RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

THIRD YEAR

B.A./B.SC. FIFTH SEMESTER (July – December), 2012

Mid-Semester Examination, September 2012

Date : 10/09/2012 **CHEMISTRY (Honours)**

Time : 2 pm – 4 pm Paper : V Full Marks : 50

[Use Separate Answer Script for each Group]

Group – A

(*Attempt **any one** from each unit*)

Unit - I

1. a) Justify or criticize the followings : [2×2]
   i) For a BCC lattice, the only reflections that occur are those for which the sum of the indices is even.
   ii) Ferrocene is a well known molecule with C_5 symmetry axis. But 5-fold rotation axis is absent in crystals.
   b) The μ of HBr is 0·78D and its dielectric constant at 20°C and 1atm pr. Is 1·00313. Calculate its distortion polarisability. [Given $E_0 = 8{\cdot}854 \times 10^{-12}\ J^{-1}c^2m^{-1}$]. Do you expect any change in the same, if Br is replaced by D? Explain. [4]
   c) Draw the (III) plane for FCC lattice. [1]

2. a) How does one determine the dipole moment of a molecule by measuring the molar polarisation? Explain. [3]
   b) Molar polarisation does not have the contribution from orientation of a molecule at higher frequency than microwave. Justify it. [2]
   c) The X-ray spectrum of a cubic metal using radiation of $\lambda = 1{\cdot}5418\,A$ gives lines at the following values of θ :
   21·8 25·4 37·2 45·4
   i) Index the lines i.e. determine the hkl values of the planes.
   ii) Calculate the edge length.
   iii) Identify the unit cell. [4]

Unit - II

3. a) Differentiate between a classical and a quantum mechanical harmonic oscillators. [2]
   b) The wave function of a harmonic oscillator at its lowest energy state is given by $\psi_0(x) = A.e^{-dx^2/2}$. Find out A. [2]
   c) Show that $< x^2 >= \dfrac{\hbar\left(n+\frac{1}{2}\right)}{(\mu k)^{1/2}}$ for a harmonic oscillator. [4]

4. a) 'Zero point energy of a quantum mechanical harmonic oscillator can not be zero'. —Explain. [2]
   b) The wave function $\psi_1(x)$ of a harmonic oscillator is given by $\psi_1(x) = \left(\dfrac{4d^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$, where $\alpha = \dfrac{\sqrt{\mu k}}{\hbar}$. Show that the expression for the corresponding energy is given by $E_1 = \dfrac{3}{2}h\nu$, where ν is the oscillating frequency. [3]

c) The fundamental vibrational frequency of H_2 is $4{\cdot}33\times10^3 cm^{-1}$ and to is 74 pm. Calculate the rms displacement in the n = 0 state and compare it with the equilibrium bond length l_0.

Unit - III

5. a) Derive the relationship between the elevation of boiling point of the solvent with the molality of the solute, the later being nonvolatile and nonelectrolyte. [4]

   b) Consider the following equilibrium :

   $AlCl_3+3H_2O = Al(OH)_3 + 3HCl$

   Write down the number of components, phases and degrees of freedom in the system (Use your knowledge of general chemistry!) along with proper explanations. [3]

   c) Calculate the highest number of phases that can coexist in a two component system. [1]

6. a) Show from thermodynamic consideration that the osmotic pressure of a solution is proportional to the concentration of the solution and its temperature. [4]

   b) A solution containing 4·13gm LiCl per litre freezes at –0·343 C. Calculate van't Hoff factor and the degree of dissociation. [3]

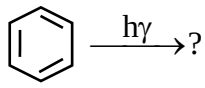
   c) Explain why the degrees of freedom at upper critical solution temperature in phenol-water system is zero (when pressure is constant). [1]

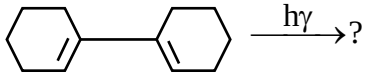
Group – B

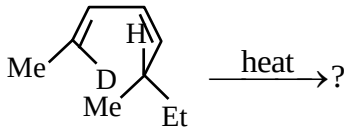
(*Attempt **any one** from each unit*)

Unit - I

7. Predict product with stereochemistry & possible orbital interaction at transition state :

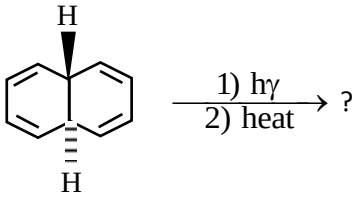
   a) 

   b) 

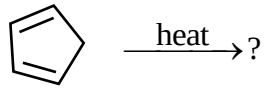
   c) 

   [1½+1½+3]

8. Predict product with stereochemistry & possible orbital interaction at transition state :

   a) 

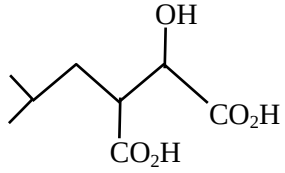
   [3]

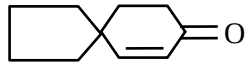
   b) 

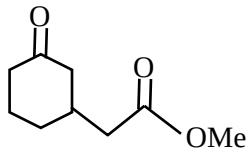
   [3]

Unit - II

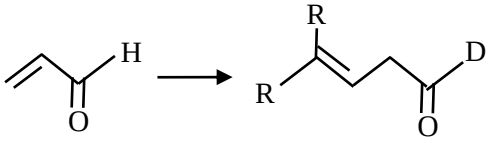
9. Give retrosynthetic analysis and an efficient synthesis of each of the following compounds ; [3×2]

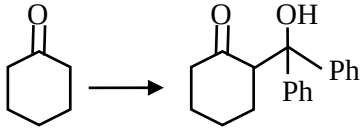
   a) 

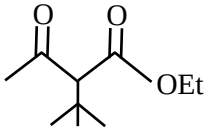
b) 

c) 

10. Carry out the following conversions. Mechanism is not necessary. [3×2]

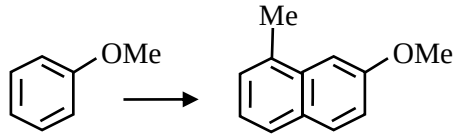
a) 

b) 

c) EAA 

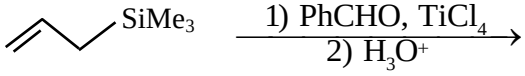
Unit - III

11. a) Carry out the following conversion. [2]



b) How would you prepare β-naphthol from naphthalene? What happens when β-naphthol is treated with nitrous acid?

c) Predict the products(s) of the following reaction and give mechanism. [1½]



d) Give product(s) and explain the stereochemical course of the following reaction.

threo - $C_3H_7-\underset{OH}{CH}-\underset{SiMe_3}{CH}-C_3H_7 \xrightarrow{KF/THF}$ [1½]

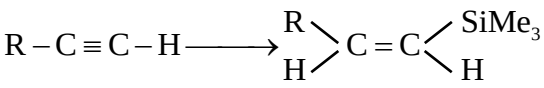
12. a) What happens when β-naphthol is heated with ammonia in the presence of aqueous sodium bisulphite solution. Give mechanism of the reaction. [2]

b) How would you distinguish chemically between anthraquinone and phenanthraquinone? Give the reaction. [1]

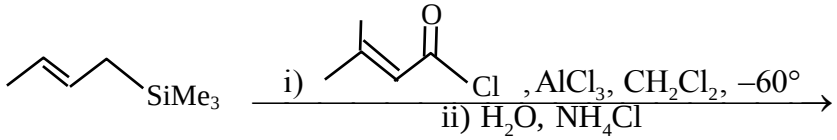
c) Write the product(s) of the following reaction and explain the regioselectivity of the process. [1]

Phenanthrene $\xrightarrow[t-BuOK]{CHCl_3}$

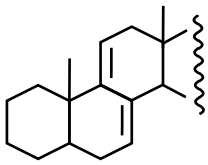
d) Carry out the following conversion : [1½]

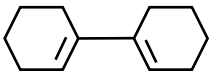


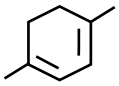
e) Predict the product(s) of the following reaction and give plausible mechanism. [1½]



13. a) The following dienes have λ_{max} at 231 nm (ε_{max} 21000), 236nm (ε_{max} 12000), 245nm (ε_{max} 18000), 265nm (ε_{max} 64000), and 282nm (ε_{max} 11900) in ethanol. Which is which? [5]


A


B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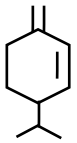
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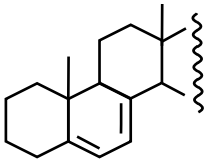
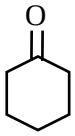
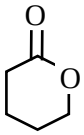

E

b) What is 'end absorption' in UV spectroscopy? [1]

14. a) Which will occur at a larger wavenumber?
   i) the C – N stretch of an amine or the C – N stretch of an amide
   ii) the C –O stretch of phenol or the C – O stretch of cyclohexanol
   iii) the stretch or the bend of the C – O bond in ethanol [3]

b) List the following compounds in order of decreasing wavenumber of the C = O absorption band. [3]

i) 

ii) 

iii)