RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

FIRST YEAR [BATCH 2017-20]

B.A./B.Sc. SECOND SEMESTER (January – June) 2018

Mid-Semester Examination, March 2018

Date : 14/03/2018 — **CHEMISTRY (Honours)**

Time : 11 am – 1 pm — Paper : II — Full Marks : 50

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

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

<u>Group – A</u>

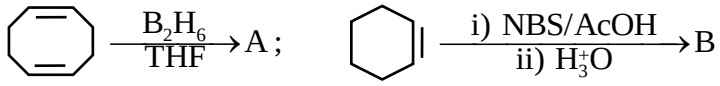
[16 marks]

<u>Unit - I</u>

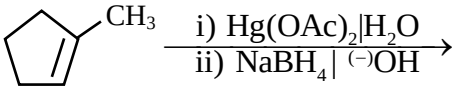
1. a) Arrange the following compounds in the order of increasing heat of hydrogenation with proper reason : 1 – butene, E – 2 – butene, Z – 2 – butene [2]

   b) Bromine addition on trans – 1 – phenyl propene yielded 70% antiproduct where trans – 2 – butene yielded 100% anti product. — Explain. [2]

   c) Identify product of following reactions (no mechanism required.) [2]

   d) Write down the product with proper mechanism [2]

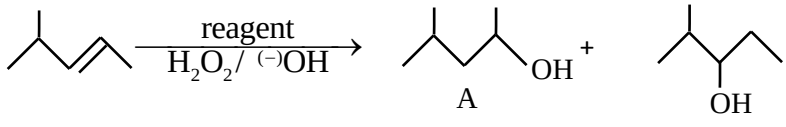
   

2. a) HBr addition to C – C double bond via Markonikoff rule is a regioselective reaction. —Explain with one example. [2]

   b) Write down the products in the following reactions with proper reason. [2]

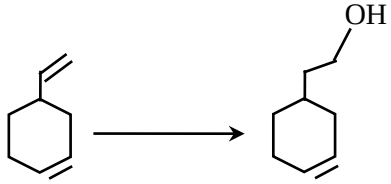
   

   c) Explain the different product ratio is with the use of different reagents. [2]

reagent	A	B
B_2H_6	57%	43%
$Si\alpha_2BH$	97%	3%

   d) Write down the proper reagents for the following conversion. [1]

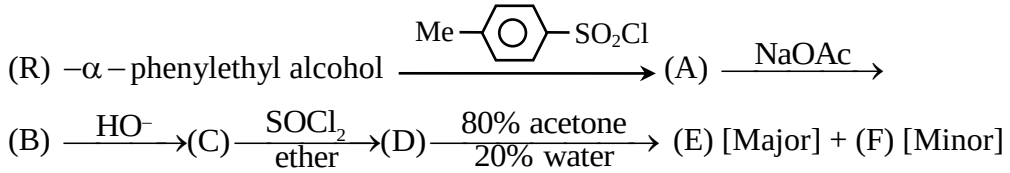
   

   e) Write down the product for the following reaction. [1]

   $CH_2 = CH - \overset{(+)}{N}Me_3\overset{(-)}{I} \xrightarrow{HI} ?$

Unit - II

3. a) Trace the following interconversions by appropriate 3D formulae. [3]

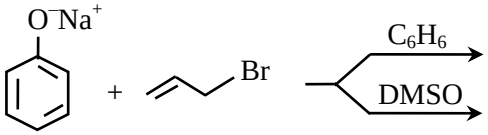


b) Which one of the following is a better nucleophile? Justify your answer. [3]

i) LiCl or $Bu_4\overset{+}{N}Cl^-$ in acetone

ii) KOH or H_2O_2 in H_2O

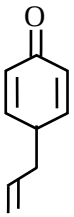
c) Predict the major product of the following reaction. Explain your answer. [2]



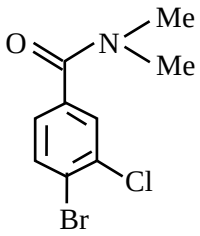
4. a) Explain with is meant by primary kinetic isotope effect. Give the mechanism of oxidation of 2-propanol with chromic acid. Indicate whether kinetic isotope effect is operative here. Cite a labelling experiment and its result in favour of your answer. [4]

b) Give the IUPAC nomenclature of the following compounds : [2]

i)



ii)



c) Compare the S_N^2 reactivity of ROTs and ROTf. [1]

d) 2, 6–Di–t–butylpyridine is a better scavanger than pyridine. —Explain. [1]

Group – B [18 marks]

Unit - III

5. a) Applying VSEPR model, predict and justify the structure of BrF_4^- and XeO_2F_2. [3]

b) Starting with gaseous NH_3 and HCl, construct a Born-Haber cycle leading to the formation of solid NH_4Cl. [2]

c) Derive the limiting value of radius ratio in tetrahedral co-ordination. [3]

d) Lithium perchlorate is hydrated, comment. [1]

6. a) The heat of formation of CaCl is –182 KJ/mole. Calculate the heat of formation of $CaCl_2$ from the given data and compare the stability of CaCl and $CaCl_2$. [3+1]

Heat of Sublimation of Ca = +201 KJ/mole

Heat of dissociation of Cl_2 = +242 KJ/mole

$I.E_1$ of Ca = +590 KJ/mole $I.E_2$ of Ca = +1146 KJ/mole

E.A of CI = –349 KJ/mole

Lattice energy of $CaCl_2$ = –2280·4 KJ/mole

b) $NaClO_4$ is about 1000 times as soluble as $KClO_4$ in water. Explain with reason. [2]

c) Calculate the lattice energy of CaO using the following data : Madelung constant = 1·75, interionic distance = 2·4Å. [2]

d) Anhydrous $AlCl_3$ is convalent while $AlCl_3 \cdot 6H_2O$ is ionic. [1]

Unit - IV

7. a) How can you extract lithium from one of its important ore? Write down the reactions involved in the process. [4]

b) When burnt in air, lithium forms Li_2O, sodium given Na_2O_2 but other alkali metals form superoxides. —Explain. [3]

c) Discuss the structure of basic beryllium acetate. [2]

8. a) Explain the following : [2+2]

i) Solubility of BeO increases in aqueous $BeSO_4$ solution.

ii) Magnesium does not impart any colour to flame.

b) Compare the stability of complexes of the alkali metal ions with 18–crown–6 ether and explain the variation. [3]

c) Discuss the structure of beryllium chloride in vapour state and in solid state. [2]

Group – C

[16 marks]

Unit - V

9. a) Starting with Clausius inequality show that at constant temperature and pressure for any spontaneous process $\Delta G < 0$. [3]

b) Write down the thermodynamic definition of entropy. [2]

c) For a Carnot cycle $\frac{q_h}{T_h} + \frac{q_l}{T_l} = 0$. Prove that for a reversible cycle that uses any arbitrary number of reservoirs, $\sum_i \frac{q_i}{T_i} = 0$. [3]

10. a) Starting with Clausius inequality show that the entropy of the universe is increasing. [3]

b) You are being asked to increase the efficiency of a Carnot engine. This can be done either by increasing the temperature of the source or by decreasing the temperature of the sink. Which of the two ways will be more effective? Explain. [2]

c) Give proper arguments to arrive at the statistical definition of entropy $S = k\ln(\omega)$. Where ω is the number microstates corresponding to a given macrostate. [3]

Unit - VI

11. a) If the reaction : $A \rightarrow$ Product; is zero order with respect to A, derive the integrated rate law and draw the graph of [A] versus time. [2]

b) What is the method of initial rate and why is it used in chemical kinetics? [2]

c) When the concentration of A in the simple reaction $A \rightarrow B$ was changed from 0·502 mol/dm^3 to 1·002 mol/dm^3, the half life dropped from 51 seconds to 26 seconds at 26°C. What is the order of the reaction? [2]

d) A sampling milk kept at 25°C is found to sour 40 times as rapidly as when it is kept at 4°C. Estimate the activation energy for the souring process. [2]

12. a) What is steady state approximation and when do we employ this approximation? [2]

b) Explain why the reactions of higher molecularity are rare. [2]

c) The reaction $A + 2B + C = D$ occurs by the mechanism

$A + B \rightleftharpoons X$ (very rapid equilibrium)

$X + C \rightarrow Y$ (slow)

$Y + B \rightarrow D$ (very fast)

Derive the rate law for the equation. [2]

d) A drug product is known to be ineffective after it is decomposed 25%. After 20 months the original concentration was dropped from 5·0 mg/ml to 4·2 mg/ml. Assuming that the decomposition is first order, what should be the expiration time on the label? [2]

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