M.Sc. 4th Semester Examination, 2012

CHEMISTRY

PAPER—CEM-403

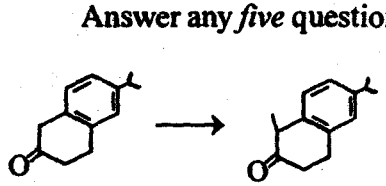
Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

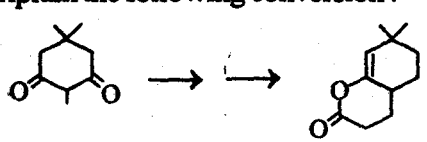
(*Organic Special*)

Answer any *five* questions

1. (*a*) 

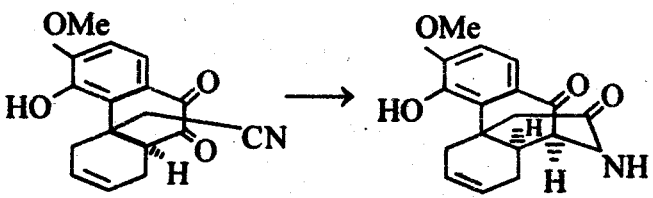
Name the reaction involved in this process and mention its advantage over simple ordinary methylation. 3

(*b*) Explain the following conversion : 4

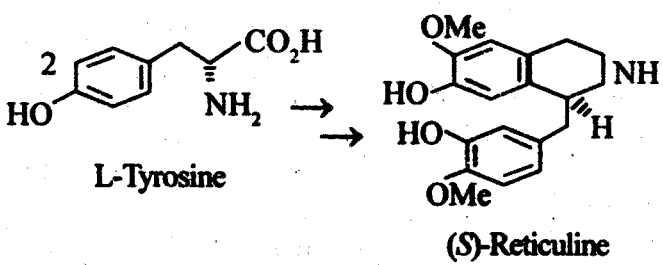


(*c*) Define natural products. 1

2. (*a*) Explain the following reductive cyclization mechanistically. 3

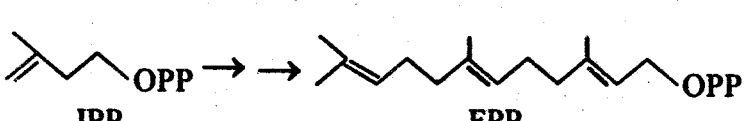


(*b*) Explain the following biosynthetic conversion : 5



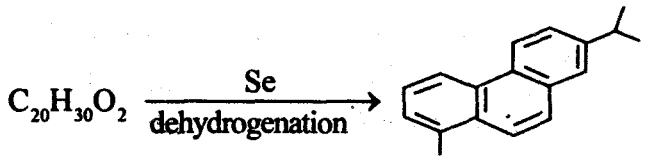
3. Explain the following with mechanism : 5

(*a*)



(*b*) Define the primary and secondary metabolites in natural product chemistry. 3

4. (*a*) Abietic acid



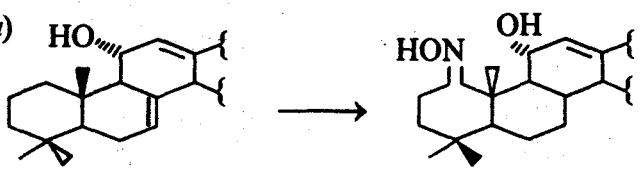
How much information could be procured from the above conversion regarding the structure of abietic acid. 4

(*b*) Show schematically biogenetic conversion of GGPP to abietic acid. 2

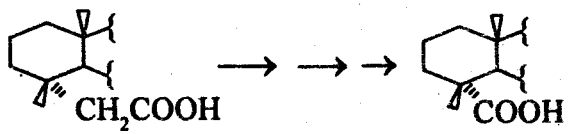
(*c*) Calculate the UV absorption maximum of abietic acid. 2

5. Mechanistically explain the following conversions :

(*a*)

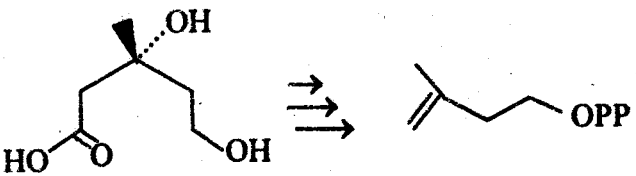


4

(*b*) 

4

6. (*a*) How do you establish the participation of three molecules of ATP durings the following conversion : 4



(*b*) Establish the configuration of the double bonds in abietic acid. 4

7. (*a*) Write down the stereostructures of reserpine and isoreserpine. Give the (*R*, *S*)-designation of the six stereogenic centers of reserpine. 3

(*b*) How was the absolute configuration of the 18-OH of reserpic acid determined ? 2

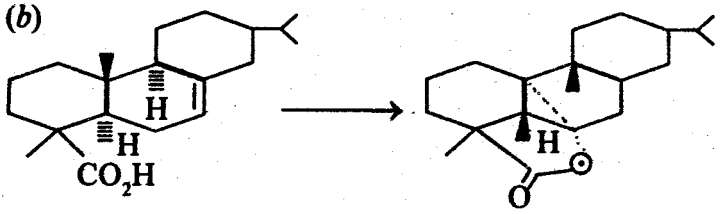
(*c*) Explain from conformational grounds the greater stability of isoreserpine than reserpine. 3

Or

(*a*) Carry out the following conversion : 4 x 2

Dehydroabietic acid (±) ⟶ Abietic Acid (±)

(*b*)



8. Biogenetically flavonoids are of mixed origin. Name the two pathways involved in the biogenesis of flavonoid skeleton. Delineate the biosynthesis of flavonoid skeleton from cinnamoyl coenzyme A and malonyl coenzyme A. 8

9. (*a*) How does a flavonoid act as an antioxidant. Give four examples of differently classified flavonoids. 4

(*b*) What are the relationship of four natural *Cinchona* alkaloids. Designate the stereogenic centers of these alkaloids. 4

10. (*a*) Name two important reactions used in the synthesis of (±)-dehydroabietic acid. Give examples of their applications. 4

(*b*) In squalene biosynthesis the carbocation is quenched by NADPH. How can one prove the fate of the carbocation in absence of NADPH. 4

(*Inorganic Special*)

Answer any *four* questions

1. (*a*) A certain substance absorbs 3×10^{16} quantas of light per second. On irradiation for 10 min, 0·002 moles reactant was found to have reacted. Calculate the quantum efficiency of the process. 2

(*b*) Distinguish between "internal conversion" and "intersystem crossing". 2

(*c*) The percentage transmittancy of an aqueous solution of a dye at 450 nm and at 25 °C is 30% for a 2×10^{-3} M solution in a 2 cm cell. Calculate the optical density and molar extinction coefficient. Find the concentration of the same dye in another solution where the percentage transmittance is 20% in a 1 cm cell at the same temperature and wavelength of light. 3

(*d*) Distinguish between fluorescence and phosphorescence. 2

(*e*) Is Einstein's law of photochemical equivalence always valid ? 1

2. (*a*) What do you mean by thexi state ? Write the characteristics of this state. 3

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

(*c*) Write short note on temperature dependence of photochemical processes. 4

3. (*a*) Briefly discuss the luminescence in lanthanoid complexes with qualitative energy level diagram. 4

(*b*) Complete the following reaction : 2

(*i*) $CeF_3 \xrightarrow[298\ K,\ 6\ days]{F_2 \text{ in liq. HF}}$

(*ii*) $Ln(NO_3)_3 \xrightarrow{\Delta}$

(*c*) Predict the product and write down the structure of the final product for the following reaction 4

(*i*) $YbCl_3 + Na[C_5H\ ^iPr_4] \xrightarrow{1,2\text{-dimethoxyethane}}$

(*ii*) $LaCl_3 + Na[C_5H\ ^iPr_4] \xrightarrow[\text{followed by recrystallization from } Et_2O]{THF,}$

4. (*a*) Give a concise definition of the term "supramolecular chemistry". Explain the distinction between molecular and supramolecular interactions. 1 + 2

(*b*) What is 'Preorganisation' in supramolecular chemistry ? 2

(*c*) What do you mean by 'dipole-dipole' interactions. 2

(*d*) What is π - π stacking ? How many types of π - π stacking are possible ? 2

(*e*) What do you mean by a Clathrate complex ? 1

5. (*a*) Write short note on "nuclear processing". 3

(*b*) What is the most important source of uranium ? 1

(*c*) How MCl_3 [M = Ln, Ce, -------] can be extracted from monazite ore ? Briefly discuss the process of separation of Ln^{3+} complexes in pure form. 3 + 3

6. (*a*) Derive London equation for a superconductor and hence find an expression of penetration depth. 6

(*b*) Clearly distinguish type I and type II superconductor. 4

7. (*a*) Find the density of states in a metal according to Sommerfeld model. 5

(*b*) Derive an expression of Hall coefficient for a metal. 3

(*c*) What is Boltzman tail ? Explain. 2

(*Physical Special*)

Answer *four* questions taking *one* from each Group

GROUP – A

Answer any *one* of the following

1. Write down the characteristic features of exciplex emission. Schematically draw the gas phase as well as solution phase potential energy curves for exciplex as

a function of donor acceptor distance and hence explain the emission characteristic of exciplex. 3 + 7

2. Describe the methods for the determination of ground and excited state acidity constant of salicylic acid. How do you obtain the excited state acidity constant of an aromatic acid from its UV-vis absorption spectroscopic data ? 3 + 7

GROUP – B

Answer any *one* of the following

3. (*a*) Give a schematic plot of potential energy curve for the inversion vibration of ammonia. Write down an empirical mathematical expression which support the inversion vibration of NH_3. 2 + 2

(*b*) What do you understand by ring puckering and torsional vibrational modes of molecules ? Explain each with examples. Write down the most general form of the torsional potential function. 2 + 2 + 2

4. (*a*) What do you understand by Non-linear optical (NLO) properties of materials ? Write down the principle involved for the generation of second harmonic from a given frequency of radiation. 2 + 3

(*b*) What do you mean by Hyper Raman Scattering ? Give a schematic energy level diagram to explain the appearence of (*i*) Hyper Rayleigh, (*ii*) Hyper Raman Stokes and Hyper Raman Anti-stokes scattering processes. 2 + 3

GROUP – C

Answer any *one* of the following

5. (*a*) Write down the expression of Hamiltonian for free radical in esr transition. How do you obtain '*g*' value from esr transition of a free radical. 2 + 3

(*b*) Depict the energy levels with possible M_I and M_S values, the possible esr transitions and the ratio of intensities of transitions of the following free radicals. $2\frac{1}{2} \times 2$

(*i*) $[SO_3NO]^{2-}$

(*ii*) CH_3.

6. Use perturbation theory to obtain 1st order correction to wavefunction for second order correction to energy of magnetic energy levels of hydrogen atom. Show

that $\psi_1 \rightarrow \psi_4$ is allowed for second order transition, though it is forbidden during zero as well as first order transition. 5 + 5

GROUP – D

Answer any *one* of the following

7. (*a*) What do you mean by Resonance Energy Transfer (RET) ? 2

(*b*) How can you differentiate between quenching process and RET process ? 3

(*c*) 'RET solely depends on the distance between donor and acceptor' – Justify the statement. 3

(*d*) Why is the total intensity required $(I_{11} + I_{1r})$, during anisotropy measurement ? 2

8. (*a*) What is the effect of RET during anisotropy measurement ? 3

(*b*) Write a short note on 'solvent re-orientation. 3

(*c*) Show that anisotropy (r) is equal to 4

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