

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [BATCH 2015-18]

B.A./B.Sc. FOURTH SEMESTER (January – June) 2017

Mid-Semester Examination, March 2017

Date : 15/03/2017

Time : 11 am – 1 pm

CHEMISTRY (Honours)

Paper : IV

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

[Attempt one question from each Unit]

Unit – I

[8]

1. a) Define ionic mobility. [1]
b) Discuss the conductometric method for finding the value of dissociation constant of a weak monobasic acid. [4]
c) Consider a cell with cell reaction $\text{Zn} + 2\text{AgCl(s)} = \text{ZnCl}_2(0.555\text{m}) + 2\text{Ag(s)}$. The EMF of the cell is 1.015 volt and its temperature coefficient of EMF is $-4.02 \times 10^{-4} \text{ volt K}^{-1}$. Find out ΔG , ΔS and ΔH of this reaction. [3]
2. a) Construct the cells having the following cell reactions
(i) $\text{NiO(s)} + \text{Fe(s)} = \text{Ni(s)} + \text{FeO(s)}$, (ii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell)$ [4]
b) At 25°C, ΔG of formation of $\text{H}_2\text{O}(\ell)$ is -237.244 kJ/mol and that of its ionization is 79.709 kJ/mol . Calculate the EMF of the cell $\text{H}_2(\text{g}, 1\text{atm}) | \text{H}^+ || \text{OH}^- | \text{O}_2(\text{g}, 1\text{atm})$.
The heat of formation of $\text{H}_2\text{O}(\ell)$ is 285.864 kJ/mol and its heat of ionization is 56.905 kJ/mol . Calculate the value of the temperature coefficient of EMF of this cell. [4]

Unit – II

[8]

3. a) Starting with the condition for equilibrium between the solvent in solution in the liquid state and the same in pure solid state prove that the elevation of boiling point for a solvent due to dissolution of solute is proportional to the molality of the solute. [4]
b) Explain with reason the order of freezing point in the following solutions :
 0.1 N NaCl , 0.1 N MgSO_4 , $0.1 \text{ N CH}_3\text{COOH}$ and 0.1 M sugar [4]
4. a) i) Define 'Ideal solution'. [2]
ii) Show that for such a solution $\mu_i = \mu_i^0 + RT \ln x_i$. [3]
iii) How would you express the chemical potential for a real solution, with a mole fraction x_i ? [2]
b) Why of all the units molality is generally used to describe the properties of solutions like elevation of boiling point or depression of freezing point. [1]

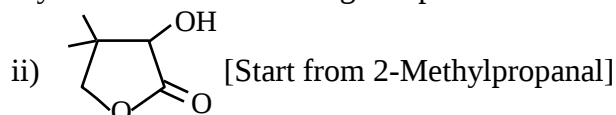
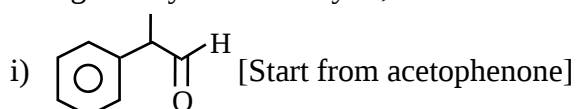
Group – B

[Attempt one question from each Unit]

Unit – I

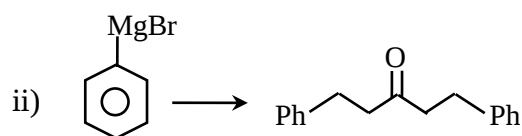
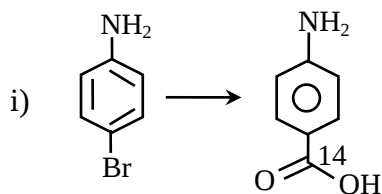
[8]

5. a) Using retrosynthetic analysis, outline an efficient synthesis of the following compounds [4]



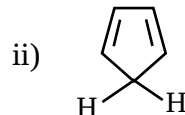
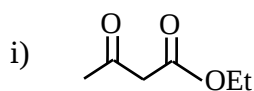
b) Carry out the following conversions :

[4]



6. a) Give the product(s) of reaction of MeMgI (one mole) with each of the following compounds :

[1]

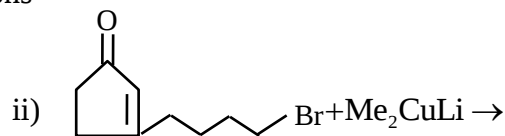
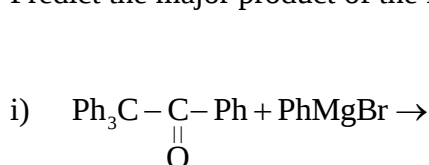


b) What happens when di-isopropyl ketone is allowed to react with Me₂CHMgBr? Give mechanism. Do you expect the same product if di-isopropyl ketone is allowed to react with Me₂CHLi? Explain.

[3]

c) Predict the major product of the following reactions

[2×2]

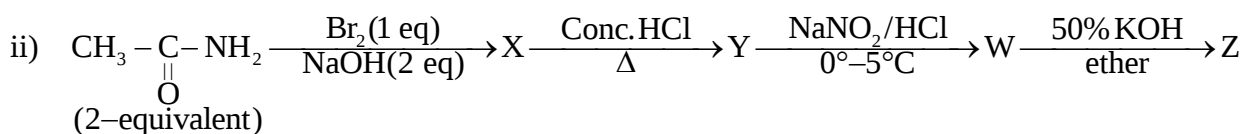
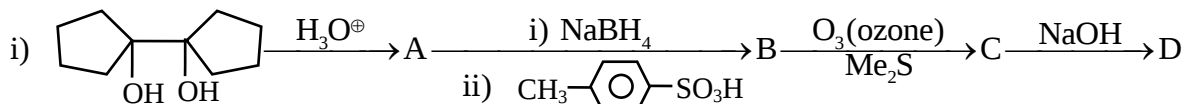


Unit – II

[8]

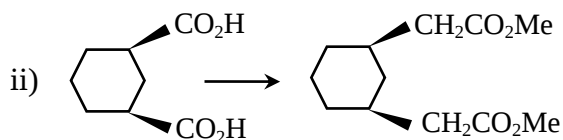
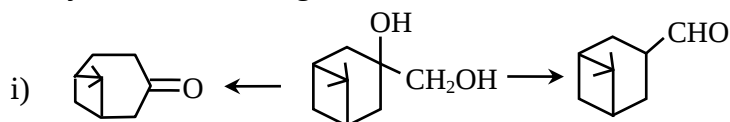
7. a) Complete the following reaction sequence.

[2×2]



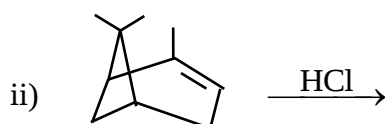
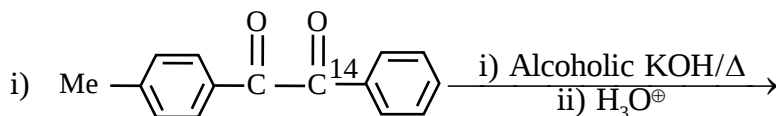
b) Carry out the following conversions.

[2×2]



8. a) Predict the product of the following reaction with proper mechanism

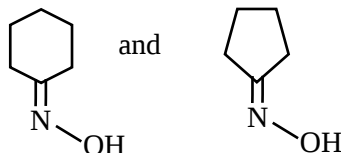
[2×2]



b) Dienone phenol rearrangement is considered as reverse pinacol rearrangement —Explain it.

[2]

- c) Which one of the following oxime undergoes Beckmann rearrangement in faster rate and why? [2]



Group – C

[Attempt one question from each Unit]

Unit – I

[9]

9. a) Suggest a reaction where B-alkane bond forms. [2]
 b) Write down the structure of X and Y of the following reaction : [2]

$$\text{NH}_4\text{Cl} + \text{BCl}_3 \xrightarrow[\text{PhCl}]{\Delta} [\text{X}] + \text{other product and } \text{X} + \text{NaBH}_4 \xrightarrow{\Delta} [\text{Y}] + \text{other product}$$

 c) Chlorine dioxide, though an odd electron molecule, does not dimerise. Explain. [2]
 d) Perchloric acid on hydration produces $[(\text{H}_2\text{O})_n\text{H}]^+\text{ClO}_4^-$ while the product of periodic acid on hydration is quite different. Explain. [3]
10. a) Starch forms blue colour with iodine in presence of iodide ion. Explain. [2]
 b) If phenol is treated separately with (i) ICl vapour and (ii) with ICl in CCl_4 solution, products are different. Explain. [3]
 c) Molten GaCl_2 conducts electricity. Why? [2]
 d) Proposed balanced chemical equation (or indicate no reaction) for reactions between (i) $\text{Et}_3\text{AsBCl}_3$ and $\text{Et}_3\text{NGaCl}_3$ in toluene. (ii) $\text{Et}_3\text{NGaCl}_3$ and GaF_3 in toluene. Explain each with proper reason. [2×1]

Unit – II

[9]

11. a) How are the two peroxosulfuric acids prepared? What are their structures? [5]
 b) i) Assign with experimental support, the oxidation state of Tl in TlI_3 .
 ii) Predict the probable products of the following reactions, and write the balanced chemical equations. [2]
 c) BF_3 and NaF (excess) in acidic aqueous solution. [2]
12. a) Explain with reasons :
 i) Formula of telluric acid is H_6TeO_6 but analogous H_6SO_6 is not formed.
 ii) Oxygen is a gas, but sulphur is solid at room temperature. [5]
 b) Predict the probable products of the following reactions and write the balanced chemical equations. [2×2]
 i) BCl_3 and NaCl (excess) in acidic aqueous solution.
 ii) BBr_3 and HNMe_2 (excess) in a hydrocarbon solvent.

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