RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, MAY 2018

THIRD YEAR [BATCH 2015-18]

Date : 04/05/2018 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** VIII [Gr. A&B] Full Marks : 50

[Use a separate Answer Book for <u>each group</u>]

Group – A

[***Attempt <u>one question</u> from each Unit***]

Unit – I

1. a) Confirm that a Morse oscillator has a finite number of bound states, and determine the value of v_{max} for the highest bound state. [3]

   b) Explain the following : [3]

   i) 'Stokes' line are more intense than 'anti-stokes' lines.

   ii) $\Delta J = \pm 1$ transitions are the specific selection rule for all rotational transitions (Consider only rigid rotor).

   c) For $^{14}N_2$, the transitional lines observed are due to $v = 1 \leftarrow 0$, $2 \leftarrow 0$ and $3 \leftarrow 0$ and are seen with the values 2345·15, 4661·40 and 6983·73 cm^{-1}. Calculate $\tilde{\nu}$ and x_e. [Assume y_e to be 0] [4]

   d) Why is laser used in Raman Spectrometer? [2]

2. a) Show that the lines in the rotation spectrum of a diatomic molecule are equispaced under rigid rotor approximation. [3]

   b) Which of the following molecules show (i) rotational, (ii) infrared, (iii) Raman spectrum and why? [3]

   HCl, CS_2, Br_2, CCl_4

   c) The rotational spectrum of HF has lines 41·9 cm^{-1} apart. Calculate the moment of inertia and bond length in HF. [3]

   d) The fundamental vibrational frequency of $H^{35}Cl$ is $8 \cdot 667 \times 10^{13}\ sec^{-1}$. What would be the positions of fundamental vibrational frequency for $H^{35}Cl$ and $H^{37}Cl$, if the force constants of the bonds are assumed to be constant? [3]

Unit – II

3. a) Discuss with an example what is meant by photostationary equilibrium. [3]

   b) Monochromatic light is passed through a 1 mm pathlength cell containing 0·005 moles/dm^3 solution. The light intensity is reduced to 16% of its value. Calculate the molar extinction coefficient of the sample. What would be the transmittance if the cell path is 2 mm? [3]

   c) At 460 mm, a blue filter transmits 75% of the light and a yellow filter 40% of the light. What is the transmittance at same wavelengths of the two filters in combination? [3]

   d) The photochemical decomposition of HI consists of the following steps :

   $HI + h\nu \rightarrow H + I$

   $H + HI \rightarrow H_2 + I$

   $2I \rightarrow I_2$

   Applying steady state approximation for [H], calculate the quantum yield of the reaction. Does it violate the Einstein's law of photochemical equivalence? [3+1]

4. a) What are the factors on which the optical density of a solution depends? [2]
   b) Can quantum yield be greater than 1? Explain. [3]
   c) Why are the lifetime of phosphorescent molecules are greater than fluorescent molecules? [2]
   d) Write down the mathematical form of the Lambert-Beer's law for the case when two components in a solution absorb in the range of light that is used. [3]
   e) In a wavelength vs intensity plot depict the three phenomena : absorption, the consequent fluorescence and phosphorescence. [3]

Group – B

[***Attempt <u>one question</u> from <u>each Unit</u>***]

Unit – III

5. a) Explain the mechanism of osazone formation with special reference to Amadori rearrangement. Why osazone formation does not proceed beyond the first two carbon atoms. (2 + 1)
   b) What is anomeric effect? In dry methanol 'α'– and 'β'–D(+) glucose exist in equal amounts, Explain. (1 + 2)
   c) An aldopentose [P] can be oxidised with dil HNO_3 to an optically active aldaric acid. A Kiliani-Fischer synthesis starting with [P] gives two new aldoses [Q] and [R]. Aldose [Q] can be oxidised to an optically inactive aldaric acid, but aldose [R] is oxidised to an optically active aldaric acid. Assuming the [D] configuration give the structures of [P], [Q] and [R] and also justify the assignments. (3)
   d) Show the reaction steps and the mechanisms involved in N-terminal amino acid determination by Edman method. (2)
   e) Get adenosine from its triphosphate. (1)
   f) Write the different interactions responsible for stabilizing the secondary structure of a protein. (1)
   g) Outline a synthesis of Citral. (2)

6. a) Identify compounds (A–D) in the following sequence of transformation.

$$\text{D-glucose} \xrightarrow[\text{reflux}]{CH_3OH/HCl} A \xrightarrow[NaOH]{(CH_3)_2SO_4} B \xrightarrow{\text{dil HCl}} C \xrightarrow{Br_2/H_2O} \xrightarrow{90^oC} D$$ (2)

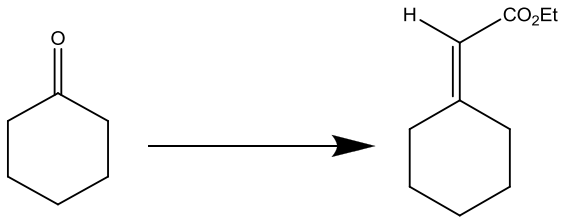
   b) Explain the formation of the products, when D–glucose is separately allowed to react with acetone/dry HCl and benzaldehyde / dry HCl. (2)
   c) Justify or criticise: Mutarotation of δ-Gluconolactone is not a case of first order asymmetric transformation. (2)
   d) Utilizing the structural illustration, explain the non-reducing property of sucrose. (2)
   e) Using chemical reactions justify the importance of the following reagents in peptide sequence analysis. (2 × 1.5)
      (i) Ph–N = C = S
      (ii) Br – CN
   f) How will you separate the constituents from a mixture of glycine, lysine and aspartic acid? (The respective isoelectric points are 6.0, 9.5 and 3.0) (2)
   g) Draw the H-bonded complementary base pairing structure in DNA. (2)

Unit – IV

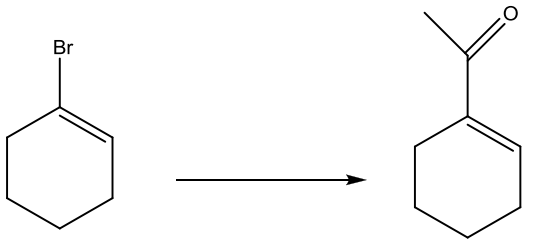
7. a) Explain the following reaction on the basis of FMO theory. (2)
   2E, 4Z, 6E – 2, 4, 6 – Octatriene is heated.

   b) Carry out the following conversion using organosilicon reagent. (2 + 2)

   (i)

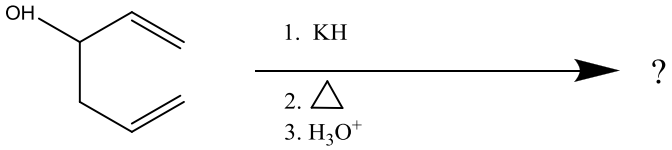


   (ii)

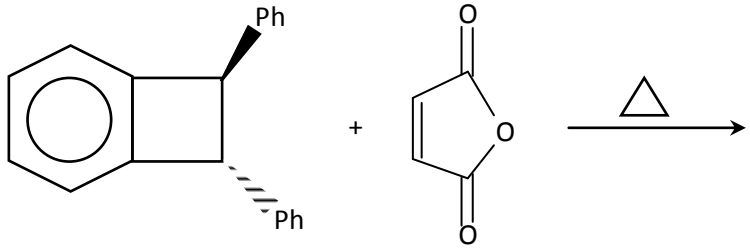


   c) Thermal [1,5] hydrogen shift is facile but [1,3] hydrogen shift is not observed. Explain (2)

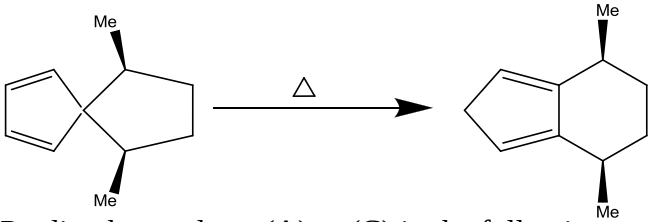
   d) Predict the product(s) of the following reactions with plausible mechanism. (2)



8. a) Predict the product of the following reaction indicating FMO interactions. (3)

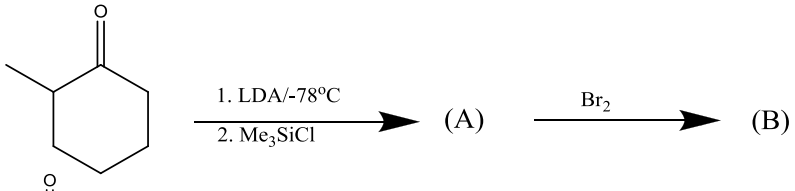


   b) Write down the mechanism of the following transformation: (2)

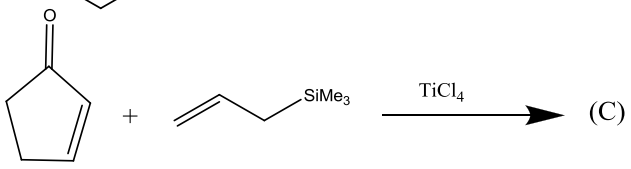


   c) Predict the products (A) to (C) in the following reactions. Give mechanism of formation of (C). (3)

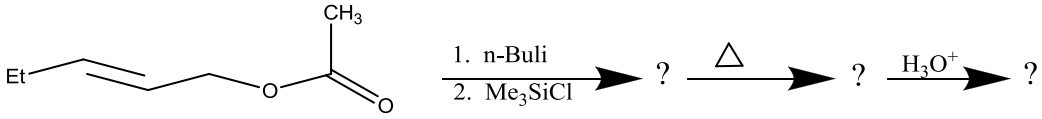
   (i)



   (ii)



d) Predict the product(s) of the following reactions with plausible mechanism: (2)



(4)