

2015

M.Sc. 3rd Seme. Examination

CHEMISTRY

PAPER—CEM-302

Full Marks : 40

Time : 2. Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *four* questions, taking at least *two* from each group.

Group—A

1. Define grand partition function for fermions and derive Fermi-Dirac distribution law. 4+6
2. (a) Define quantities α and β for exchanges between suitable ensembles and derive the relation between these.

(Turn Over)

(b) Calculate the translational partition function for benzene in a volume of 1 m^3 at 25°C . 7+3

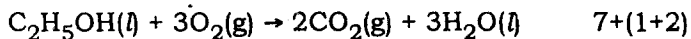
3. Derive the expression of ideal gas equation given by Einstein. 10

4. (a) For a polarizable interface prove that

$$d\gamma = -q_M dv - \frac{q_M}{Z_j F} d\mu_j - \sum \Gamma_i d\mu_i$$

where $d\gamma$ is the infinitesimal change in surface tension and the other terms bear usual significance.

(b) Define fuel cell and calculate the efficiency of the fuel cell



Group—B

5. (a) Derive an expression for Gibb's energy of ionic solvation using Born model.

(b) What are the disadvantages of Born model.

7+3

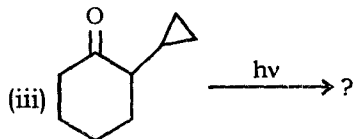
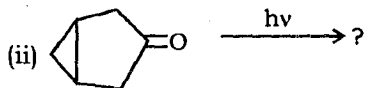
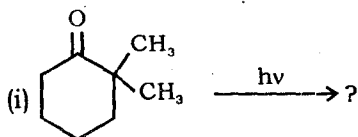
6. (a) Trace out the course of the reaction between hydrogen atom and hydrogen molecule using appropriate diagrams of potential energy surfaces.
- (b) Estimate the diffusion-controlled rate constant for the recombination of iodine atoms in n-hexane solution at 25°C, given that η for hexane is 0.325 cP. 7+3
7. (a) How does the rate of a Kinetic reaction between two ions depend on the dielectric constant of the solvent ?
- (b) For the first-order isomerization of an organic compound at 130°C, the activation energy is 108.4 kJ and the rate constant is $9 \cdot 12 \times 10^{-4} \text{ s}^{-1}$. Calculate the standard Entropy of activation for this reaction. 6+4
8. (a) "The plot of $\log K_r$ (where K_r = rate constant) against $\sqrt{\mu}$ (μ = ionic strength) for the reaction of base catalyzed hydrolysis of ethyl acetate is parallel to the X-axis" — Justify.
- (b) Derive the rate constant by appropriate statistical calculation of a gaseous bimolecular reaction. 3+7
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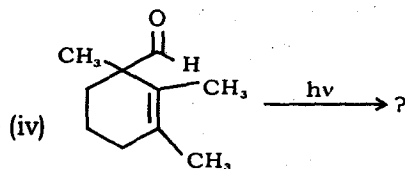
(Organic Special)

Answer any *five* questions, taking at least *two* from each group.

Group—A

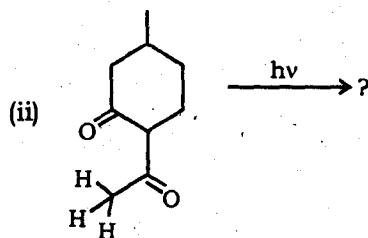
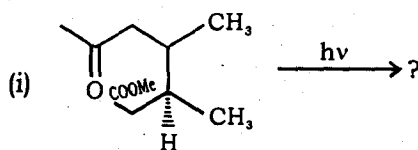
1. (a) What is 'Norrish-type - I' reaction? Explain the reaction mechanism with proper example. 2
- (b) Predict the product of the following reaction (any *three*): 3×2





2. (a) What are the condition/s for breaking on organic molecule in 'Norrish-type - II' reaction (r-Hydrogen abstraction). Show with pictorial diagram. 2

(b) What products are obtained from the following reactions and explain with mechanism indicating the differences with Norrish type - II reaction ; 3+3

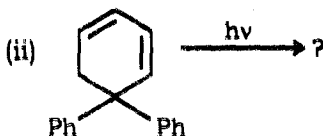


3. (a) Explain 'Di- π -methane' Rearrangement reaction with an example indicating the Zimmermann 'Frontier-Orbital Interaction'.

2

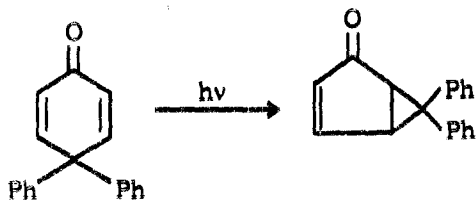
(b) Predict the product of the following reactions :

1+1

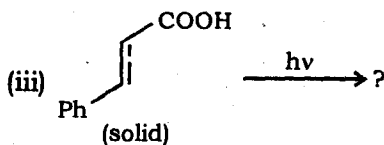
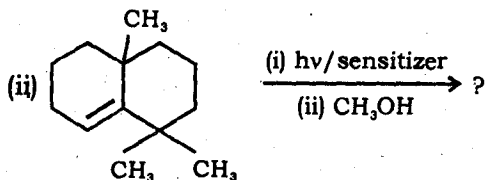
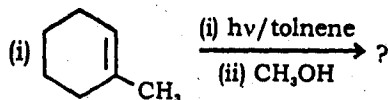


(c) Complete the following transformation indicating the kind of reaction taking place in each step :

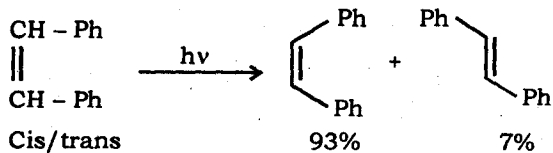
4



4. (a) Predict the product of the following reaction indicating mechanism (any two) : 2×2

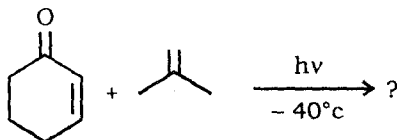


- (b) The following reaction gives the products as :



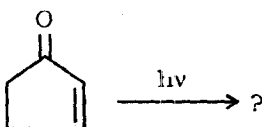
Explain the formation of the products with proper explanation. 4

5. (a) How many products are obtained from the following reaction. Indicate the mechanism of formation of each of the product.

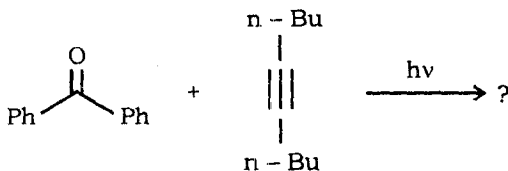


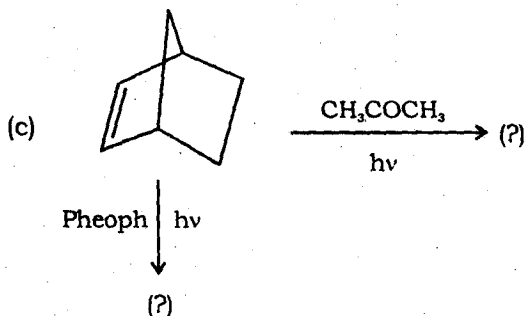
- (b) Indicate the product/s with ratios of following reaction irradiated separately in *methanol* and *benzene* medium :

3



or

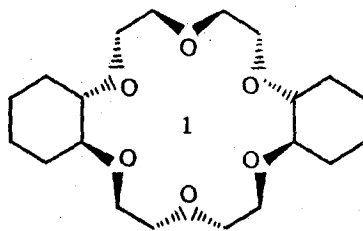




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Group—B

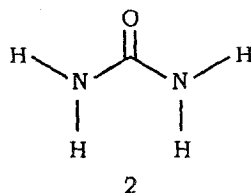
6. (a) What is template effect ?
- (b) How does macrocyclization work even though it is an entropically unfavorable process ?
- (c) How does 18-crown-6 bind a monovalent cation? Name a naturally occurring ionophore having similar selectivity.



- (d) Write the IUPAC name of compound 1 and propose a synthetic route. 2×4

7. (a) Define molecular recognition and write the principal forces involved in this process.
- (b) How can one use 'U'-tube transport experiment for the separation of ions/molecules?
- (c) Design a suitable receptor for aspartic acid, synthesize it and show the mode of its complexation. 2+2+4
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 utilising aromatic-aromatic interaction. 2×4

9. (a) Design a receptor for urea **2**, synthesize it and show the mode of its complexation.

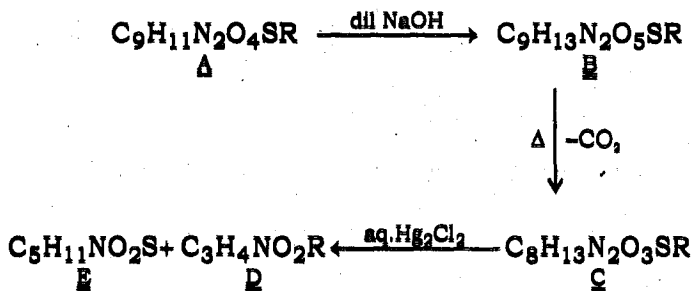


- (b) Design, synthesize and explain the mode of action of a protease enzyme mimic. 4+4

10. (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

or

The following transformation gives the product as follows :



Deduce the structure of E & D and establish the possible structure A drawing backwards of the above transformation. 8

(Inorganic Special)

Answer any *four* questions, taking at least *two* from each group.

Group—A

- (a) Briefly discuss the catalytic cycle for 'Monsanto acetic acid' process using $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyst. Mention oxidation states of 'Rh' in each step. 4

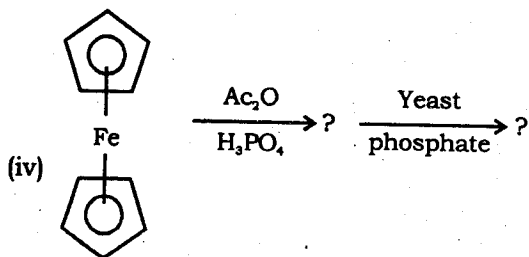
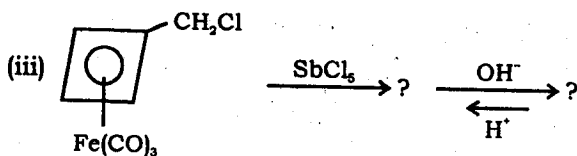
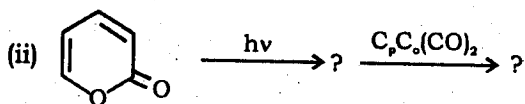
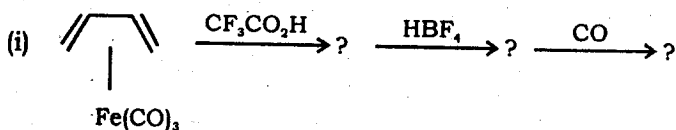
(b) Mention the draw back of Monsanto process. 2

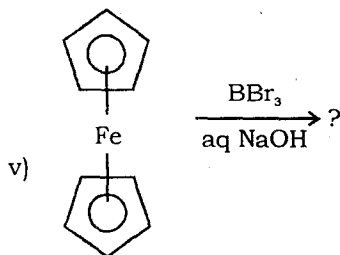
(c) Draw the catalytic cycle for the efficient and cost effective Cative process for the production of 'acetic acid'. 4
2. Write down the complete reaction for the production of CH_3CHO from C_2H_4 by Wacker process. Write down the rate equation for this process. Draw the catalytic cycle for this process. Discuss the role of CuCl_2 in Wacker process. 2+2+4+2
3. What is oxidative addition reaction? Mention the essential requirements of oxidative addition reaction? Write about the stereochemistry involved in oxidative addition reaction. What do you mean by orthometallation? What is oxidative coupling? 2+2+2+2+2

Group—B

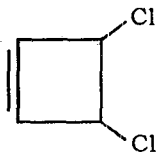
4. Complete the following reaction :

1×10





5. (a) What characteristic bands are observed for a DNA conformation in CD spectroscopy? 2
- (b) What are the characteristic bands and transition responsible for β -sheet and random Coil structure of a protein in CD spectroscopy? 3+3
- (c) Write down the behaviour of different types of polarised light. 2
6. (a) How will you synthesize $(\eta^4 - \text{C}_4\text{H}_4) \text{Fe}(\text{CO})_3$ starting from



2

(b) Discuss the diamagnetism in $(\eta^4 - \text{C}_4\text{H}_4) \text{Fe}(\text{CO})_3$ complex. 4

(c) Predict the product in the following reaction — 1×4

