

**DEPARTMENT OF CHEMISTRY**  
**RANI RASHMONI GREEN UNIVERSITY**  
**M. Sc. COURSE IN CHEMISTRY**  
**SEMESTER III FINAL EXAMINATION: 2024**  
**Course ID: CHEM-C33**

**Full Marks:40**

**Time: 2hrs**

Answer any **ONE** question from each **UNIT** in your own words with proper scientific justification.

**Unit-1: Inorganic Reaction Mechanism**

**Q-1.** (a)  $k_{aq}(s^{-1}, 25\text{ }^{\circ}C)$  of  $Cl^{-}$  ligand for  $[CoCl(NH_3)_5]^{2+}$  and  $[CoCl_2(NH_3)_4]^{+}$  are  $10^{-6}$  and  $10^{-2}-10^{-3}$ , respectively. Which type of reaction pathway has been followed in these reactions and explain why?

(b) Write the Eyring reaction rate equation and how  $\Delta H^{\ddagger}$  can be evaluated from it? [4+4 = 8]

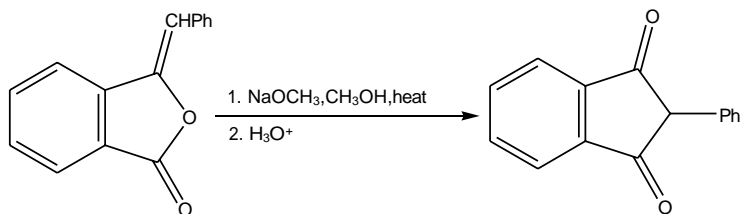
**Q-2.** (a) What is Outer Sphere Electron Transfer (OSET) process?

(b) Explain all steps involved in the outer sphere oxidation of  $[Fe(CN)_6]^{4-}$  by  $[Fe(phen)_3]^{3+}$ .

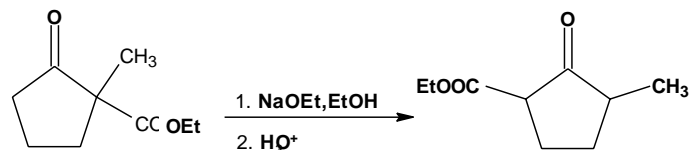
(c) Write the factors favouring the OSET process. [2+4+2= 8]

**Unit-2: Organic Reaction Mechanism**

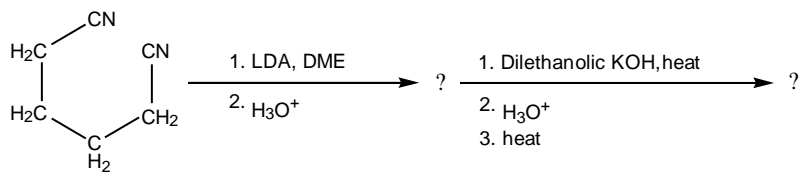
**Q-3.**(a) Account for the following observation:



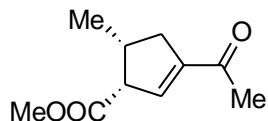
(b) Explain the following transformation:



(c) Complete the following:

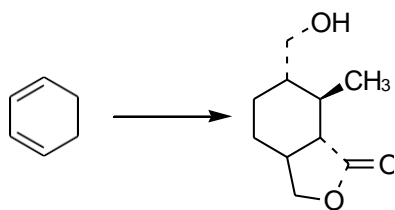


(d) Synthesize the following molecule using Diels-Alder reaction as one of the steps

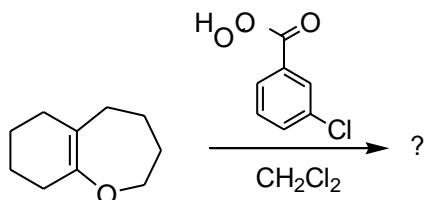


[2+2+2+2 = 8]

Q-4.(a) Carry out the following conversion.



(b) Predict the product with plausible mechanism:



(c) Predict the product of the following reaction with proper logic when D-glucose is treated with excess of Ph-N(Me)-NH<sub>2</sub>?

(d) What will happen when *p*-benzoquinone is treated with excess of aniline?

[2+2+2+2 = 8]

### Unit-3: Supramolecular Chemistry

Q-5.(a) Describe ion-dipole interaction in a suitable Ru 2,2' - bipyridyl complex.

(b) Define the following terms

(i) supramolecular isomerism (ii) reticular synthesis

(c) Illustrate a smart material with suitable example.

[3+2+2+1 = 8]

**Q-6. (a)** Describe pi-pi interactions in hexafluorobenzene.

(b) Define the following terms

(i) supramolecular devices (ii) secondary building units in a supramolecular assembly.

(c) Illustrate hierarchical super structure with suitable example.

[3+2+2+1 = 8]

#### Unit-4: Asymmetric Synthesis

**Q-7. (a)** Titanium (IV) alkoxide forms a complex with tartarate and allylic alcohol substrate.

(i) Propose a stepwise mechanism for the formation of the active titanium complex.

(ii) How does the coordination environment of Ti(IV) complex dictate in the facial selectivity of the epoxidation?

(b) The Sharpless asymmetric dihydroxylation (AD) reaction utilizes OsO<sub>4</sub> as the oxidant and a chiral ligand such as (DHQD)PHAL or (DHQ)PHAL.

Predict the major enantiomeric product when using (DHQD)PHAL versus (DHQ)PHAL on a simple alkene such as *trans*-β-methyl styrene with the help of a suitable mnemonic device.

[4+4 = 8]

**Q-8. (a)** Consider the following two allylic alcohols:

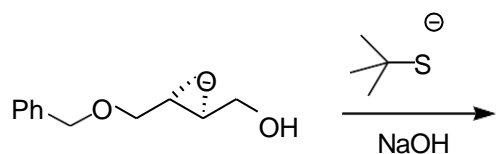
(i) CH<sub>3</sub>-CH=CH-CH<sub>2</sub>OH

(ii) Ph-CH=CH-CH<sub>2</sub>OH

Which substrate will undergo Sharpless epoxidation faster? Justify your answer based on steric and electronic factors.

(b) Give two examples of C<sub>2</sub>-symmetric bidentate amine ligands used in asymmetric dihydroxylation reaction.

(c) Predict the structure of the product with proper stereochemistry and mechanism of the following reaction:



[3+2+3 = 8]

### Unit-5: Valency and Perturbation Theory

**Q-9.**(a) How does the Virial theorem relate total energy and the kinetic energy of a system?

(b) Explain the assumptions made in the Born-Oppenheimer approximation.

(c) Derive the expression for first-order correction for energy using Rayleigh-Schrödinger perturbation theory. [2+3+3 = 8]

**Q-10.** (a ) Why does the von Neumann-Wigner theorem prevent actual level crossing?

(b) Assuming the potential energy function,  $V(r)=-ar^{-n}$ , where a and n are constants, derive the expression for the average kinetic energy of a particle in this potential using the virial theorem.

(c) Compare non-degenerate vs. degenerate perturbation theory.

[2+3+3=8]