RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2017

SECOND YEAR [BATCH 2016-19]

Date : 12/12/2017 **CHEMISTRY (Honours)**

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

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

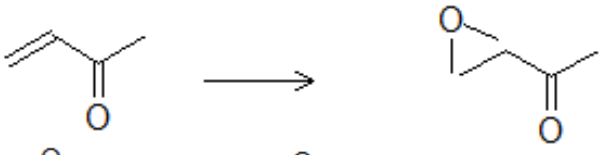
(Attempt one question from each Unit)

Unit I [15 marks]

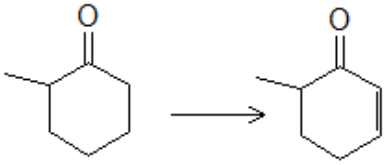
Answer **any one** question (1 or 2):

1. a) Complete the following conversion with proper reagents and mechanism. 2+2+2

i)

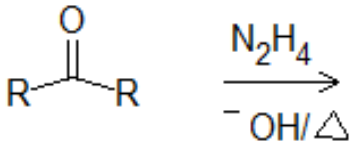


ii)

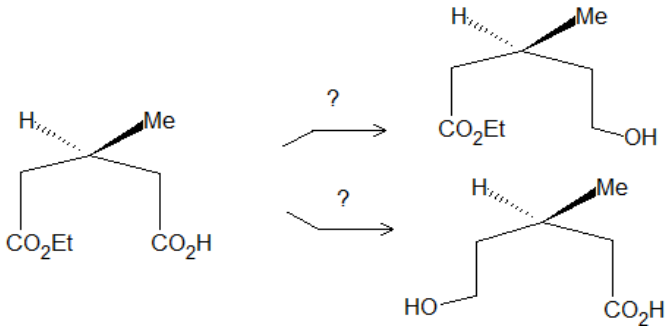


iii) Acetaldehyde to ethylacetate.

b) Write down mechanism for the following reactions: 2



c) Write the proper reagent for the following conversions: 2



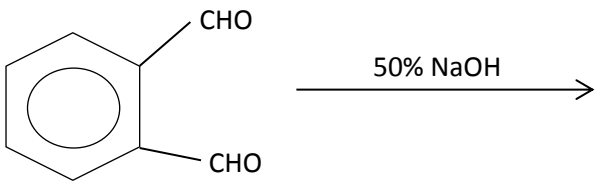
d) Suggest a mechanism for deprotection of dithioketals with $HgCl_2$. 2

e) Mesitoic acid does not undergo esterification under normal acid catalysed conditions– explain why? State the actual process of esterification in this case. 2

f) Write down the major product for the following reaction (no mechanism required): 1

$$CH_2=C=CH_2 \xrightarrow[(1eqv)]{dry\ HCl}$$

2. a) Write down the major product for the following reaction (no mechanism required): 1



[1]

b) Predict the products for the following reactions with proper mechanism: 2 + 2

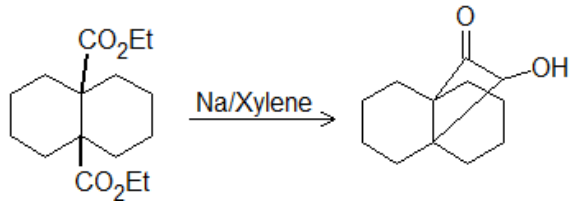
(i) $RCO_2Ag \xrightarrow[\Delta]{Br_2/CCl_4}$

(ii) $H_3C-C\equiv C-CH \xrightarrow[H_2O_2/NaOH]{Si\alpha_2BH/THF}$

c) α-chlorocarbonyl compounds are very good substrate for S_N2 process — explain. 2

d) "In Perkin reaction, salt of same carboxylic acid as that anhydride is taken". Justify the observation with an example. 2

e) Explain this following conversion with mechanics. 2



f) How can you convert: Hex-2-yne to meso-2,3-dibromohexane. 2

g) How can you convert: $CH_3CHO \rightarrow CH_3CDO$ 2

UNIT-II [13 marks]

3. a) Consider a reaction $A \rightarrow B+C$ that has reached equilibrium. What is the effect on the value of K_x if suddenly a gas which does not take part in the reaction is introduced into the reaction mixture (i) at constant pressure (ii) at constant volume. 3

b) Show that,

$$\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j s(j\neq i)} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j s\,(j\neq i)}$$

where the terms have their usual significance. 3

c) AT 2000 K and one bar, water vapour is 0.53% dissociated. AT 2100 K and one bar, it is 0.88% dissociated. Calculate the value of ΔH^o for the dissociation of water vapour at one bar, assuming the enthalpy of reaction is constant over the range from 2000 K to 2100 K. 3

d) The partition coefficient of an alkaloid between chloroform and water is 20, the alkaloid being more soluble in chloroform. Compare the weights of the alkaloid remaining in aqueous solution after 100 cm^3 containing 1 g has been shaken with,

(i) 100 cm^3 chloroform and,

(ii) two successive quantities of 50 cm^3 chloroform. 4

4. a) Discuss what effects are produced on the equilibrium position of the reaction

$$SO_2(g)+\frac{1}{2}O_2(g) \cap SO_3(g)$$

when,

(i) An inert gas of n_i moles is added keeping volume of the system constant,

(ii) An inert gas of n_i moles is added keeping pressure of the system constant. 3

b) Consider the two equations:

(i) $CO(g)+H_2O(g)=CO_2(g)+H_2(g)$ $\quad K_1 \quad \Delta G_1$

(ii) $CH_4(g)+H_2O(g)=CO(g)+3H_2(g)$ $\quad K_2 \quad \Delta G_2$

Also we have the equation which is the sum of the above two reactions

(iii) $CH_4(g)+2H_2O(g)=CO_2(g)+4H_2(g)$ $\quad K_3 \quad \Delta G_3$

Show that $K_3 = K_1K_2$ and $\Delta G_3 = \Delta G_1 + \Delta G_2$ 4

c) Consider the following gas phase reaction, 3

$N_2O_4(g) \cap 2NO_2(g)$

Show that the degree of dissociation is given by,

$$\alpha = \left[\frac{K_p}{K_p + 4P}\right]^{1/2}$$

What happens when $P \to 0$ and $P \to \alpha$.

d) State Le Chatelier principle and explain it from thermodynamic view point. 3

UNIT-III [12 marks]

5. a) Derive the operator equation $\frac{d}{dx}x^n = nx^{n-1} + x^n\frac{d}{dx}$ and then show that $\left[\frac{d}{dx}, x^n\right] = x^{n-1}$. 3

b) Show that eigenfunctions corresponding to a Hermitian operator having different eigenvalues are orthogonal to each other. What happens if two or more eigenfunctions have the same eigenvalues? 3

c) The terms state and energy level are not of same meaning Q.M. For the particle in a cubic box, consider the energy range $E < 15h^2/(8ma^2)$.

i) What are the states, which lie in this range?

ii) Write down the wave function for the highest possible energy state within this energy range. 2+1

d) Find the eigenfunctions and eigenvalues of the operation: 3

(i) d/dx ; (ii) $\int(\ )\,dx$

6. a) Calculate the maximum percentage change in wavelength due to Compton scattering for incident photons of wavelengths $1\overset{o}{A}$ and $10\overset{o}{A}$. What conclusion do you draw from these results? 3

b) Which of the following functions, when multiplied by a normalization constant, would be acceptable one dimensional wave functions for a bound particle? 3

(i) e^{-ax}, (ii) e^{-bx^2}, (iii) ie^{-bx^2}

a, b and positive constants and *x* goes from $-\alpha$ to $+\alpha$.

Given that, $\int_0^{\alpha} e^{-bx^2}dx = \frac{1}{2}\left(\frac{\pi}{b}\right)^{1/2}$, $b > 0$.

c) Show that if Ψ_1 and Ψ_2 are two eigenfunctions of the operator $\hat{A}$ corresponding to the dynamical variable *M*, with eigenvalues m_1 and $m_2 (m_1 \neq m_2)$, the state represented by $\Psi = c_1\Psi_1 + c_2\Psi_2$ is not an eigenstate of $\hat{A}$. Which state is then represented by Ψ . 3

d) At what value of *x* (in terms of *L*) the probability density of a particle enclosed in a 1D box of length extending from 0 to *L* will be 25% of the maximum value for *n* = 2 state? 3

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