

2016

M.Sc. Part-II Examination

CHEMISTRY

PAPER—VII

Full Marks : 75 / 100

Time : 3 / 4 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)

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

(Turn Over)

Group—A

1. (a) Write down the steps involved and the rate of each steps for Unimolecular photophysical processes.

Show that,

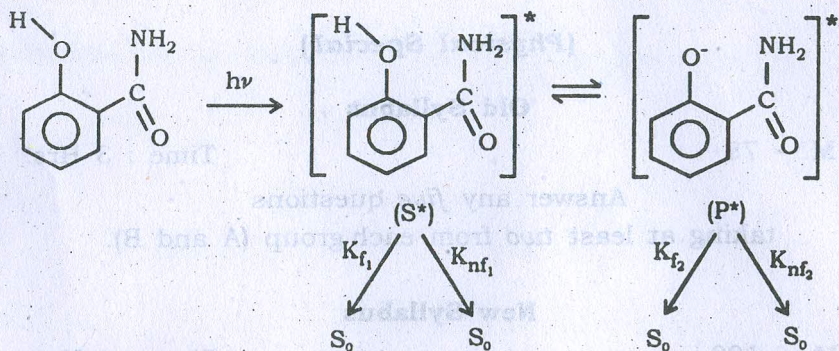
$$K_{ISC} = \frac{1}{\tau_f} \left(\frac{1 - \phi_f}{\phi_f} \right)$$

Assume $\phi_P + \phi_f + \phi_{ISC}^T \cong 1$

Here all the symbols have their usual significances.

7

- (b) The following photophysical process takes place in trans-silylamide.



Show that quantum yield of fluorescence of S^* and P^* at high pH are given by,

$$\phi_f(S^*) = \frac{K_{f1}}{K_{f1} + K_{nf1} + K_{nf2}}$$

$$\& \quad \phi_f(P^*) = \frac{K_{f2} \cdot K_1}{(K_{f1} + K_{nf1} + K_{f1})(K_{f2} + K_{nf2})}$$

where symbols have their usual significance. 4+4

2. (a) Write down the steps involved and the rate of each steps of a fluorophore in presence of quencher (Q).

Deduce the expression of quantum yield of fluorophore

in the absence ϕ_f^0 and presence ϕ_f of quencher. Hence show that,

$$\frac{\phi_f^0}{\phi_f} = 1 + K_{sv}[Q]$$

where K_{sv} is the Stern-Volmer quenching constant and all other symbols have their usual significances.

3+2+2+3

- (b) What is meant by exciplex emission? Give one such example. Write down the characteristics of exciplex emission with the change of solvent polarity. 2+1+2
3. (a) What is meant by induced absorption and induced emission?
Show that inversion of population is an essential criterion of a system to show lasing activity.
Write down the characteristics of LASER radiation. 3+2+2
- (b) "Inversion of population can be achieved for a three level system." — Justify or criticize the statement. 8
4. (a) What is Stark effect? Derive an expression for the second order correction in the rotational energy of a molecule in an electrostatic field.

$$\text{Given : } \langle (J+1)M / \cos \theta / JM \rangle = \sqrt{\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}}$$

where M is the eigen value of J_z . 2+8

- (b) Derive expression for spherical top molecule in rotational spectra. 5

Group—B

5. (a) Why do the spin lattice and spin-spin relaxation mechanism is so important in NMR spectroscopy?

Show that in spin-lattice relaxation mechanism,

$$P_- > P_+$$

where P_- is the total probability per unit time of a spin undergoing transition from higher to lower state and P_+ is the total probability per unit time of a spin undergoing transition from lower to higher state.

3+7

- (b) Write down the spin wavefunctions and the magnetic interaction Hamiltonian of an isolated proton.
Show that energy gap between the spin states of proton increases with the increase in magnetic field strength.

2+3

6. Write down the magnetic interaction Hamiltonian and spin wave functions for A-X spin system. Obtain the zero order as well as first order correction to energy of all the spin state and hence show the frequency of all the possible transitions.

2+4+4+5

8. (a) Explain with reason the effect of bias on depletion width in a p-n junction. 4
- (b) Calculate the Schottky defect concentration in an ionic crystal of MX type. 4
- (c) Colour centre is due to lattice defect which absorbs light. Explain the mechanism of absorption process. 3
- (d) Cerium crystallizes as a face centred cubic lattice and the length of the unit cell is 516 pm. Given that density of Cerium is 6.773 g cm^{-3} . Calculate the Avogadro Constant. 4

Group—C

9. Answer any *five* of the following : 5×5
- (i) State and Proof Eckart's theorem.
- (ii) Use variational principle to obtain the energy of the MO's of ethylene.
- (iii) Write down Hartree-Fock equation and the explicit form of Hamiltonian for 2N electron system.
"Hartree-Fock equation is called Integro-differential equation" — Explain.
- (iv) Use time independent non-degenerate perturbation theory to obtain first order correction to energy.
- (v) What is a projection operator ? Show that it is idempotent.
- (vi) What is Faraday ?
- (vii) What is polarizability ?

(Organic Special)

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. - 100

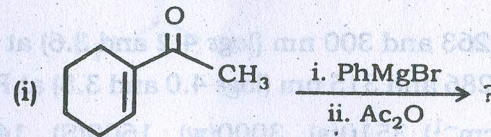
Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B)
and also group C.

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

Group — A

1. (a) Derive a mathematical expression of the Curtin-Hammett principle with the help of an energy profile diagram, and explain the same. Mention clearly the conditions where the principle will be valid, cite an example corresponding to Curtin-Hammett system where less populated conformer gives major product. 4+2+2
- (b) Write down the structure of product(s) with stereochemistry of the following reactions.



(Organic Special)**Old Syllabus**

F.M. - 75

Time : 3 Hrs.

Answer any five questions

taking at least two from each group A and B.

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer any five questions

taking at least two from each group (A and B) and answer any five questions from group C.

Group - A

1. (a) Predict the theoretical number of non-equivalent proton in each of the following compounds.
 trans-1,2-dimethylcyclopropane, 2-chloro-3-methylbutane. 2
- (b) What is Nuclear Overhauser Effect? Explain it with example. 4
- (c) Compound A (C₁₀H₁₂O₂) shows the following spectral data :
 UV : λ_{max} = 263 and 300 nm ($\log \epsilon$ 4.2 and 3.6) at pH = 7
 λ_{max} = 286 and 315 nm ($\log \epsilon$ 4.0 and 3.8) at pH = 13
 IR : ν_{max} (cm⁻¹) 3510(s), 3000(w), 1600(s), 1430(s).

C/17/DDE/M.Sc./Part-II(N&O)/Chem./7

(Continued)

965(m) and series of bands below 900 cm⁻¹.

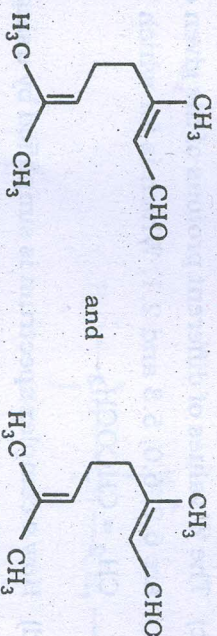
¹H NMR : δ 6.0 (1H, dq, J₁ = 7.0 Hz and J₂ = 16 Hz), 6.2 (1H, d, J = 16 Hz) 5.60 (1H, broad. Singlet disappeared on deuterium exchange), 6.70 (3H, m showing ABX type splitting patterns), 1.81 (3H, d, J = 7Hz) and 3.75 (3H, s).

Suggest a structure for the compound from its above spectral data and justify your choice. 6

(d) The magnetically equivalent nuclei are chemically equivalent nuclei but the reverse is not true? Explain. 3

2. (a) What is spin decoupling in NMR spectroscopy? How it is carried out? Illustrate the phenomenon with pure ethanol. 6

(b) Distinguish the following compounds using PMR spectroscopy? 2

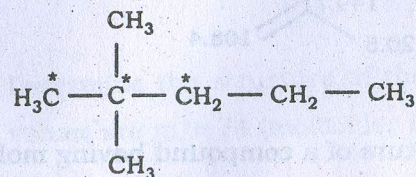


C/17/DDE/M.Sc./Part-II(N&O)/Chem./7

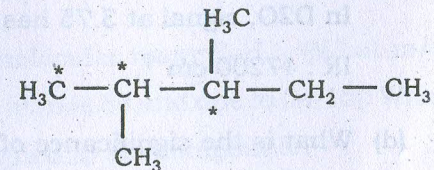
(Turn Over)

- (c) Acetylacetone shows in its ^1H NMR spectrum run at room temperature (30°C) the signals at δ 1.97(s), 2.14(s), 3.57(s), 5.50(s) and 14.92(s) having relative integral values 0.84, 0.16, 0.1066, 0.28 and 0.28 respectively. Assign the above signals to the protons of the keto- and enol-form of the compound and calculate the percentage of its keto- and enol-forms from the integral values of the signals. 5
- (d) How will differentiate among the three following compounds using ^{13}C NMR spectroscopy. o-dimethoxybenzene, m-dimethoxybenzene and p-dimethoxybenzene. 2
3. (a) What are the relations between intensity of a NMR active nuclei and its spin-lattice relaxation time T_1 ? 2
- (b) How intensity of a carbon nuclei depends on its degree of protonations? 2
- (c) The δ ' values of different protons of the given compound are 6.2, 6.0, 5.8 and 2.1. Which is for which?
 $\text{CH}_2 = \text{CHCOCH}_3$. 2
- (d) How a complex spectrum is simplified by using high field FT-NMR spectroscopy? 3

- (e) What are the advantages of Fourier Transform (FT-NMR) technique over CW-NMR technique? 3
- (f) Is it possible to differentiate the two methyl protons of Me_2NCHO ? 1
- (g) The ^1H NMR spectrum of cyclohexane is temperature dependent. — Explain. 2
4. (a) Calculate the δ_{C} values of the carbon atoms marked with asterisk of the following pairs of isomeric compounds and show how they can be distinguished from each other.

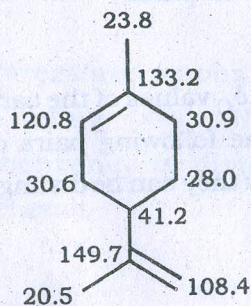


and



Additive parameters in ppm: base value : -2.5; α , β and γ -effects have their usual values; δ -effect : +0.3, $1^\circ(4^\circ)$: -3.4; $4^\circ(1^\circ)$: -1.5; $4^\circ(2^\circ)$: -8.4 ; $2^\circ(4^\circ)$: -7.2 ; $1^\circ(3^\circ)$: -1.1 ; $3^\circ(3^\circ)$: -9.5 ; $3^\circ(2^\circ)$; -3.7]. 2

- (b) Draw the expected DEPT, and ATP, spectra of the following compound. 4



- (c) Propose the structure of a compound having molecular formula $C_4H_8O_2$ and it shows the following spectral data.

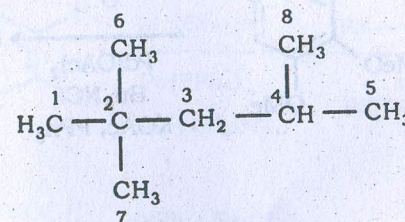
1H NMR : δ 1.35 (d, 3H), 2.15 (s, 3H), 3.75 (bs, 1H), 4.25 (q, 1H).

In D_2O , signal at 3.75 has disappeared.

IR : 17200 cm^{-1} . 3

- (d) What is the significance of Spin-lattice Relaxation time in NMR spectroscopy? Which carbon atoms of the

following compound have highest and lowest spin-lattice Relaxation time? 3+1



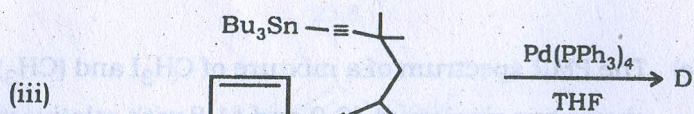
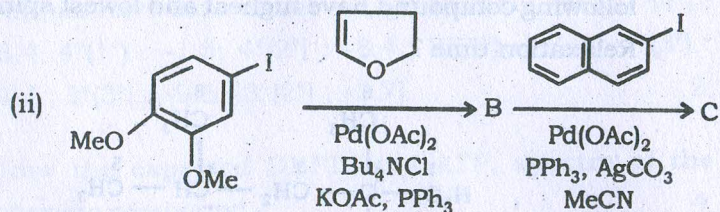
- (e) The PMR spectrum of a mixture of CH_3I and $(CH_3)_3C-Br$ shows two singlets at δ 2.2 and δ 1.8 with relative integral of 5:1. What is the mole percent of each compound in the mixture? 2

5. (a) Determine the structure of the compound whose m/e values are m/e 74 (molecular ion), 56, 43 and 31 (base peak). 3

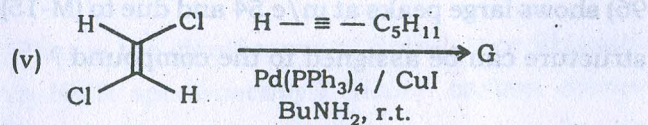
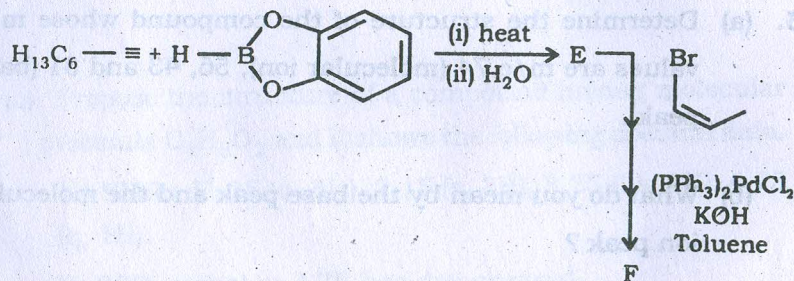
- (b) What do you mean by the base peak and the molecular ion peak? 2

- (c) A hydrocarbon with molecular mass C_7H_{12} (M^+ at m/e 96) shows large peaks at m/e 54 and due to $(M-15)$. What structure can be assigned to the compound? 3

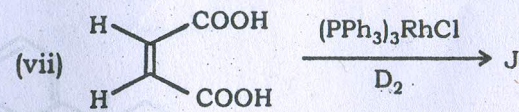
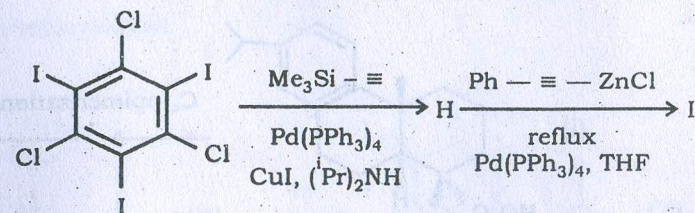
- (d) Give the mass spectral fragmentation of 1-phenylethanol. 2



(iv)



(vi)

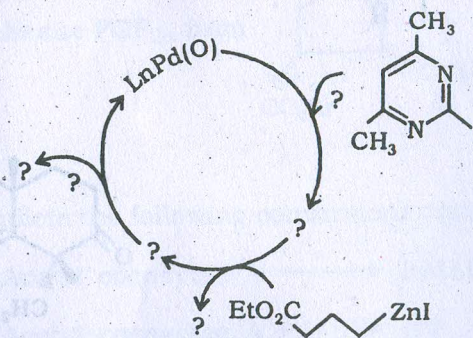


(c) What is hepto number ? 1

(d) Show the synthetic use of Ziegler Natta Catalyst. 2

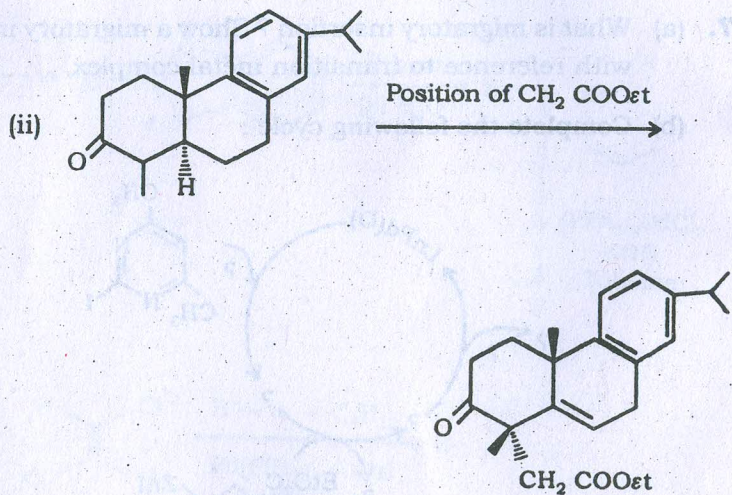
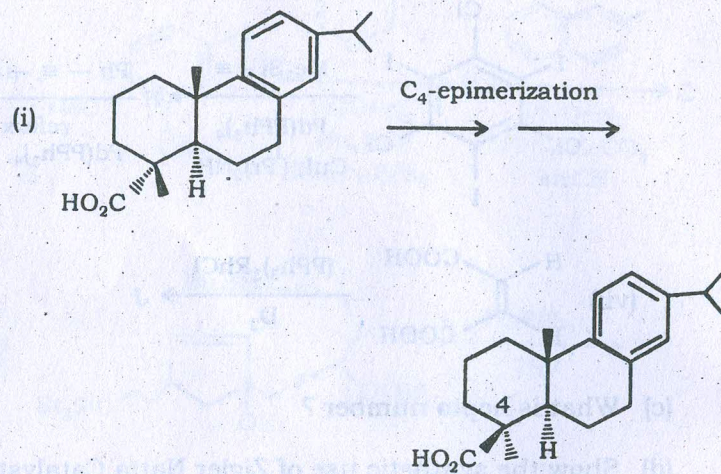
7. (a) What is migratory insertion ? Show a migratory insertion with reference to transition metal complex. 2+3

(b) Complete the following cycle : 4



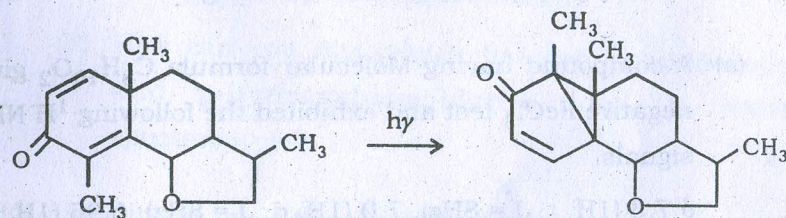
(b) Explain the following conversions :

4+4



(c) Write down the mechanism for photochemical transformation.

3



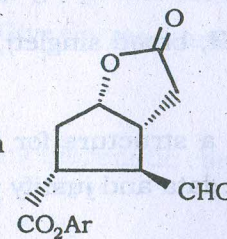
10. (a) Write down the chemical structure of the following :

(i) PGF_{2α}(ii) PGE₂

2+2

(b) Synthesize PGF_{2α} from

5



(c) Complete the following conversions : (any two)

3×2

(i) Acetyl coenzyme A \longrightarrow DMAPP(ii) Acetyl coenzyme A \longrightarrow IPP(iii) IPP \longrightarrow Geraniol

Group—C

11. Answer any five questions from following : 5×5

(a) A compound having Molecular formula $C_8H_{10}O_2$ gives negative $FeCl_3$ test and exhibited the following 1H NMR signals.

δ 7.3 (1H, t, $J = 8Hz$), 7.0 (1H, d, $J = 8Hz$), 6.95 (1H, s), 6.9 (1H, d, $J = 8Hz$), 5.3 (1H, broad singlet, D_2O exchangeable), 4.6 (2H, s), 3.9 (3H, s). Suggest a structure for the compound from its above spectral data and justify your choice. 5

(b) A compound having Molecular formula $C_{10}H_{12}O_2$ exhibited the following spectral data 1H NMR signals :

δ 7.3 (5H, broad singlet), 4.3 (2H, t), 2.97 (2H, t), 2.08 (3H, s)

Suggest a structure for the compound from its above spectral data and justify your choice. 5

(c) (i) The 1H NMR spectrum of ethyl 2-butenoate (ethyl crotonate), $CH_3CH = CH - CO_2CH_2CH_3$, shows the following signals $\delta = 6.95$ (dq, $J_1 = 16$, $J_2 = 6.8$ Hz, 1H), 5.81 (dq, $J_1 = 16$, $J_2 = 1.7$ Hz, 1H), 4.13 (q, $J = 7$, 2H), 1.88 (dd, $J_1 = 6.8$, $J_2 = 1.7$ Hz,

3H) and 1.24 (t, $J = 7$, 3H) ppm. Assign these δ values to various hydrogens, and tell if the double bond is cis or trans substituted. 3

(ii) How can you distinguish between salisaldehyde and p-hydroxybenzaldehyde by 1H NMR spectroscopy? 2

(d) Explain the basic theory of FT-NMR spectroscopy? 5

(e) How can you establish the Presence of cyclobutane ring in caryophyllene with suitable experiment? 5

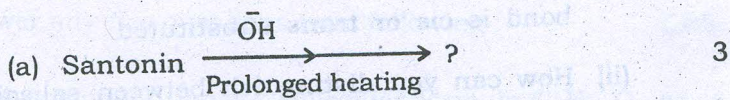
(f) How yohimbine and pseudo-yohimbine can be differentiated by using $Hg(OAc)_2$ in acetic acid. Why both of them produce the same compound when treated with tert-butyl hypochlorite? Give the mechanism in both the cases. 5

(g) (i) Delineate the following biogenetic conversion from GPP to abietic acid.

(ii) Designate the absolute configuration of (+) mevalonic acid. 4+1

(h) How can you establish the Location of isopropyl grouping and the double bonds in abietic acid with suitable experiment? 5

(i) Predict the product for the following reactions :



(b) Discuss the mechanism of isomerisation reaction of santonin in presence of HCl. 2
