

M.Sc. 4th Semester Examination, 2014

CHEMISTRY

PAPER — CEM - 403

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(Organic)

Answer any five questions

1. (a) Write the most elegant approach of E.J. Corey for construction of a nine-membered ring with desired stereochemistry and functionalities. Write the step where this approach has been successfully used in the synthesis of caryophyllene. 3 + 2

- (b) Establish the fact that alkylation of Indole at position 2 occurs *via* migration of alkyl group from 3. Design a suitable experiment to prove the fact. 3

(Turn Over)

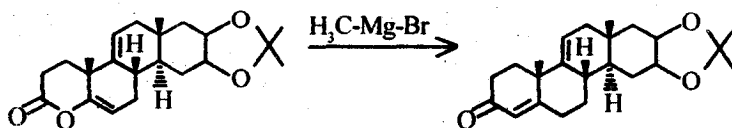
2. (a) In a schematic form show that both Indole and Cinchona alkaloids originates from same precursor loganin. 4
- (b) How can you establish the fact that all cinchona alkaloids have same stereochemistry at C₃ and C₄ and hence deduce their absolute configuration. 4
3. (a) Show that abietic acid and podocarpic acid has opposite configuration of -CO₂H group at C₄ and establish their configurations. How can you relate the two compounds ? 2 + 2
- (b) Show that cholesterol has homoallylic -OH group and also establish how the position of attachment and the length of side chain has been established by Barbier-Wieland degradation. 1 + 3
4. (a) Yohimbine and Ψ-yohimbine both can be oxidized to give same product by using tertiarybutyl hypochlorite. Write a plausible mechanism for such an oxidation. On the

other hand yohimbine can only be oxidized by mercuricacetate, give a reasonable explanation for the same. 3 + 1

- (b) What are 'acetogenin'? Show that catechin and epicatechin are diastereoisomers and hence establish their absolute configuration. 1 + 3
5. (a) Show that caryophyllene contains two rings and hence deduce their ring size. 6
- (b) Give a plausible mechanism for the conversion of morphine to apomorphine. 2
6. (a) How morphine can be converted to heroin and show that morphine contains a phenanthrene skeleton with a vernarable ethylamine side chain. 6
- (b) How can you establish that abietic acid has a heteroannular diene skeleton? 2
7. (a) Carry out the following conversion : 3 + 2
- (i) Yohimbine \longrightarrow yohimbine Oxi indole
- (ii) Quinine \longrightarrow Quinidine.

(4)

- (b) Suggest a plausible mechanism for the following transformation as carried by Woodward in one of his steps for the synthesis of cholesterol. 3



(Inorganic)

Answer any **five** questions taking at least **two** from each Group

GROUP – A

1. Discuss the photochemical cleavage of water molecule using $[\text{Ru}(\text{bipy})_3]^{2+}$ as a sensitizer. (bipy = 2,2' - bipyridine) 8
2. (a) Distinguish between fluorescence and phosphorescence. 3
(b) Define "actual life time" and "inherent life time" of a photochemical reaction. 2

(5)

- (c) What do you mean by "DOSENCO" and "Thexi" states? Write the characteristic of "Thexi" State. 3
3. (a) Write down the differences between 4 *f* and 5 *f* orbitals. 2
- (b) Discuss the luminescence property of lanthanoid complexes. 4
- (c) Explain the role of lanthanoids as shift reagent. 2
4. (a) What is critical field and critical temperature? 4
- (b) Find out the average kinetic energy of an electron in a metal at $T = 0\text{K}$. 3
- (c) What is Boltzmann tail? 1

GROUP – B

5. Write short notes on : 3 + 2 + 3
- (i) Stimulated absorption

- (ii) Radiationless transition
- (iii) Charge transfer excited state.
6. (a) Explain the term 'preorganisation' in the light of supramolecular chemistry. 2
- (b) Discuss the differences between 'molecular' and 'supramolecular' – chemistry. 2
- (c) What do you mean by Π - Π stacking ? How many types of Π -stacking are possible ? 2
- (d) Write notes on "dipole-dipole" interaction. 2
7. (a) What is superconductivity ? 2
- (b) Derive an expression of Hall coefficient for a metal. 2
- (c) Find out the fermi energy expression of an electron at $T > 0\text{K}$. 4
8. (a) Discuss the separation of lanthanoids by ion exchange method. 3
- (b) Mention two important sources of Uranium. 1

(7)

- (c) Draw the flow chart of isolating uranium metal from its ore. 2
- (d) Discuss the nature of absorption spectra of lanthanoids. 2

(*Physical Special*)

GROUP – A

Answer any **two** of the following

1. What is exciplex emission? Give one such example. State the characteristic features of exciplex emission. Give a schematic potential energy diagram of exciplex formation and explain its emission behaviour from the potential diagram.
1 + 1 + 3 + 5
2. What is twisted Intramolecular charge transfer (TICT) emission? Give one such example. State and explain the emission characteristics of TICT processes in terms of solvent polarity and solvent viscosity.
2 + 1 + 4 + 3
3. "Excited state acidity constant of an organic acid is less than its ground state value" – Explain.

How do you obtain the excited state acidity constant of an aromatic acid from its UV-VIS absorption spectra ? 10

4. (a) What is meant by Non-linear optical (NLO) properties of materials ? Write down the principle involved for the generation of third harmonic ($3\gamma_0$) frequency from a given frequency (γ_0) of radiation. 2 + 4
- (b) What is Hyper Raman scattering ? Give a schematic energy level diagram to explain the appearance of (i) Hyper Rayleigh, (ii) Hyper Raman Stokes and (iii) Hyper Raman Antistokes scattering. 4

GROUP -B

Answer any two of the following

5. (a) State and explain the zero field splitting parameter of molecular triplet electronic state. 6

- (b) Draw the energy levels with possible M_l and M_s values for $[\text{SO}_3\text{NO}]^{2-}$ radical and hence show the possible esr transitions. 4
6. (a) Write down the magnetic interaction Hamiltonian of Hydrogen atom. Use Fermi contact interaction as the perturbing term to obtain first order correction to wave function and second order correction to energy.
- (b) Ψ_1 (lowest level) \rightarrow Ψ_4 (highest level) of the above problem is allowed for second order transition but is forbidden during zero as well as first order transition. 10
7. (a) Write down the differences between steady state and time resolved fluorescence spectroscopy. 4
- (b) What is stoke's shift in fluorescence ? How does solvent molecule affect stokes shift of a fluorophore ? 3

- (c) "Intrinsic fluorophore is a better choice than extrinsic one during fluorescence imaging"
– Explain. 3

8. (a) Deduce the following expression of fluorescence anisotropy(r),

$$r = \frac{3\langle \cos^2 \theta \rangle - 1}{2}$$

where symbols have their usual significances.
Show that during co-linear dipolar absorption and emission anisotropy, $r = 0.4$. 4 + 3

- (b) "Total intensity of fluorescence during anisotropy measurement is equal to $(I_{||} + 2I_{\perp n})$ "
– Explain. 3