

**M.Sc. 3rd Semester Examination, 2013**

**CHEMISTRY**

**PAPER—CEM - 302**

*The figures in the right-hand margin indicate marks*

*( Organic Special )*

*[ Marks : 40 ]*

*Time : 2 hours*

Answer any **five** questions taking  
at least **two** from each Group

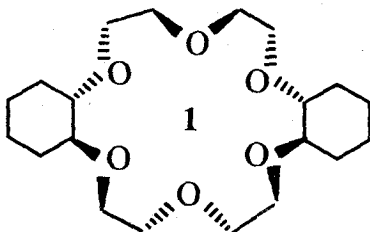
**GROUP – A**

1. (a) What is molecular recognition ? 2
- (b) What are the principal forces involved in molecular recognition ? 2
- (c) Design, synthesize and depict the mode of complexation of an adipic acid receptor. 4

*( Turn Over )*

( 2 )

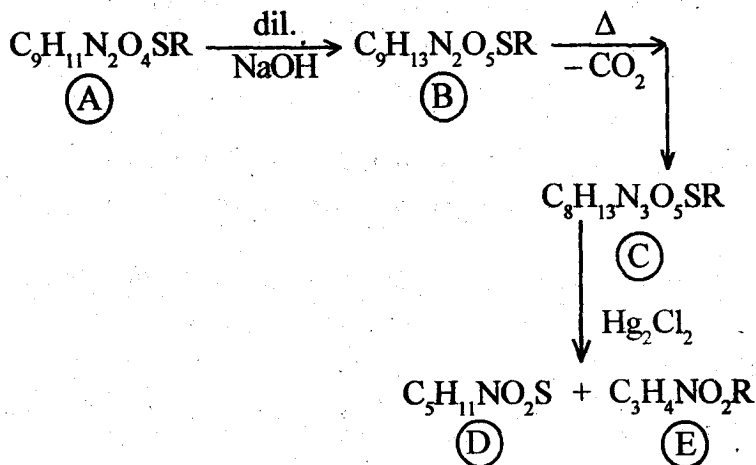
2. (a) Define template effect. 2
- (b) How does macrocyclization work even though it is an entropically unfavorable process? 2
- (c) How does 18-crown-6 bind a monovalent cation? 2
- (d) Name the compound 1 and propose a synthetic route. 2



3. (a) Write the applications of crown ethers. 2
- (b) How can one use 'U' - tube transport experiment for the separation of ions/molecules? 2
- (c) Design a suitable receptor for monopotassium salts of a dicarboxylic acid, synthesize it and show the mode of its complexation. 4

( 3 )

4. The following transformation shows the products as : 4 + 4



Draw backwards and identify the structure of  $\textcircled{\text{A}}$  and confirm its structure through its spectroscopic evidences.

5. (a) What are the different pathways by which the antibiotics destroy the pathogenic micro-organism ? How benzyl penicillin destroy the microbial cell wall. 4
- (b) How penicillin is biosynthesized in the culture medium of *Penicillium chrosogenum*. 4

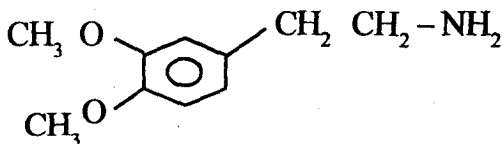
GROUP – B

6. (a) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation. 2
- (b) Design a suitable **chiral** host for complexing **L-Trp** and show the mode of its complexation. 2
- (c) Design, synthesize and explain the mode of action of a protease enzyme mimic. 4
7. (a) What are cyclodextrins ? 2
- (b) *p*-chlorination of anisole is preferred in water in the presence of  $\beta$ -CD with rate acceleration. How do you explain this observation ? 2
- (c) Describe the use of a cyclodextrin derivative as a Ribonuclease enzyme mimic. 4
8. (a) Define hydrophobic effect. 2
- (b) How can water act as a better solvent than common organic solvents for a simple

- Diels-Alder reaction? Illustrate with examples. 3
- (c) What are 'salting in' and 'salting out' agents? 3
9. (a) What is aromatic-aromatic ( $\pi$ - $\pi$ ) interaction? 2
- (b) Show schematically the potential energy diagram for two interacting  $\pi$ -atoms as a function of their orientation. 2
- (c) Charge transfer transitions observed for EDA complexes are a consequence not a cause of the more general  $\pi$ - $\pi$  interaction. 2
- (d) Give an example of Host-Guest complexation utilizing aromatic-aromatic interaction. 2
10. (a) What are the synthetic equivalents of  
 $\ominus$   $\text{CH}(\text{CO}_2\text{Et})_2$ ,  $\ominus$   $\text{CH}_3$ ,  $\oplus$   $\text{Ph CH}_2$  3
- (b) Demonstrate the use of Functional Group

( 6 )

Interconversion in retrosynthetic analysis  
by which catechol is found as the starting  
material for



( *Inorganic Special* )

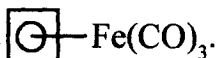
[ Marks : 40 ]

Time : 2 hours

Answer any five questions taking  
at least two from each Group

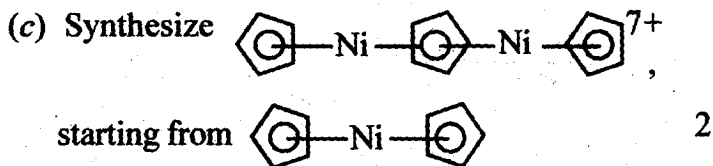
GROUP – A

1. (a) Synthesize 'Cubane' starting from

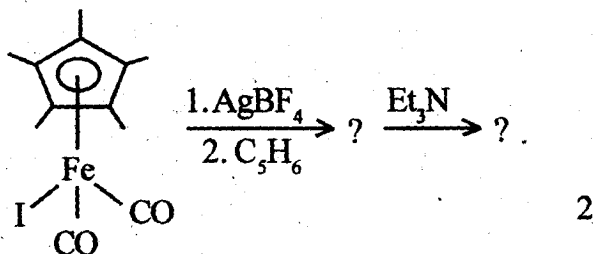


(b) Write down the synthesis procedure of  
( $\eta^6$  - arene)<sub>2</sub> Cr by Fisher-Haffner method. 2

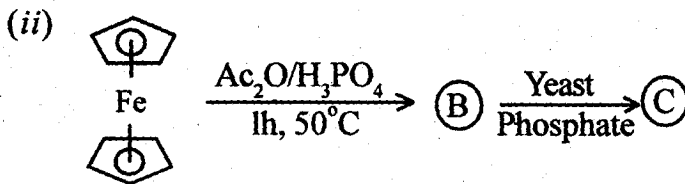
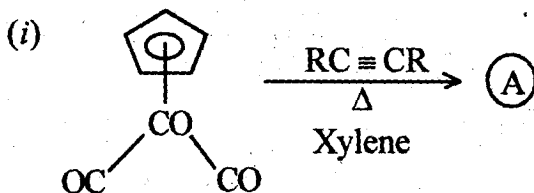
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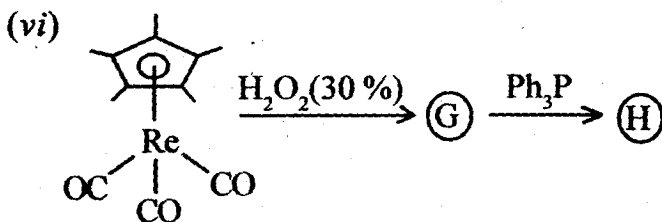
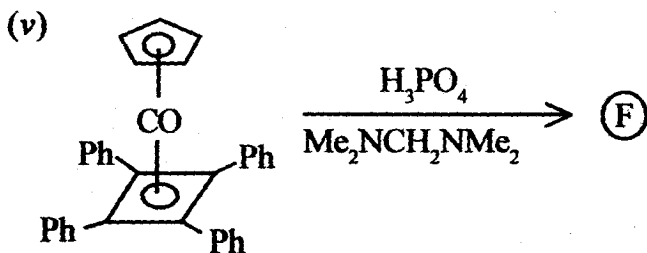
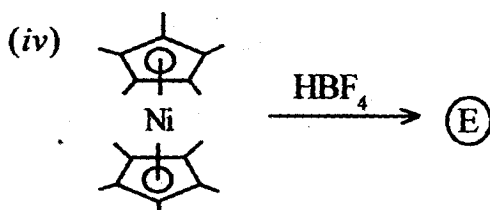
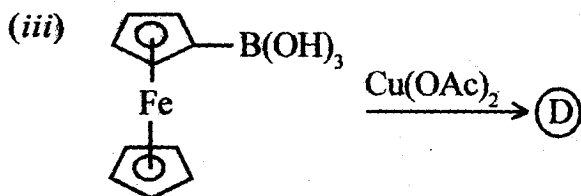
(d) Complete the reaction --



2. Write down the product (A - H): 1 × 8



( 8 )





3. (a) Explain ' $\beta$ -hydrogen elimination' reaction in the light of organometallic chemistry. 2
- (b) Write explanatory note on 'alkyl/hydrogen migration'. 3
- (c) Discuss the catalytic cycle of Rh-catalysed 'Monsanto acetic acid synthesis'. 3
4. (a) Describe the three broad classes of DNA adducts that can be made by biofunctional  $pt$ -complexes. 4
- (b) Explain the biological consequences of  $pt$ -DNA binding. 4

GROUP – B

5. (a) State and explain different point groups for hexagonal system. 4
- (b) For an orthorhombic system the three sides of an unit cell are  $a = 5\text{\AA}$ ,  $b = 10\text{\AA}$  and  $c = 20\text{\AA}$ . Then what will be the volume of an unit cell
- (i) of the direct lattice
- (ii) of the reciprocal lattice. 2 + 2

6. (a) Define Screw axis. 1
- (b) How will you classify different crystal systems in respect of different unit cell parameters ? 5
- (c) What is reciprocal lattice ? 2
7. (a) What is 'Oxidative coupling' reaction ? What are the driving forces for this type of reaction ? 2
- (b) Write short note on 'Catalytic Converter'. 2
- (c) Draw the catalytic cycle for 'Hydroformylation reaction'. 3
- (d) Write down the name and structure of two hydrogenation catalysts other than Wilkinson's catalyst. 1
8. (a) Explain convergent and divergent approach for the formation for dendrimers. 2
- (b) Discuss the spectral properties of transition metal based dendrimers. 3

( 11 )

- (c) Write explanatory notes on "Interaction of metal ions with nucleic acid". 3

( *Physical Special* )

[ Marks : 40 ]

Time : 2 hours

Answer any four questions taking  
at least two from each Group

GROUP – A

- (a) What is partial microscopic diffusion control reaction ? Derive the expression for partial microscopic diffusion control reaction. 2 + 5

(b) Write down the principle and schematic diagram for the most suitable method to study the high temperature fast gas-phase reactions. 3
- (a) A reaction between two ionic species of opposite charge is carried out separately in

ethyl acetate and hexane. What will be the fate of reaction in two different solvents – Explain. 6

(b) The full diffusion control reactions the combination of iodine atoms in water and the combination of methyl radicals in toluene occur spontaneously. If the viscosities of water and toluene at 20°C are  $1.002 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}$  and  $5.90 \times 10^{-4} \text{ kg m}^{-1}\text{s}^{-1}$ , respectively, estimate the ratio of the rate constants of the two reactions at that temperature. 4

3. (a) "In a reaction between two ions entropy of activation always decreases after formation of activated complex due to electrostriction" – Criticise the statement. 4

(b) What is the utility of potential energy surface (PES) in kinetic reaction? With the help of PES define 'COL' and draw the potential energy diagram as well as contour diagram showing the actual path of a reaction.  $\left(1 + 2 + 1\frac{1}{2} + 1\frac{1}{2}\right)$

4. (a) Distinguish between :

(i) Polarizable and non-polarizable interface

(ii) Chemical potential and electro-chemical potential.

$$\left(2\frac{1}{2} + 2\frac{1}{2}\right)$$

(b) Prove that for a polarizable interface

$$d\gamma = -q_{\mu} dV - (q_{\mu}/z_j F) d\mu_j - \Sigma \Gamma_i d\mu_i$$

where the terms bear usual significance. 5

GROUP - B

5. (a) Elucidate/Justify

(i) The electro-capillary curve is a perfect parabola for a parallel plate condensor model an electrified interface.

(ii) The efficiency of an ideally operating fuel cell can be even greater than one.

3 + 3

(b) How does the transmission co-efficient help in determining the mechanism of hydrogen evolution reaction ? Give examples of two mechanisms.

4

6. (a) Obtain the expression for the rotational contribution to the molar entropy of a heteronuclear diatomic molecule. 6
- (b) Define the ensemble average and the time average and state the Ergodic hypothesis. 4
7. (a) Considering two microcanonical ensembles in thermal equilibrium define the Lagrangian energy multiplier ' $\beta$ ', evaluate the quantity and establish the relation between ' $\beta$ ' and the particle number multiplier  $\alpha$  in terms of its chemical potential. 6
- (b) Show that the chemical potential of Bosons are negative. 4
8. Define grand partition function for a system of fermions and derive the Fermi-Dirac distribution law. 10
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