2016

M.Sc. 4th Seme. Examination

CHEMISTRY

PAPER—CEM-403

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(*Physical Special*)

Answer any *four* questions, taking *two* from each group.

Group—A

1. (a) What is pumping ? How can it achieve population inversion ? 4

(b) What are the differences between optical pumping and electrical pumping ? 3

(c) What are semiconductor lasers ? Give an example. 3

2. (a) What is Stern-Volmer quenching ? How can you assign a quenching to be of Stern-Volmer type ? 4

(b) Write down the mathematical expression that may be used to determine the fluorescence anisotropy value. 2

(c) How is the fluorescence of pyrene influenced by solvent polarity ? 2

(d) Schematically show the P.E. curves I_2 molecule in its ground and higher energy states. 2

3. (a) Write down the relation between the spin energy level of a free electron with the magnetic field strength and spin number. 2

(b) Comment on the esr spectra of radical anion of benzene. 3

(c) Mention the range of the applied magnetic field strength in an esr spectrometer ? 1

(d) How does the snesetivity of an esr spectrometer depend on temperature ? 2

(e) What is the role of an optical circulator in an esr spectrometer ? 2

4. Write notes on (any *four*) : $4 \times 2\frac{1}{2}$

(a) Vibrationless transition ;

(b) Stoke's shift ;

(c) Onsager field ;

(d) Optical cavetus ;

(e) Brewster angle.

Group—B

5. (a) What do you mean by coherence in laser spectroscopy ? Explain different types of coherences with the help of suitable diagrams. 1+3

(b) The coherent length of a light source is 2.5×10^{-2} m and its wavelength is 5500Å. Calculate the frequency and coherence time. 3

(c) What do you mean by gain in lasers ? What is the condition for a threshold gain ? 3

6. (a) How can the solvent polanity affect excited state dipolemoment of a substance ? 3

(b) Comment on the pK_a values of phonolic substances in the ground and excited states. 4

(c) When ferrous sulphate and methylene blue are mixed together, the bleaching occurs only in presence of light. Explain. 3

7. (a) Hyperfine splitting, not the energy, is the marker in esr spectroscopy — why ? 2

(b) Why do we get quintet of quintets is the esr spectra of pyrazine amion ? 3

(c) What is the typical wavelength range in esr spectroscopy ? 1

(d) What do you mean by saturation in esr spectroscopy ? 2

(e) Why is the differential plot more preferred in esr spectroscopy ? 2

8. Write short notes on (any *four*) : $4 \times 2\frac{1}{2}$

(a) He-Ne laser ;

(b) Excimer laser ;

(c) Excited state dipole moment ;

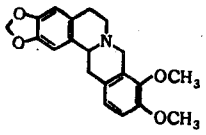
(d) First vibronic peak ;

(e) Optical band gap.

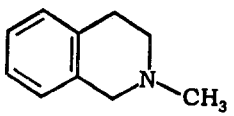
(*Organic Special*)

Answer any *five* questions.

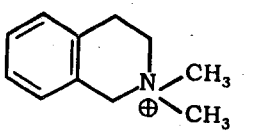
1. (a) Give the products with mechanism :

(i) 

3

(ii) 

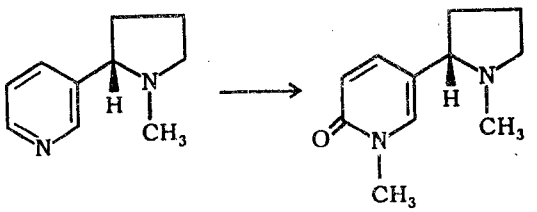
$1\frac{1}{2}$

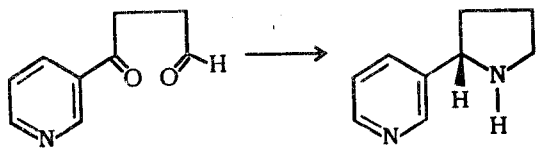
(iii) 

$1\frac{1}{2}$

(b) How would you detect the presence of both $-OCH_3$ and $\diagdown N - CH_3$ group in any alkaloid using same reagent ? Explain the reaction condition to be employed. 2

2. (a) Carry out following conversion. Mention the reagents and reaction conditions for each step.

(i)  3

(ii)  3

(b) Prove that (–) quinine possesses erythro relationship between $C_8 - C_9$ from the pk_a values of (–) quinine and (+) 9-epiquinine. 2

3. Predict the products with mechanism (Any *four*) : 4×2

(i) Quinine $\xrightarrow[\text{Warm}]{\text{dil HOAc}}$

(ii) Quinidine $\xrightarrow{\text{dil } H_2SO_4}$

(iii) 9 – deoxyquine $\xrightarrow[O_2,\ 25°C]{\text{NaH, DMSO}}$

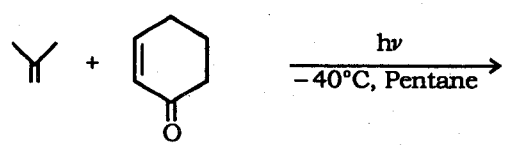
(iv) Quinine $\xrightarrow[\text{Benzo phenone dry toluene}]{\text{tBuOK}}$

(v) Quinine $\xrightarrow{25\%\ H_3PO_4,\ \text{boil}}$

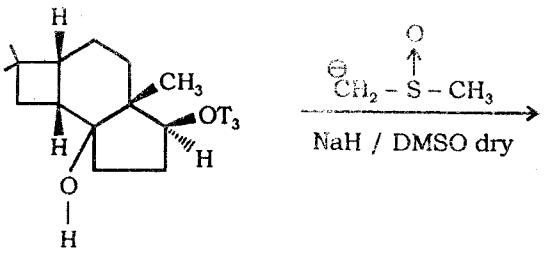
4. Predict the product with mechanism when the baine is separately treated with (a) Conc. HCl, (b) Conc. HCl containing $SnCl_2$, (c) dil. HCl with warming, (d) Phenyl maquesium bromide in dry ether. 4×2

5. (a) Write down the structure of etorphine which is used for immobilisation of large animals. Outline the synthesis of etorphine from the baine. 1+3

(b) Predict with mechanism (any *two*) : 2×2

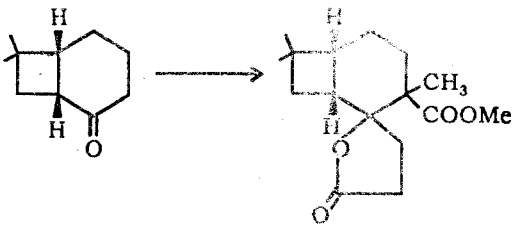
(i) 

(ii) Caryophyllene $\xrightarrow{\text{dil } H_2SO_4}$

(iii) 

6. (a) Carry out following conversions :

(i) Caryophylene ⟶ Isocaryophylene 2

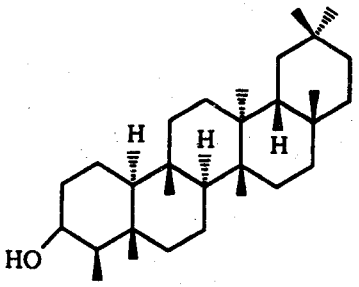
(ii) 
 3

(b) Outline a mechanism for the biosynthesis of squalene from two units of farnesgl pyrophosphate. In which type of plants, biosynthesis stops at presqualene pyrophosphate and why ? 3

7. Predict the product/s of the following with mechanism :

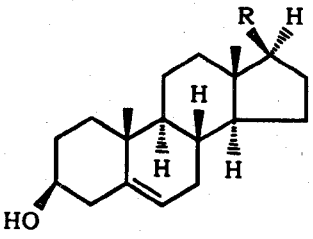
3+3+2

(i)



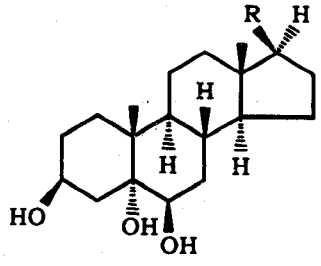
Conc HCl
reflux

(ii)



KOAc

(iii)



$H_2SO_4/AcOH/H_2O$

(Inorganic Special)

Answer any *five* questions
taking at least two from each group.

Group—A

1. (a) Calculate the equilibrium concentration of Frenkel defect in a crystal.

(b) Write short notes on following :

(i) Edge dislocation ;

(ii) Screw dislocation. 4+2+2

2. (a) Draw the E-K diagram for direct and indirect lattice.

(b) Derive the expression of energy gap for an electron passing through a crystal. 2+6

3. (a) Calculate the Fermi energy of an electron when $T > 0$.

(b) Derive the expression for specific heat of electron gas.

(c) Distinguish among metal insulator and semiconductor. 3+3+2

4. (a) Write down the differences between 4f and 5f orbitals.

   (b) How Uranium is extracted from its ore ?

   (c) Write down the separation of lanthanoid metal ions.

3+3+2

Group—B

5. (a) What do you mean by "X-band frequency" and "Q-band frequency" in ESR spectroscopy ? What are the advantages and limitations in using "Q-band frequency".

   (b) An ESR instrument is operating at a frequency of 9.1 GHz, and measurements are made with atomic hydrogen. Resonance is observed at a magnetic flux density of 0.3247 T. Calculate the g value for the electron in the hydrogen atom.

   (c) Show that "orbital angular momentum" of electron acts just opposite in direction with "orbital magnetic moment".

3+2+3

6. (a) Write short notes on "solvent used in ESR measurement".

   (b) What do you mean by hyperfine splitting in ESR spectroscopy ?

   (c) Explain the appearance of three lines in the esr spectrum of napthalene diradical. 3+1+4

7. (a) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of the $\dot{N}H_2$ radical.

(b) Explain why the energy of α-spin $\left(m_s = +\frac{1}{2}\right)$ of electron increases linearly whereas that of β-spin $\left(m_s = -\frac{1}{2}\right)$ decreases with increasing external magnetic field.

(c) Explain the EPR activity of the ions Mn(II) and Cr(II).

3+3+2
