RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

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

SECOND YEAR (BATCH 2016-19)

Date : 19/05/2018 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm Paper : IV [Gr-A] Full Marks : 40

[Use one Answer Book for Unit I and another Answer Book for Unit II & III]

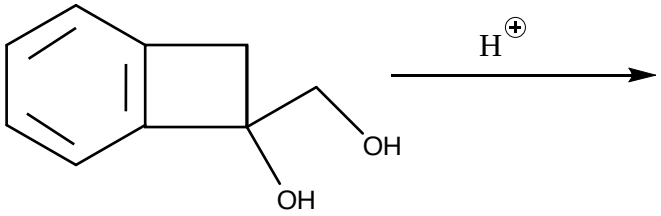
(Attempt one question from each Unit)

Unit I

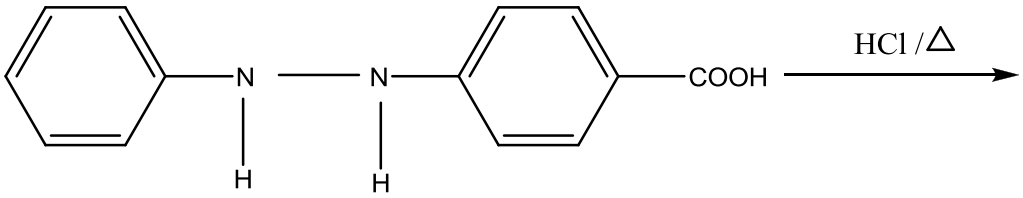
[15 marks]

1. a) Complete the following reactions with plausible mechanism: 2 + 2

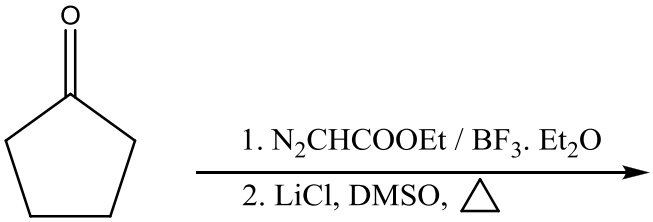
(i)



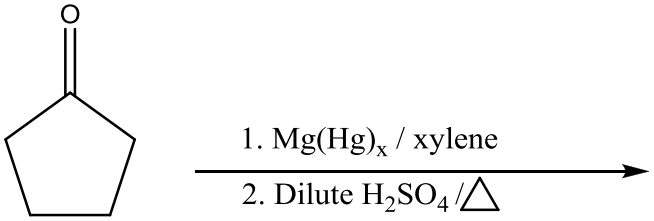
(ii)



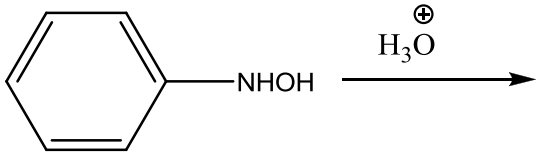
b) Explain the following reaction with mechanism along with the product: 2



c) Complete the following reaction with plausible mechanism: 2

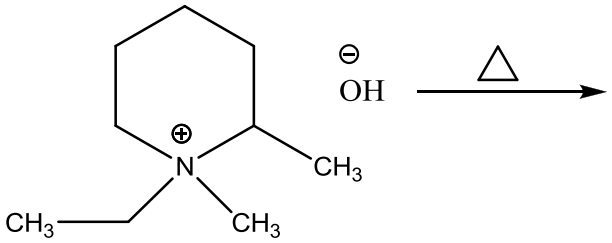


d) Complete the following: (show the mechanism) 2

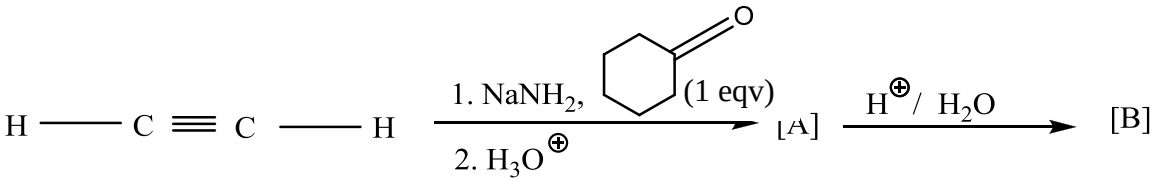


e) The diazocoupling reaction with phenol should be carried out at pH = 9.00. What will happen if this reaction is carried out at pH > 10? Why is the diazocoupling reaction with aromatic tertiary amine carried out at pH = 5.6? 3

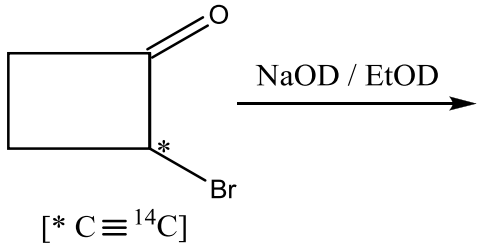
f) Complete the following reaction along with mechanism: 2



2. a) Identify [A] and [B] in the following reactions. Give mechanism for formation of [B] from [A]. 3

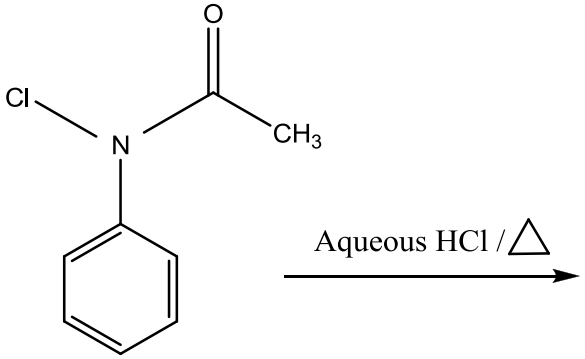


b) Predict the product with plausible mechanism: 2



[* C ≡ ^{14}C]

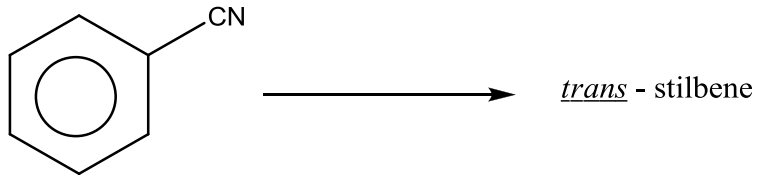
c) Complete the following reaction with mechanism: 2



d) How can you prepare allyl cyanide and allyl isocyanide separately from allyl alcohol? 2

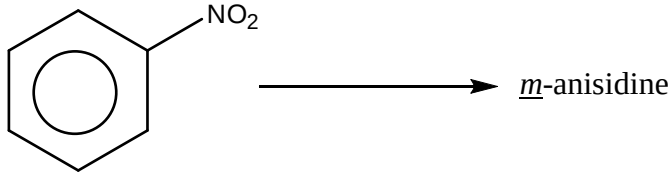
e) Carry out the following conversions: 2+2

(i)



trans - stilbene

(ii)



m-anisidine

f) Identify [C] and [D] in the following reactions (No mechanism needed): 2

$$PhCH_2NH_2 \xrightarrow[2.\ NaNO_2 / dil.\ HCl]{1.\ ClCO_2Et} [C] \xrightarrow{NaOH / H_2O} [D]$$

Unit II [13 marks]

3. a) Consider the following concentration cell with transference,
$Pt|H_2$ (g, 1 atm) | HCl (aq, a_1) ⋮ HCl (aq, a_2) | H_2 (g, 1 atm) |Pt find out the expression for the emf of the cell. 4

b) Depict the cell that corresponds to the reaction, Ag^+ (aq)+Cl^- (aq) ⇆ AgCl (s). Calculate the equilibrium constant for the reaction at 25°C. 3
Given: $E^0_{Ag^+/Ag} = 0.799V;\ E^0_{Cl^-/AgCl/Ag} = 0.222V$

c) At 25°C in a saturated solution of $BaSO_4$, Ba^{2+} and SO_4^{2-} ions take 151 seconds and 121 seconds respectively to cover a distance of 1 cm across a potential difference of 10 volts. The solubility product of $BaSO_4$ is 10^{-10}. The conductance of the solution is 2.2×10^{-6} ohm^{-1} in a cell of which the conductance of water is 0.8×10^{-6} ohm^{-1}. If in the same cell, the conductance of 0.01(N) KCl solution be 1.4×10^{-3} ohm^{-1}, what would be the specific conductance? 4

d) Arrange the following electrolytes in increasing order of their λ_m^0 in water, HCl, KCl and NaOH, with proper explanation. 2

4. a) Given the cell
$Pt|Cl_2$ (g, 1 atm) | NaCl (0.1 M) | Nacl (0.01 M) | Cl_2 (g, 1 atm)| Pt
(i) Neglecting the liquid junction effects, write down the net cell reaction and the thermodynamic EMF of the cell at 25°C.
(ii) Including the liquid junction effects, write the net cell reaction per Faraday. If t_+ is 0.39, calculate the EMF of the cell with transference and the liquid junction potential, ε_j. 2+4

b) Construct a reversible electrochemical cell in which the following overall reaction takes place:
H_2(g, 1 bar)+2AgCl(s) ⇌ 2HCl (a=0.1)+2Ag(s).
If E_{cell} = 0.2812 V at 25°C, and $\partial E / \partial T\ _P = -1.8 \times 10^{-4} VK^{-1}$, calculate (i) $E^0_{AgCl(s)/Cl^-,Ag(s)}$ and (ii) ΔG^o, ΔH^o and ΔS^o for the above cell reaction at 25°C. 2+3

c) How can a concentration cell be used to determine the valency of mercurous ion? Explain 2

Unit III [12 marks]

5. a) The 1s wavefunction for the hydrogen atom is $\phi = \frac{1}{\pi a_0^{3\ \frac{1}{2}}} e^{-r/a_0}$

Calculate the probability of the electron being within a distance of a_0 (the first Bohr radius) from the nucleus. 4

b) Verify that the function $Ae^{-Bx^2/2}$ is an eigenfunction of a linear harmonic oscillator with $B = \frac{\sqrt{mk}}{\hbar}$. 3

c) For the simple harmonic oscillator, the ground state function $\Psi_0 = C_0 e^{-\alpha x^2/2}$ and the 2nd excited state function $\Psi_2 = (C_0 + C_2 x^2)\ e^{-\alpha x^2/2}$

where the recursion relation is $C_{n+2} = \frac{2\alpha(n-\nu)}{(n+1)(n+2)} C_n$ with 'α' being the molecular parameter. Show that the two functions are orthogonal. 3

d) What is the physical origin of quantization for a harmonic oscillator? 2

6. a) For a harmonic oscillator at 300K, the population of the 1st excited state relative to the ground state is found as 6.4×10^{-5}, following the Boltzmann distribution law

$$\frac{n_1}{n_0} = e^{-\Delta\epsilon_1 / K_B T}$$

'n' being the population of the respective levels and $\Delta\in$ being the energy dif. of the levels (above mentioned).

(i) What is the 'zero point energy'?

(ii) If the force constant for this harmonic oscillator is found as 4.09×10^5 dyn/cm, then calculate the reduced mass of the oscillator. 2+2

b) Show that the most probable value of the radial distance, r_{mp}, in a 1s state of the hydrogen atom is a_0 (the first Bohr radius). 3

c) Show that the total probability density of the 2p orbitals is spherically symmetric by evaluating $\sum_{m=-1}^{1} \psi_{2lm}^2$. Given that 3

$$\psi_{2lm} = \begin{cases} \psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta \\ \psi_{21\pm1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\phi} \end{cases}$$

d) For a hydrogen like atom the radial function of 1s orbital has a finite value at $r = 0$, but the radial distribution function is zero at the origin – explain. 2

——— × ———