

M.Sc. 4th Semester Examination, 2010

CHEMISTRY

PAPER—CH-2203

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

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

(Organic Special)

Answer any **five** questions

1. (a) Discuss the biogenetic origin of three main classes of indole alkaloids. 3

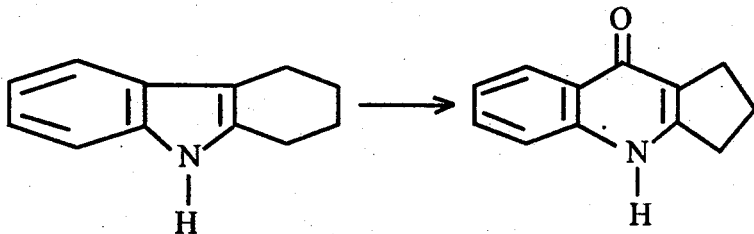
- (b) Although structurally altogether different, quinine originates from the same biogenetic precursor as those of indole alkaloids. Justify the statement. 5

2. Carry out the following transformation with plausible mechanism (any *two*) : 4 × 2

(i) yohimbine \longrightarrow yohimbin oxindole and vice versa.

(ii) *o*-nitrotoluene \longrightarrow tryptamine.

(iii)



3. (a) Write a short note about transannular cyclisation. 3
- (b) Discuss the elegant approach of Corey for rupture of transannular bond in bicyclic system using 1, 3-tertiary secondary glycol. How this has been successfully used in the synthesis of caryophyllene ? 5

4. How can you carry out the following conversions ?
- (a) Meroquinine \longrightarrow 1,2-Diethylcyclohexane. 5
- (b) Quinine \longrightarrow Quinidine 3

Or

Yohimbine \longrightarrow Ψ -yohimbine.

5. (a) How can you establish the absolute stereochemistry of C_{16} and C_{17} centre of yohimbine ? 3
- (b) Caryophyllene is macrocyclic sesquiterpene containing two rings :- establish the ring size. 5
6. (a) Catechin and *epi*-catechin are diastereoisomers :- establish their absolute stereochemistry. 5
- (b) Write the biogenesis of flavanoid compounds. 3
7. (a) Briefly discuss how the stereochemistry of A and B ring of abietic acid has been established. 4

- (b) How the Barbier-Wieland degradation has been used to determine the nature and side chain of cholesterol ? 4
8. (a) In a flow diagram briefly discuss how the various oxidation level of C₃-fragment i.e. B-ring of a flavanoid compound can originate by biogenetic oxidation of chalcone /dihydroflavone. 4
- (b) Write the synthesis of angelicin from resorcinol. 4
9. (a) What are acetogenin ? How they originates ? Discuss the role of polyketide chain for biogenesis of aromatic phenolic compounds. 5
- (b) Give Baker-Venkatraman rearrangement for synthesis of a typical flavone. 3

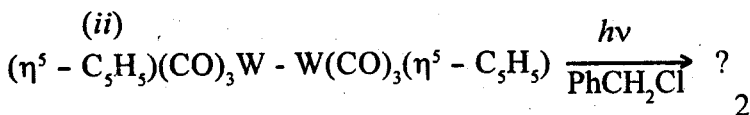
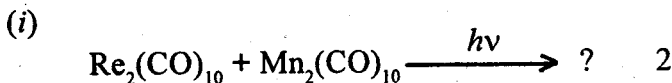
(Inorganic)

Answer any **four** questions

1. (a) State the essential requirements for carrying out a photochemical experiment. 3

(b) State the essential criteria for developing a photochemical energy-storage cycles. 3

(c) Write down the product(s) of the following photochemical reactions and suggest plausible mechanism :



2. (a) The parity selection rule for radiationless transitions is precisely opposite to the selection rule for radiative transitions. Explain. 2

(b) Write short notes on : 3+3

(i) Stimulated absorption

(ii) Charge transfer excited states.

(c) Define "actual life time" and "inherent life time" of a photochemical reaction. 2

3. (a) How will you synthesize LnF_3 ? 2
- (b) Briefly discuss 'Oxide superconductors'. 2
- (c) Explain the role of lanthanides as shift reagents. 3
- (d) Discuss the 'Electronic spectroscopy of L_n^{3+} '. 3
4. (a) What is self-assembly ? How does self-assembly differs from host-guest chemistry ? What is a clathrate ? 3
- (b) What do you mean by calixarenes ? Write down the structure of *p-t*-butylcalix [4] arene. 2
- (c) What is a 'Podand' ? 1
- (d) Give a discussion on the different π -interactions found in supramolecular systems. 4
5. (a) State and explain 'band theory' of metals. How this theory is applied to semiconductors ? 7
- (b) What are the advantages of "Differential Thermal Analysis" ? 3

6. Write notes on any *two* : 5 + 5
- (i) Superconductors
 - (ii) BCS theory
 - (iii) Thermogravimetric analysis of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
7. (a) What is a zeolite ? 1
- (b) What are the important characteristics of the lanthanides ? 3
- (c) Write note on 'magnetic behaviour' of L_n^{3+} . 3
- (d) How will you get a "molecular square" with suitable molecular analogues by self assembly ? Explain with an example. 3

(Physical Special)

Answer any **four** questions taking
two from each Group

GROUP-A

Answer any *two* of the following :

1. What do you mean by exciplex and excimer ?

Draw a schematic potential energy diagram to explain the characteristics of exciplex emission. State and explain the effect of solvent polarity on exciplex emission. 2+3+5

2. What is TICT emission? Write down the characteristic features of TICT emission with an example. Explain the effect of medium viscosity and polarity on TICT emission. What do you understand by 'static' and 'dynamic' polarity effect of TICT emission? 1+2+5+2
3. (a) What do you mean by stimulated Raman spectroscopy? Discuss the origin of $\gamma_0 - 2\gamma_1$, $\gamma_0 - 3\gamma_1$ frequency of radiation from a given LASER frequency, γ_0 in benzene (where γ_1 is the ring breathing vibration of benzene). 1+4
- (b) State the principle of cavity ring-down spectroscopy (CRDS). Why it is called cavity ring-down spectroscopy? 5
4. (a) Draw a schematic potential energy diagram of the ground as well as the excited state for a

molecule showing excited state intramolecular proton transfer. Give one example of such molecule. 3

(b) Describe the principle involved for the determination of excited state acidity constant using UV-VIS absorption spectrophotometer. 7

GROUP-B

Answer any *two* of the following :

5. Write down the magnetic interaction Hamiltonian of hydrogen atom in presence of an applied magnetic field along the z-axis. Write the spin wave functions of the above system (H-atom) and evaluate energy of the magnetic levels by considering zero order and first order correction to energy. Draw the energy levels and the possible esr transitions. 1+1+6+2
6. (a) Give schematic presentation of energy levels (up to first order correction to energy) and

the possible transitions for the following radicals : 2+2



(b) What do you mean by optically detected magnetic resonance (ODMR) spectroscopy ? How does it differ from the conventional esr spectroscopy ? Give a qualitative discussion on the splitting of triplet energy level of naphthalene at zero applied magnetic field.

1+2+3

7. (a) Time resolved fluorescence spectroscopy is more informative than the steady state fluorescence spectroscopy. Explain. 3

(b) Define intrinsic and extrinsic fluorophore ? 3

(c) What is the difference between Resonance Energy Transfer (RET) and Dexter interaction ? 4

8. (a) What do you mean by fluorescence anisotropy ? 2
- (b) During measurement of fluorescence anisotropy the magic angle between excitation polarizer and emission polarizer is 54.7° . Explain. 4
- (c) What effect do you observe in fluorescence anisotropy when resonance energy transfer occurs ? 4
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