RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2019

SECOND YEAR (BATCH 2018-20)

Date : 16/05/2019 **CHEMISTRY (Honours)**

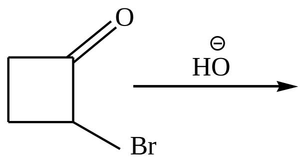
Time : 11.00 am – 1.00 pm **Paper : IV [Gr-A]** Full Marks : 40

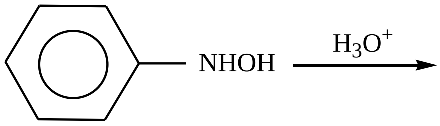
[Use one Answer Book for Unit I and another Answer Book for Unit II & III]

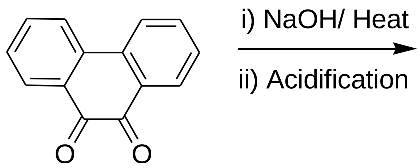
(*Attempt one question from each Unit*)

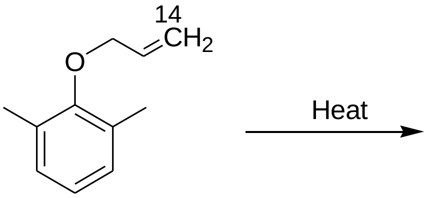
Unit I [15 marks]

1. a) Predict the product of the following reaction. Give mechanism in each case. [2×4]

(i) 

(ii) 

(iii) 

(iv) 

b) Alkaline hydrolysis of C_6H_5CN affords the salt of an acid but in the presence of H_2O_2 an amide is formed. Explain. [2]

c) Explain the following statements with proper justification. [4]

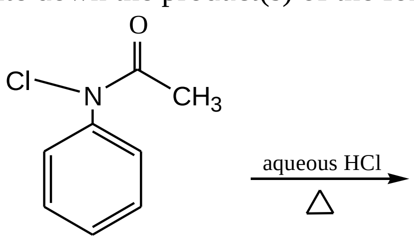
i) 3,3-Dimethyl-2-bromobutane, $Me_3CCH(Br)Me$, undergoes S_N1 hydrolysis with rearrangement whereas its phenyl analogue, $Me_3CCH(Br)Ph$, undergoes hydrolysis without rearrangement.

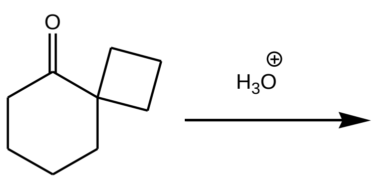
ii) Hofmann, Lossen, Curtius and Schmidt rearrangement are mechanistically similar.

d) Comment on the choice of phthalimide in the preparation of pure primary amine by Gabriel's method. [1]

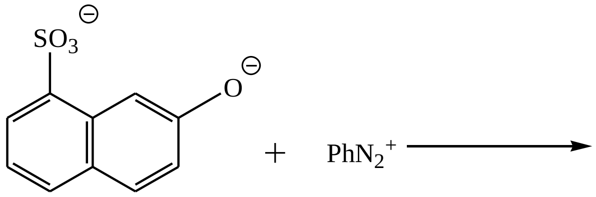
2. a) Two isomeric α-chloroketones having the molecular formula C_9H_9ClO when treated separately with aqueous NaOH, give the sodium salt of β-phenylpropionic acid. Explain with mechanism. [3]

b) Write down the product(s) of the following reactions with proper mechanism. [2×2]

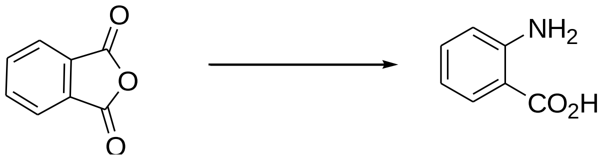
(i) 

(ii) 

c) Predict the product of the following reaction and write the mechanism. Comment on the rate determining step and pH of the reaction medium. [2]



d) Carry out the following transformation with mechanistic detail. [2]



e) Explain what happens when — [2×2]

i) Diazoaminobenzene is treated with dilute HCl.

ii) Cyclopentanone is treated with concentrated H_2SO_4.

Unit II [13 marks]

(Take T = 298 K and P = 1 atm, if not mentioned)

3\. a) The specific conductance of pure water at 30°C is 38.4×10^{-9} S cm^{-1}. The $\lambda_m^0(H^+)$ and $\lambda_m^0(OH^-)$ are 315 S cm^2 mol^{-1} and 173.8 S cm^2 mol^{-1}, respectively. Calculate the ionic product of water. Is this water alkaline or acidic with respect to water at 25°C (pH = 7). (1 lit of water weighs 998.5 kg at 30°C) [2]

b) Show that the metal-metal ion half-cell potential $E_{Ag+/Ag}$ is related to corresponding metal-insoluble salt-anion half-cell potential, $E_{X^-/AgX/Ag}$ through the relation — [3]

$$E^{\mathbf{o}}_{\mathbf{X^-/AgX/Ag}} = E^{o}_{\mathbf{Ag+/Ag}} - \frac{2.303RT}{F}\, pk_{\mathbf{SP}}(AgX)$$

[where X^- is the halide ion (Cl^-, Br^-, I^-)]

If K_{sp} (AgCl) > K_{sp} (AgBr)> K_{sp} (AgI), then arrange the potential $E^{o}_{\mathbf{X^-/AgX/Ag}}$ (where $X^- = Cl^-$, Br^-, I^-)

c) Explain the term ‘electrophoretic effect’ in context to electrical conductance of an ion in aqueous solution. [2]

d) $$Pt\,|\,H_2(g, 1\text{ atm})\left|\begin{array}{l} HA_2\,(pk_a = 6) \\ C_1 \text{ at } 298K \end{array}\right|\left|\begin{array}{l} HA_1\,(pk_a = 4) \\ C_1 \text{ at } 298K \end{array}\right| H_2(g, 1\text{ atm})\,|\,Pt$$

Calculate the e.m.f of the above cell at 25^{o}C. What are the assumption(s) which must be made in order to solve the problem? [4+2]

4\. a) How do you explain the experimental observation that H^+ conductance increases with increase in temperature? [2]

b) Specific conductance of a sample of distilled water is $5.5 \times 10^{-6} Sm^{-1}$. Also given :

$\lambda^o(H^+) = 3.498 \times 10^{-2} S\ m^2\ mol^{-1}$

$\lambda^o(OH^-) = 1.980 \times 10^{-2} S\ m^2\ mol^{-1}$

density of water = 1.0 gcm^{-3}

Find (i) degree of dissociation (α) of water and ii) the ionic product of water (K_w). [4]

c) Why the equivalent conductance at infinite dilution cannot be obtained by plotting equivalent conductance is $\sqrt{c}$ for weak electrolytes? [3]

d) $Pt|Cl_2$ (P = 0.9 atm) $|$NaCl (aq) $|$ Cl_2 (P = 0.1atm)|Pt

Will the cell reaction be spontaneous as written? Explain. [2]

e) Briefly explain the nature of potential variation during a potentiometric titration of Fe(II) solution with $KMnO_4$. [2]

Unit III [12 marks]

5. a) Justify that the harmonic oscillator wave functions, given below, are orthogonal to each other -

$$\psi_0(x) = \left(\alpha/\pi\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(4\alpha^3/\pi\right)^{1/4} x.e^{-\alpha x^2/2}$$

where the terms have their usual meaning. [2]

b) Zero point energy of a simple harmonic oscillator does not violate Heisenberg's uncertainly principle. Justify. [2]

c) Use the function, $\psi = \frac{1}{\sqrt{2\pi}} e^{iM\phi}$ to determine the energy eigenvalue and the expectation value for a particle in a ring of radius r. [3]

d) Find the average value of $\frac{1}{r}$ for the 1s electron of an H atom and hence obtain the average potential energy. Given, $\psi_{1s} = \sqrt{\frac{1}{\pi}} e^{-r}$. [3]

e) The 2s wave function for the hydrogen atom is $\psi_{2s} = N\left(2 - r/a_0\right)e^{-r/2a_0}$, where N is a constant, r is the distance from the nucleus and a_0 is the Bohr radius. Find the distance from the nucleus, in terms of a_o, at which the radial probability density shows a maxima. [2]

6. a) Draw a qualitative plot of probability distribution for ground and 1st excited state wave function for harmonic oscillator in same graph. Comment on satisfying the Bohr's correspondence principle for quantum harmonic oscillator. [3]

b) Justify that the radial equation of H atom has an eigenvalue $-\frac{1}{2}$ a.u. Given that, $R_{10}(r) = 2e^{-r}$ and radial equation is $\left[-\frac{1}{2}\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\right\} - \frac{l(l+1)}{r^2} - \frac{1}{r}\right]R_{nl}(r) = E_n R_{nl}(r)$ [3]

c) The 1s wave function for the hydrogen is $\psi_{1S} = \left(\pi a_0^3\right)^{-1/2}.e^{-r/a_0}$ where a_0 is the Bohr radius. Calculate the probability of finding the electron within a distance a_o from the nucleus.

Given, $\int_0^{\alpha} x^n e^{-bx} dx = \frac{n!}{b^{n+1}} : n > 1$ [3]

d) Define radial distribution function (rdf) and give the plot of rdf corresponding to the following wave function against (r/a_0), ψ -

$$\psi = A\left(2a_0 - r\right)e^{-r/2a_0}$$ [3]

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