RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2018

SECOND YEAR [BATCH 2017-20]

Date : 15/12/2018 **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]

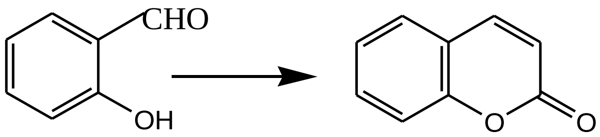
(*Attempt one question from each Unit*)

Unit I [15 marks]

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

1. a) Carry out the following transformations: 1.5×2

i)



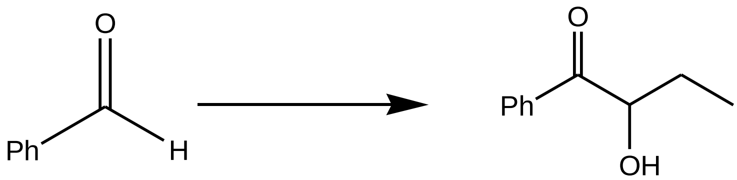
ii) $H—C \equiv C—H \longrightarrow Me—C \equiv C—CH_2—CH_2OH$

b) P-dimethyl aminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde, the condensation does occurs. Explain. 2

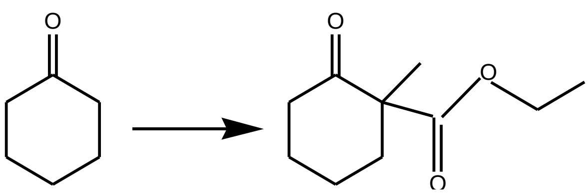
c) Explain why alkynes are less reactive than alkenes towards addition of Br_2. 2

d) Carry out the following conversions: 4

i)



ii)



e) Explain the following observations:

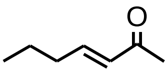
i) use of excess active methylene compound is not recommended in knoevenagel reaction.

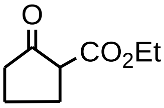
ii) on heating CH_3-CH=CH-CO_2H decarboxylates but R_3C-CH=CH-CO_2H does not. 1.5×2

f) Explain the observation that cyclopropanone forms a stable hydrate 1

2. a) Outline the synthesis of the following compounds as directed.

i) (By directed aldol)



ii) 

(By Dieckmann cyclisation using DEM) 2×2

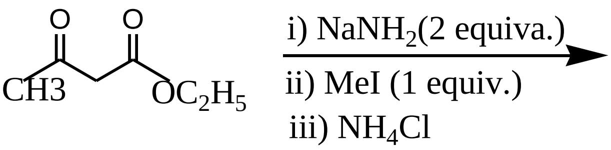
b) Carry out the following conversions:

i) $CH_3CH_2-C\equiv C-CH_2CH_3 \rightarrow \text{meso}-3,4-\text{dibromohexane}$

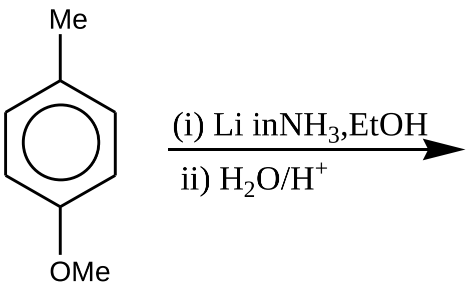
ii) $C_2H_5CH\equiv O \rightarrow C_2H_5CDO$ 1.5×2

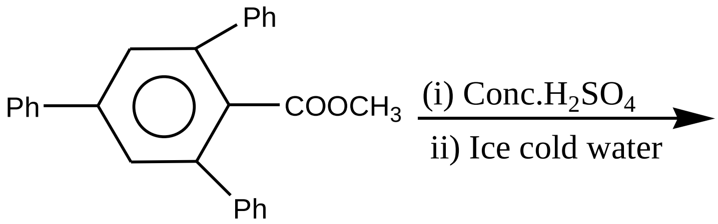
c) 2+2 cycloaddition between two alkenes is thermally forbidden but phtochemically allowed. Explain it based on FMO approach. 2

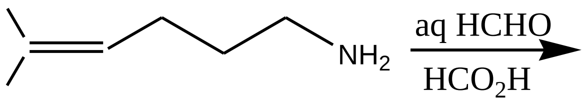
d) Write the product of the following reaction and explain its formation also.



e) Predict the product(s) of the following reactions and give possible meachansism. 3×2

i) 

ii) 

iii) 

UNIT-II [12 marks]

3. a) Write down the expression for the reaction quotient in terms of partial pressure at any arbitrary instant during the reaction and also the expression for free energy change (ΔG) in terms of standard free energy change (ΔG^o) and reaction quotient (Q_p). 2

b) How is the reaction quotient different from the equilibrium constant of a reaction (K_p)? 1

c) Does the quantity ΔG^o, for a particular equilibrium depend on the unit of concentration for a given standard state? 2

d) Show that for the following dissociation of dinitrogen tetroxide,

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

at moderately high pressure P,

$$\alpha_e = \frac{1}{2}\frac{K_P^{1/2}}{P^{1/2}}$$

where α_e = the fraction of N_2O_4 dissociated at equilibrium. 3

e) At 1000K for the equilibria,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad K_p = 4\times 10^{-2}$$

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g) \qquad K_p = 2.0$$

Solid carbon, CaO and $CaCO_3$ are mixed and allowed to attain equilibrium at 1000K . What will be the presssure of CO(g) in the mixture? 4

4. a) Consider a reaction $Cl_2(g) + Br_2(g) = 2BrCl$ at 298 K and a total pressure of one bar. Suppose that we start with one mole each of $Cl_2(g)$, $Br_2(g)$ and no BrCl. Show that

$$G(\zeta) = (1-\zeta)G^0_{Cl_2} + (1-\zeta)G^0_{Br_2} + 2\zeta G^0_{BrCl} + 2(1-\zeta)RT\ln\frac{(1-\zeta)}{2} + 2\zeta RT\ln\zeta$$

where ζ is the extent of reaction. 4

b) Suppose that we have a mixture of the gases $H_2(g)$, CO_2 (g), CO(g) and $H_2O(g)$ at 1260 K, with their partial pressures having values 0.55, 0.20, 1.25 and 0.10 bar respectively. Is the reaction described by the equation

$$H_2(g) + CO_2(g) = CO(g) + H_2O(g) \qquad [K_P = 1.59]$$

at equilibrium under these conditions? If not, in what direction will the reaction proceed to attain equilibrium? 4

c) For the dimerization equilibrium of bezoic acid in benzene and water, show that,

$$C_w / \sqrt{C_B} = \text{ constant}$$

where, C_w = Concentration of benzoic acid in aqueous layer. C_B = Concentration of benzoic acid in benzene layer. 4

UNIT-III [13 marks]

5. a) The hamiltonian operator of a given system is $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$ (where V is a constant). The corresponding eigenfunctions (not normalized) are $\psi_n = e^{\pm inx}$ (n = 1,2,3...........).

(i) What is the expectation value of $\hat{H}$, when the system is in its n = 3 stationary state?

(ii) What is the expectation value of the x-component of the linear momentum in the n = 3 state? 4

b) Which one of the following functions, when multiplied by a normalization constant, would be an acceptable wave function? Explain.

(i) $\psi(x) = e^{-bx^2} \quad \text{for } x < 0$

$\quad = 2e^{-bx^2} \quad \text{for } x \geq 0$

(ii) $\psi(x) = \sin x$ 3

c) Explain the following (Any one) 3

(i) State of a system is described by a time dependent wave function $\psi(x,t)$ but the average value of any physical quantity, M, is independent of time.

(ii) The operators $\hat{A}$ and $\hat{B}$ commute, and ψ_A is an eigenfucntion of $\hat{A}$ having the eigenvalue 'a'. Show that ψ_A is also an eigenfunction of $\hat{B}$ provided ψ_A is nondegenerate.

d) Using the wavefunction $\psi(x) = \text{Sin}\,\frac{2\pi x}{L}$ for a particle confined in the region $0 \leq x \leq L$, calculate the probability of finding the particle in the region $L/3 \leq x \leq L/2$. 3

6. a) Find <x> and <p_x> for the ground stationary state of a particle in a 3-D box. 3

b) Show that the linear momentum operator p_x is hermitian. 3

c) At what values of x (in terms of L) the probability density of a particle enclosed in a one-dimensional box extending from O to L will be 25% of the maximum value at n = 2 state? 3

d) A system is described by the operator,

$$\hat{A} = -\frac{d^2}{dx^2} + x^2$$

Show that $\psi = Cxe^{-x^2/2}$ is an eigenfunction of $\hat{A}$. What is the eigenvalue? 2

e) If the position of the electron (m = 9.1×10^{-31}kg) in H atom is determined with an accuracy of 0.01 nm, what would be the uncertainty in its velocity? Comment on the quantum nature of the particle. 2

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