain the important applications of radioisotopes in industry, agriculture and medicine. (10)
7. (a) Describe the working principle of proportional counter as a function of graphical representation. (10)
- (b) Discuss the principle and working of cyclotron. (10)



8. (a) What is the principle involved in TGA? What are the factors affecting TGA curve? (10)
- (b) Describe the principle of PES and mention its applications. (10)
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M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

Chemistry

PHYSICAL CHEMISTRY – I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Explain the different types of groups. (6)
- (b) What are the conditions for the formation of a mathematical group? (6)
- (c) Use fullerenes to explain the  $I_h$  point group. (8)
2. (a) Explain reducible and irreducible representations. (5)
- (b) Construct a character table for  $C_{3v}$  point group. (10)
- (c) Discuss the classification of vibrational modes. (5)

3. (a) Bring out the significance of the schrodinger equation. (5)
- (b) Explain :- Eigen functions and Eigen values. (5)
- (c) Discuss the postulates of quantum mechanics. (10)
4. (a) Solve the schrodinger wave equation for a particle in a one dimensional box of length  $a$  having infinitely high walls. (10)
- (b) Solve the Schrodinger equation for a diatomic rigid rotator. (10)
5. (a) Explain the application of schrodinger's wave equation to the Hydrogen atom. (10)
- (b) Discuss how the perturbation method is applied to the He atom. (10)
6. (a) Explain how fugacity of a gas is determined from equation of state. What is its significance? (10)
- (b) Give the statement of the Nernst heat theorem and explain it. (4)
- (c) Discuss the need for the III law of thermodynamics. How does this lead to the concept of probability? (6)

7. (a) What is the physical significance of the partition function? (6)
- (b) Derive an equation for canonical partition function in terms of molecular partition function. (6)
- (c) Explain the Lagrangian method of undetermined multipliers. (8)
8. (a) Derive the equation for translational partition function. (5)
- (b) The rotational constant for gaseous HCl at 500K is  $10.59 \text{ cm}^{-1}$ . Find out its rotational partition function. (5)
- (c) Derive the equation for Fermi - Dirac distribution. (10)
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