

M.Sc. 3rd Semester Examination, 2014

CHEMISTRY

PAPER—CEM-302

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(Organic Special)

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

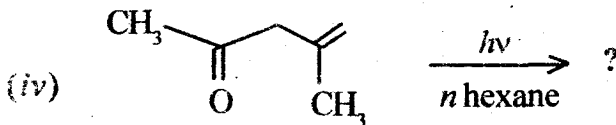
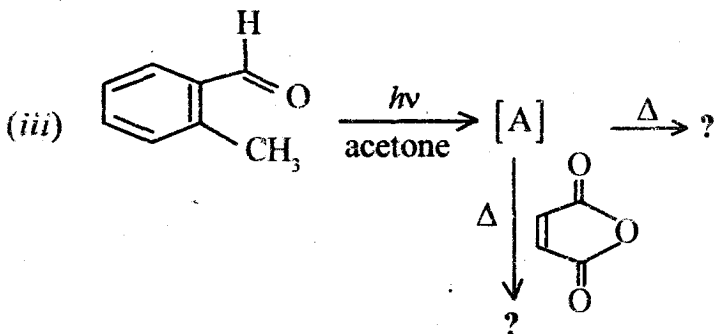
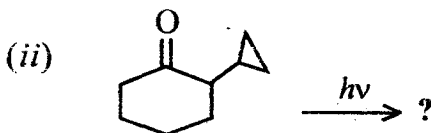
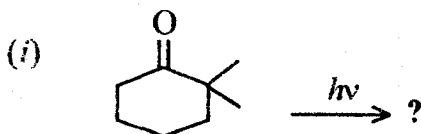
GROUP — A

1. (a) Draw Jablowski diagram and show different excited states of polyatomic molecules initiated by photochemical irradiation. Show the major events occurring in different states. 4
(b) Define and differentiate between 'Inter-system Crossing' and 'energy transfer' phenomenon with suitable examples. 2 + 2

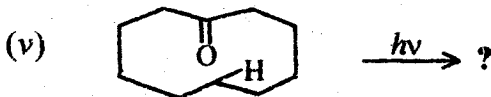
(Turn Over)

(2)

2. Predict the product/s of the following reactions showing mechanism in each case (attempt any four) : 2 × 4

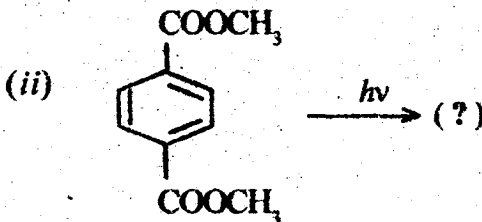
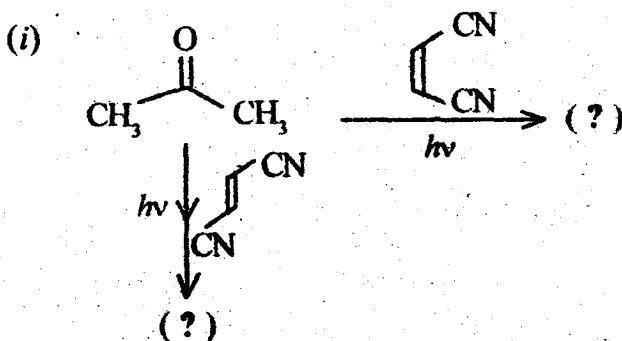


(3)

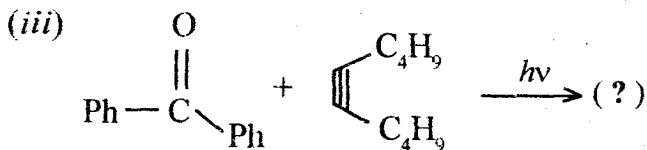


3. (a) What is Paterno-Buchi addition reaction ?
Explain the pathway of the reaction with a suitable example. 4

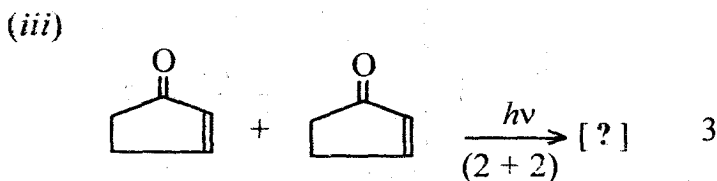
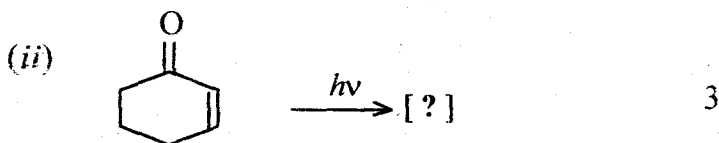
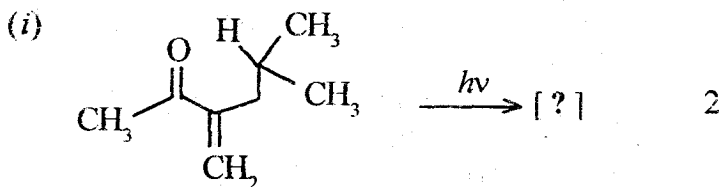
(b) Predict the product/s of the following reactions with mechanism (any two): 2 x 2



(4)

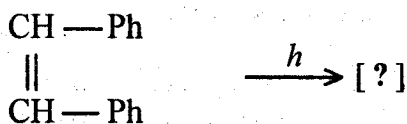


4. Predict the products of the following reaction with proper justifications :



(5)

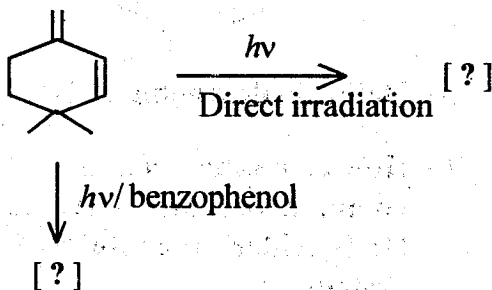
Or



cis / Trans

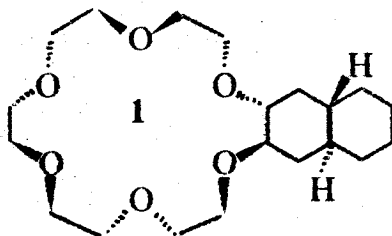
5. (a) What is Di- π -methane rearrangement reaction? Explain with a suitable example the pathway of the reaction and indicate its frontier-orbital interaction during conversion. 4

- (b) Explain free-rotor effect and hence predict the product of the following reaction : 2 + 2



GROUP – B

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



2 × 4

7. (a) Define hydrophobic effect.
- (b) How can water act as a better solvent than common organic solvents for a simple Diels-Alder reaction ? Illustrate with examples.

(7)

(c) What are 'salting in' and 'salting out' agents ?

2 + 3 + 3

Or

Establish the structure of benzyl penicillin using spectroscopic evidences. 8

8. (a) What is aromatic-aromatic (π - π) interaction ?

(b) Show schematically the potential energy diagram for two interacting π -atoms as a function of their orientation.

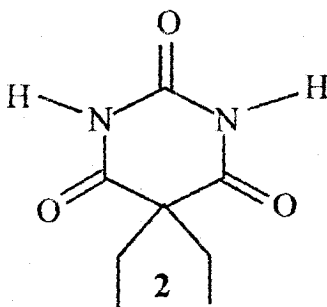
(c) Charge transfer transitions observed for EDA complexes are a consequence not a cause of the more general π - π interaction.

(d) Give an example of Host-Guest complexation utilizing aromatic-aromatic interaction. 2 × 4

9. (a) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation.

(b) Design a suitable **chiral** host for complexing **L-Trp** and show the mode of its complexation.

(c) Design a receptor for the complexation of barbital **2**.



(d) Design, and explain the mode of action of a protease enzyme mimic. 2 × 4

10. (a) What are cyclodextrins ?

(b) *p*-chlorination of anisole is preferred in water in the presence of β -CD with rate acceleration. How do you explain this observation ?

(9)

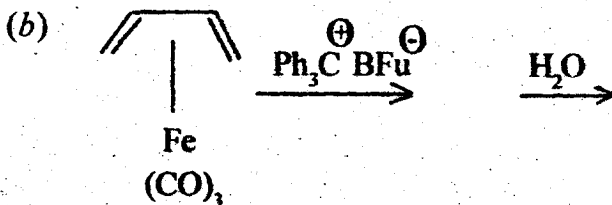
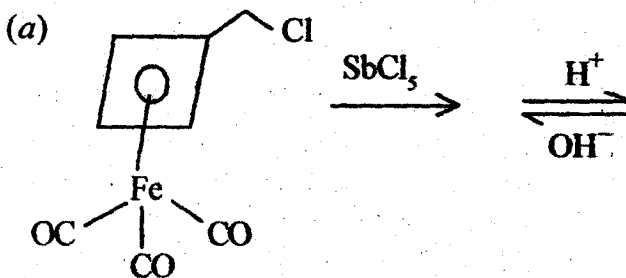
- (c) Describe the use of a cyclodextrin derivative as a Ribonuclease enzyme mimic. 2 + 2 + 4

(Inorganic Special)

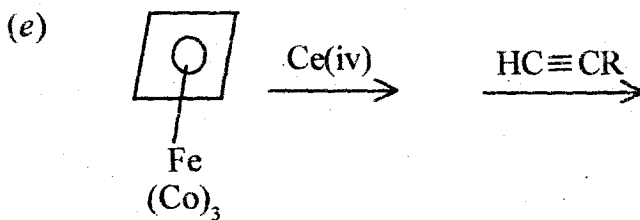
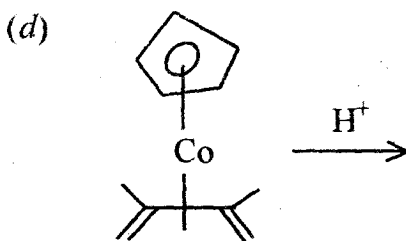
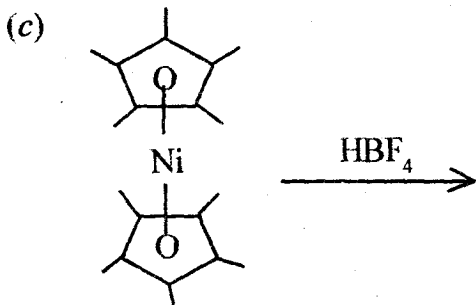
Answer any five questions taking at least two from each Group

GROUP – A

1. Complete the following reactions : 1 × 8



(10)

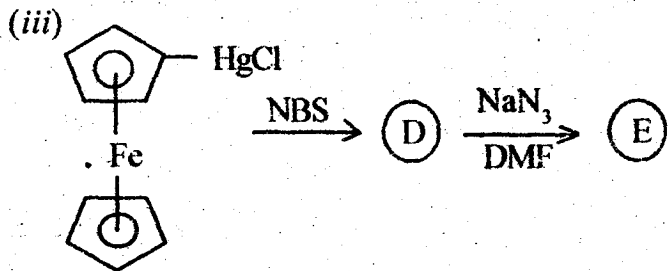
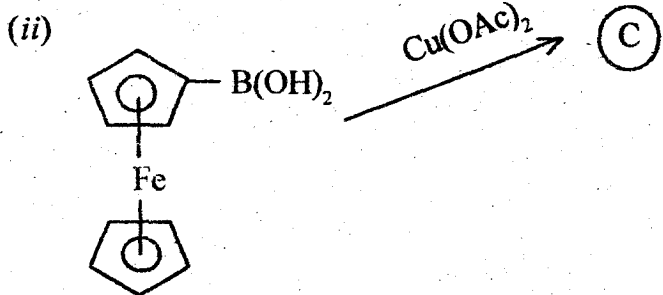
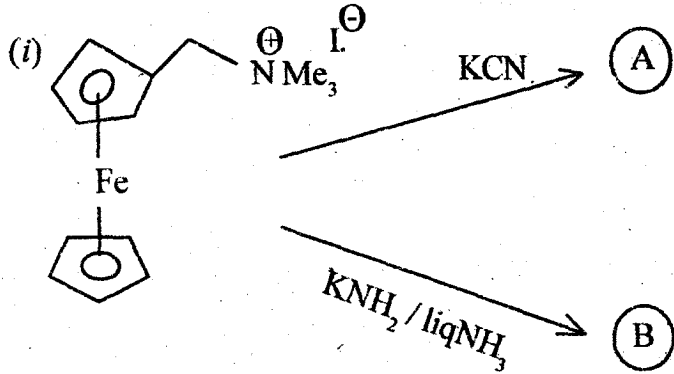


2. (a) How will you synthesize ferrocene boronic acid starting from ferrocene ?

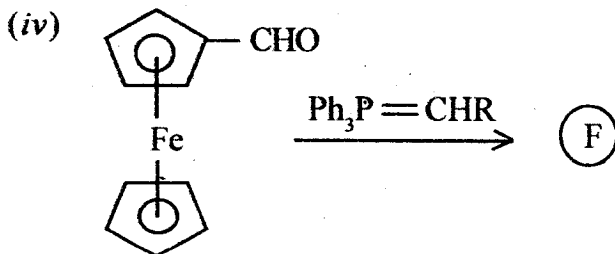
2

(b) Write down the product (A—F)

6



(12)

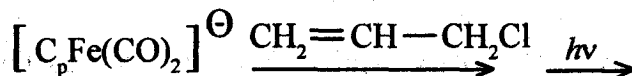


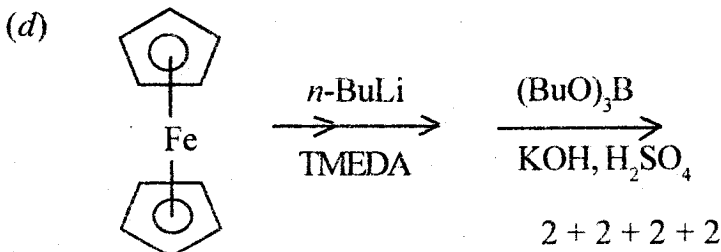
3. (a) Derive Lane diffraction conditions in case of diffraction from crystalline solids. Interpret these equations.
- (b) Show that the reciprocal of FCC lattice is BCC lattice. 4 + 4
4. (a) Write down the differences between CD and ORD spectroscopy.
- (b) Write down the differences between circular and linear polarised light ?
- (c) What do you mean by Cotton effect ? 4 + 2 + 2

GROUP – B

5. (a) Draw catalytic cycle for Wacker Oxidation.

- (b) Discuss the problems with Monsanto process.
- (c) What do you mean by Oxo-process ? Which catalyst is used for this process ? 4 + 2 + 2
6. (a) Discuss the catalytic cycle of alkene hydrogenation reaction by Wilkinson's catalyst.
- (b) Write down the chemical formulation of Schrock-Osborn's catalyst and Crabtree's catalyst.
- (c) Explain 'Orthometallation'. 4 + 2 + 2
7. (a) What are the driving forces for 'Oxidative Coupling' reaction ?
- (b) Explain β -hydrogen elimination reaction in the light of organometallic chemistry.
- (c) Complete the following reaction :





8. (a) Which type of characteristic bands are observed for Z-DNA and B-DNA conformation in CD-spectrophotometry ?
- (b) What are the characteristic bands responsible for α -helical structure of a protein in CD-spectrophotometry ? Assign the related transitions. (2 + 2) + 4

(Physical Special)

Answer any **four** questions taking **two** from each Group

GROUP – A

1. (a) Derive the expression of entropy of activation for the reaction H^+ and Br^- ions.

(15)

- (b) How does the rate of a reaction depend on the hydrostatic pressure ?
- (c) The rate of a reaction at 25°C is doubled when the pressure is increased from 1 atm. to 2000 atm. Calculate $\Delta^\ddagger V$, assuming it to be independent of pressure. 5 + 3 + 2
2. Derive the expression of viscosity co-efficient (η) using absolute reaction rate theory. 10
3. (a) "The rate of a full diffusion controlled reaction does not depend on the sizes of the reactants". Justify the statement.
- (b) The reaction between $K_2S_2O_8$ and KI is carried out separately in presence of 0.1 (M) KNO_3 and 0.5 (M) KNO_3 at the same temperature and same solvent. What will be the fate of the reaction rate and why?
- (c) State the working principle of molecular beam technique.

(d) The combination reaction of methyl radicals in toluene is full diffusion controlled. If the viscosity of toluene at 20°C is $5.90 \times 10^{-4} \text{ kgm}^{-1}\text{s}^{-1}$, find the rate constant of the reaction. 3 + 3 + 2 + 2

4. (a) What do you mean by surface excess? Show that surface excess becomes equal to moles adsorbed per unit area under certain condition. What is that condition?

(b) Starting from the thermodynamics of a polarizable interface, prove that 4 + 6

$$\left(\frac{d\gamma}{2RTd \ln a_{\pm}} \right)_{V,-} = -\Gamma_{+}$$

where the terms bear usual significance.

GROUP – B

5. (a) What are different possible mechanisms of hydrogen evolution reaction? Derive rate equation of any one of them.

- (b) How and why do the electron bands of extrinsic semiconductor change on dipping it in an electrolyte solution ?
- (c) Distinguish between photovoltaic and photo-electro-synthetic cell using schematic diagrams. (2 + 2) + 2 + 4
6. (a) Obtain the expression for molar translational entropy of a monoatomic gas.
- (b) Calculate the characteristic rotational temperature for H_2 gas at $2727^\circ C$. Given the moment of inertia of hydrogen gas molecule at this temperature = $4.60 \times 10^{-48} \text{ kgm}^2$ (given $h = 6.626 \times 10^{-34} \text{ Js}$ $K = 1.38 \times 10^{-23} \text{ JK}^{-1}$) 6 + 4
7. State the principle of equal a priori probability and derive the Gibbs canonical distribution. 2 + 8

8. What is meant by Bose-Einstein condensation ?
Derive the expression for the temperature at
which such a process may occur for a boson. 2 + 8
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