

# RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

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

FIRST YEAR (BATCH 2017-20)

CHEMISTRY (Honours)

Date : 19/05/2018

Time : 11.00 am – 1.00 pm

Paper : II [Gr-A]

Full Marks : 40

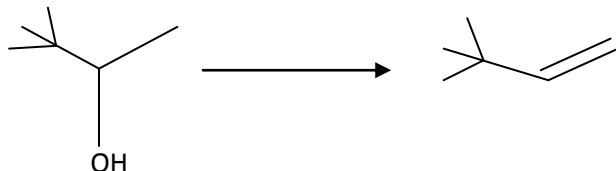
[Use one Answer Book for Unit I and another Answer Book for Unit II & III]

(Attempt one question from each Unit)

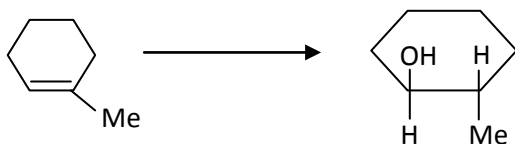
## Unit I

[15 marks]

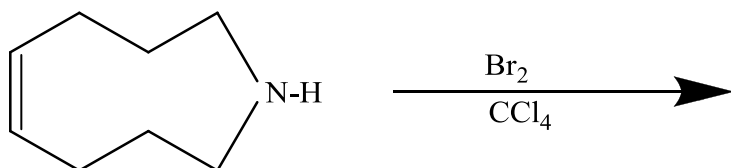
1. a) Active threo isomer of 1,2-diphenyl-1-bromopropane reacts 10 times more rapidly than the active erythro isomer, when both are treated with EtONa base to give olefin product. Give mechanism and explain the higher rate of the threo isomer. 3
- b) When  $\text{Cl}_2\text{C} = \text{CHCl}$  is treated with NaOD in  $\text{D}_2\text{O}$  then at the end of the reaction  $\text{Cl}-\text{C}\equiv\text{C}-\text{Cl}$  is formed. If the reaction is stopped at the half complete state, the recovered alkene is found to contain deuterium. — Explain mechanistically. 3
- c) Transform: 1



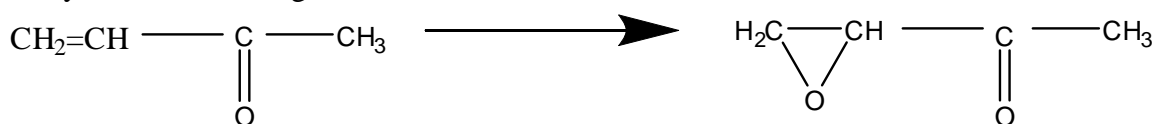
- d) Predict the major product of the reaction of  $\alpha, \alpha$ -dimethylallyl chloride with sodium thiophenoxide in ethanol. Explain. 2
- e) Carry out the following conversions: 1½
- (i) Cis-2-butene  $\rightarrow$  trans-2-butene 1½
- (ii)



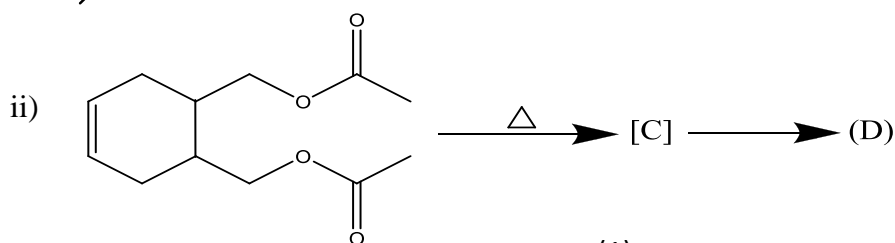
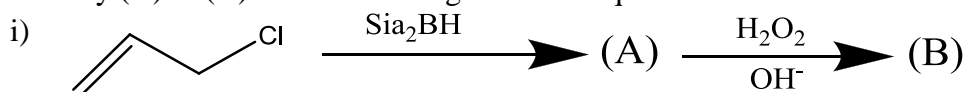
- f) Write down the product and explain its formation for the following reaction. 2



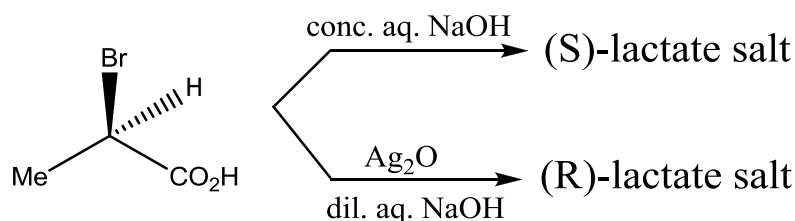
- g) Carry out the following conversions: 1



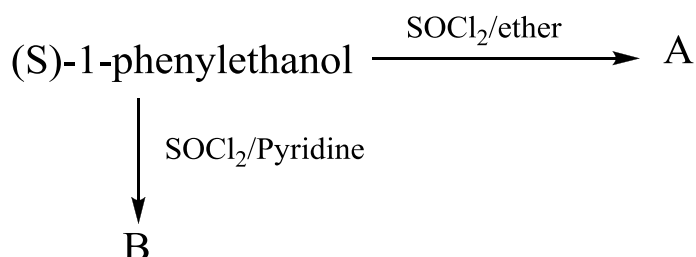
2. a) Identify (A) to (D) in the following reaction sequence: 2



- b) Write down the structure of ozonides formed when 2, 3-dimethyl-2-butene was subjected to ozonolysis in the presence of HCHO. Give mechanism of the ozonide formation. 3
- c) Between  $\text{NH}_3$  and  $\text{NH}_2\text{-NH}_2$  which one is the better nucleophile in bimolecular substitution reaction? Give explanation. 2
- d) Account for the following observations: 3



- e) Explain the following reactions with plausible mechanism and give the structure of A and B. 3



- f)  $\text{Cl}^-$  ion of  $\text{Bu}_4\text{N}^+\text{Cl}^-$  in acetone is a better nucleophile than that of LiCl in the same solvent. Explain. 2

## Unit II

[13 marks]

3. a) Show that the condition for spontaneity of a process at constant T, V is given as  $\Delta A_{T,V} < 0$ . 3
- b) Show that  $\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$  (employing the appropriate form of the thermodynamic equation of state). Now find out the value of  $\left(\frac{\partial C_V}{\partial V}\right)_T$  for a van der Waals gas. 2+2
- c) Draw T-S diagram for an ideal gas changing state by the cyclic process as given below: 2
- Step1– Reversible adiabatic expansion
  - Step2– Reversible isobaric expansion
  - Step3– Reversible adiabatic compression
  - Step4– Reversible isobaric compression to the initial state
- d) A gas may be cooled by Joule-Thomson expansion below the inversion temperature or by reversible adiabatic expansion. Which one is more effective for cooling a real gas? 2
- e) Calculate  $\Delta G$  for the isothermal (300K) expansion of an ideal gas from 5000 kPa to 200 kPa. 2
4. a) Kelvin-Planck statement and Clausius statement for the second law of thermodynamics are equivalent – justify. 3
- b) Efficiency ( $\eta$ ) of the Carnot cycle can be increased either by increasing temperature of the hot reservoir or by decreasing the temperature of the cold reservoir. Which one is more effective in order to increase the value of  $\eta$ ? 2
- c) Water has  $V_m = 18 \text{ cm}^3/\text{mol}$ ,  $C_{p,m} = 75.3 \text{ J/Kmol}$  and  $\alpha = 2.07 \times 10^{-4} \text{ K}^{-1}$ . Compute the (i) change of entropy and (ii) decrease in temperature that occurs, if water at 298 K and 1000 atm pressure is brought reversibly and adiabatically to 1 atm pressure. Assume  $k = 0$ . 3

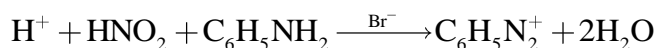
- d) If  $\Delta G = a + bT + cT^2$  (a, b, c are three temperature independent constants) then find out the expression of  $\Delta H$  by deriving Gibbs-Helmholtz equation:  $\left[ \frac{\partial(\Delta G/T)}{\partial(1/T)} \right]_p = \Delta H$ . 3
- e) Show that  $dH = C_p dT + (V - TV\alpha)dP$ , where  $\alpha$  is the coefficient of thermal expansion, and other terms have their usual significance. 2

### Unit III

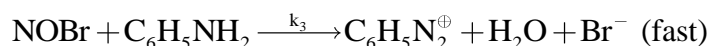
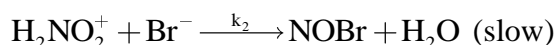
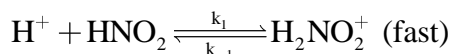
[12 marks]

5. a) Show that the ratio of  $t_{0.5} / t_{0.75}$  of any  $n^{\text{th}}$  order reaction ( $n \neq 1$ ) with identical initial concentration of the reactant can be written as a function of 'n' alone. 3
- b) Pre-exponential factor in Arrhenius equation should be temperature dependent – justify this from the simple collision theory of reaction rate. 4
- c)  $E_1$  and  $E_2$  are the activation energy for the two different reactions ( $E_1 > E_2$ ). If the temperature for both the reactions are raised from  $T_1$  to  $T_2$ , then show that rate constant of the reaction 1 will be increased more than the rate constant of reaction 2. 3
- d) Write down the characteristics of a zero order reactions with one example. 2

6. a) For the  $\text{Br}^-$  catalysed aqueous reaction



the proposed mechanism is



Find out the rate law of the reaction using rate determining step as well as steady state approximation. 4

- b) Compare Collision theory and transition state theory. 2

- c) Show that in a consecutive reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ ,  $k_1 \gg k_2$  the  $[\text{B}]_{\text{max}}$  will appear at

$$t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}.$$

$$\text{Given } [\text{B}] = \frac{k_1[\text{A}]_0}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}).$$

3

- d) Define turn-over number for an enzyme catalysed reaction. How can you determine it by using Lineweaver Burk plot if the enzyme has single active site. 1+2

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