RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [2018-21]
B.A./B.Sc. THIRD SEMESTER (July – December) 2019
Mid-Semester Examination, September 2019

Date : 16/09/2019
CHEMISTRY (Honours)
Time : 11 am – 3 pm
Paper: III
Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Unit- I

(Answer any one question from each unit)

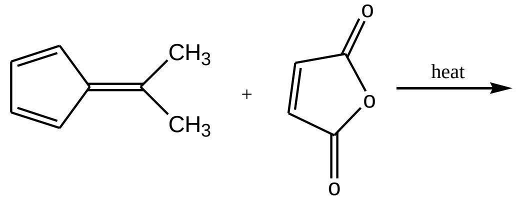
(2 × 3)

1. a) Predict the products of the following reactions with mechanism.

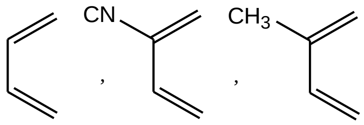
i) $CH_3\text{-}C\equiv CH \xrightarrow[NaOH,H_2O_2]{B_2H_6/THF}$

ii) $CH_3\text{-}C\equiv C\text{-}CH_3 \xrightarrow[EtOH]{Na/liq\ NH_3}$

iii)

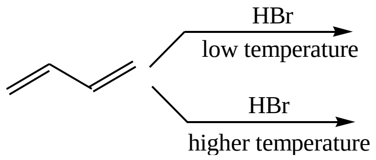


b) Arrange the following dienes in order of increasing reactivity in Diels-Alder reaction with tetracyano ethylene. Give suitable explanation in favour of your choice. [2]



2. a) Diels-Alder reaction is a thermally allowed process — Give suitable explanation for the above statement. [3]

b)

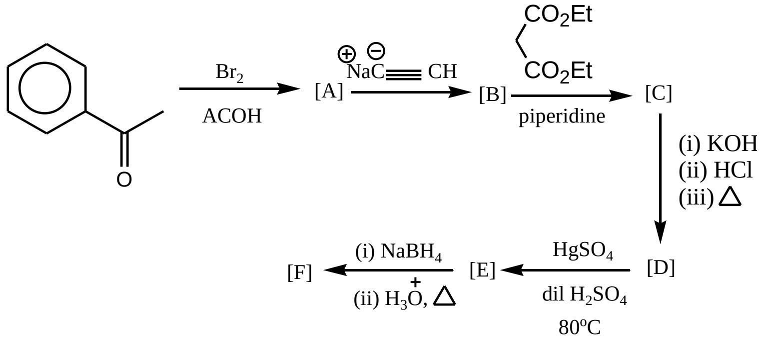


Predict the products for above reactions, also explain the formation. [3]

c) [2+2] cycloaddition is supra-supra addition process under photochemical condition – explain the above observation. [2]

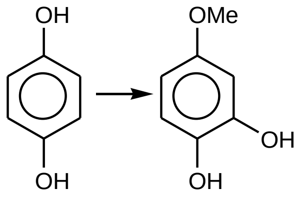
Unit -II

3. a) Identify [A] to [F] in the following reaction sequence: [4]



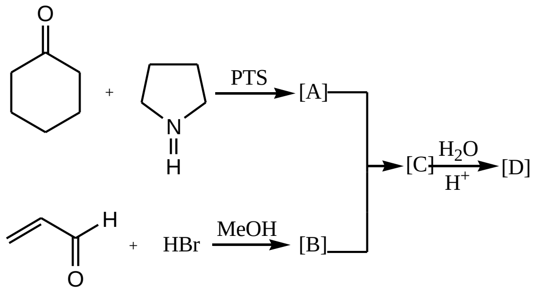
b) p-N,N-dimethylaminobenzaldehyde fails to undergo benzoin condensation with KCN/EtOH, but the condensation does take place when mixed with benzaldehyde — Explain. [2]

c) Carry out the following conversion: [2]

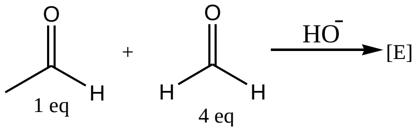


4. a) Write down the structure of [A] to [E] in the following reaction sequence: [3]

i)

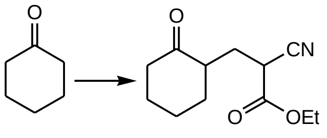


ii)

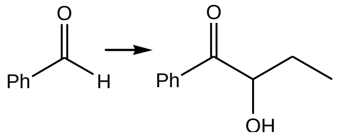


b) Carry out the following conversions: [4]

i)



ii)



c) Cyclopropane forms a stable hydrate, Justify. [1]

Group – B

Unit - III

5. a) Consider a reaction represented as $A \rightarrow B + C$

i) Write down the expression for the reaction quotient (Q_p) at any arbitrary instant in terms of partial pressure. Now write down the expression for free energy change (ΔG) of the reaction in terms of standard free energy change (ΔG^0) and reaction quotient (Q_p).

ii) Comment which of the quantities, $\Delta G, \Delta G^0, Q_p$ depend on the choice of the standard state?

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 pressure having values 0.55, 0.20, 1.25 and 0.10 bar respectively. Is the reaction described by the equation

$$H_2(g) + CO_2(g) = CO(g) \text{ and } H_2O(g) \qquad [K_p = 1.59]$$

at equilibrium under these condition? If not, in what direction will the reaction proceed to attain equilibrium? [(1+1)+(1×3)+3]

6. a) Consider a reaction represented as $A \rightarrow B$.

i) Express the net free energy of species in a reaction mixture in terms of their standard free energies and the free energy of mixing.

ii) Draw a schematic diagram which shows how standard free energy, free energy of mixing and the total free changes during the reaction.

iii) Show the location of the equilibrium and explain its origin from the graph. [2+3+(1+2)]

[Given that the standard free energy of B is greater than that of A]

Unit –IV

7. a) Derive Wien's displacement law from Planck's radiation law [3]

$$P(\lambda) = \frac{8\pi hc}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)}$$

b) i) What is the relative (w.r.t. light) wavelength of H^+ ion $(m = 1.7 \times 10^{-27}\,\text{kg})$ moving with a velocity equal to $\frac{1}{100}$ of that of light? Consider the light is of same energy to that of electron. [3]

ii) Explain the result of the double slit experiment for light, considering one slit open at a time and both slits open at a time.(only figure) [2]

8. a) A baseball (m = 200 gm) is moving with a velocity of 3000 cm sec^{-1}. If the position is located with an uncertainly of 500 cm, what will be the uncertainly in velocity? Comment. [2+1]

b) Show that energy levels of a particle in a one dimensional box are quantised. [3]

c) Write down the equations for energy and momentum conservation law in Campton effect. [2]

Group – C

Unit -V

9. a) State LCAO rules relating to molecular orbital formation. [3]

b) Which homonuclear diatomic molecules(s) of second period elements, besides O_2 should be paramagnetic? [2]

c) Explain why N_2 has a greater dissociation energy than N_2^+ whereas O_2 has a lower dissociation energy than O_2^+. [2+2]

10. a) The antibonding molecular orbital is more antibonding than the bonding molecular orbital is bonding- explain. [2]

b) Show pictorially the formation of every possible bonding and antibonding molecular orbitals from linear combinations of S and p-orbitals. [2]

c) Constructing the molecular orbital energy level diagram of CO molecule, explain the following:

i) low polarity, ii) ligating behaviour and iii) diamagnetism. [2+1+1+1]

Unit - VI

11. a) State the stereochemistry of the following compounds with suitable drawing:

i) Ethylenediaminetetraacetatocobaltate(III) ion.

ii) Bis-(acetylacetonato) oxovandium (IV)

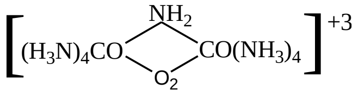
iii) Bis-(dimethylglyoximato) nickel (II). [3]

b) Differentiate π acidic and π complexing ligands with suitable example. [2]

c) Ethylenediaminetetracetic in the form of its calcium dihydrogen salt, is administered as an antidote for lead poisoning. Explain why this reagent might be an effective medicine. Why is the calcium salt administered rather than the free acid? [2]

d) Potassium alum is obtained when a solution of K_2SO_4 and $Al_2(SO_4)_3$ is concentrated by evaporation. Suggest specific experiments which might be used to determine whether potassium alum is a coordination compound. Explain what results would be expected if it were and if it were not a coordination compound. [2]

12. a) Name the following compounds or ions.

i) $K_2\left[O_sCl_5N\right]$ ii) 
$\left[(H_3N)_4CO\overset{NH_2}{\underset{O_2}{\diamond}}CO(NH_3)_4\right]^{+3}$

iii) $\left[Co\left(NH_3\right)_5\left(CO_3\right)\right]_2\left[CuCl_4\right]$ [3]

b) 'All inner metallic complexes are chetates but all chelates are not inner metallic complexes' — explain with specific examples. [2]

c) Potassium tetrathiocyanidopalladate (II) reacts with bipyridyl at $-78^{\circ}C$ to give an orange yellow compound (I) (C-SIR stretching frequency 2100 cm^{-1}) which when heated to $150^{o}C$ gives a light yellow compound (II) (C-S IR stretching frequency 800 cm^{-1} ; C-N IR stretching frequency 1980 Cm^{-1}). Both I and II on elemental analysis give the same results. Explain the phenomenon giving structure of the compounds. [2]

d) What is the difference between ambidentate and polydentate ligands. Why is glycine a bidentate ligand and not an ambidentate ligand? [2]

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