2007

CHEMISTRY

PAPER-VII

Marks : 75

Time : 3 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*

Illustrate the answers whenever necessary

Write the answers to questions of each **Group in separate books**

(**Organic Special**)

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

GROUP -A

1. (a) Show that caryophyllene is a macrocyclic sesqui-terpene containing two rings and determine the ring size. 6

 (b) (i) Discuss the biogenetic origin of three main classes of indole alkaloids. 3

 (ii) Although structurally altogether different, qui-**nine** alkaloids originate from the same precursor as that of indole alkaloids. Justify the statement. 6

2. Write the structure of the key synthon necessary for the synthesis of non-nitrogeneous part of yohimbine. In a flow diagram write the retrosynthetic steps for construction of such a synthon. 6

(b) How Barbier-Wieland degradation has been used for determining the nature and size of side chain in cholesterol ? 5

(c) Discuss how the stereochemistry of A and B ring including the stereochemistry of COOH group in abietic acid is determined. 4

3. Establish the following with experimental evidence:

(i) **Absolute configuration** of C15_ **and CZO_H of yohimbine.** **4**

(ii) **Absolute configuration of C3_H and C17_OH of** yohimbine. 4

(ii) Absolute configuration of C9 of quinine. 3

(iv) Location of isopropyl **group and double bonds in abietic acid.**

4. Carry out **following transformations** and give **plausible mechanisms**, wherever applicable : 3x5

(i) **Quinine** -i **Quinidine**

(n) **Quinine** -> **Meroquinine**

(iii) Yohimbine -) Yohimbine Oxindole

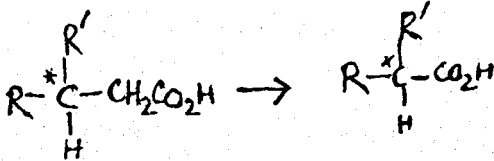*(iv)* Yohimbine -4 Pseudo-Yohimbine

(Y) Ortho-Nitrophaenol -4 Tryptamine.

5. **Outline the steps** for the following conversions :

(ii)   3

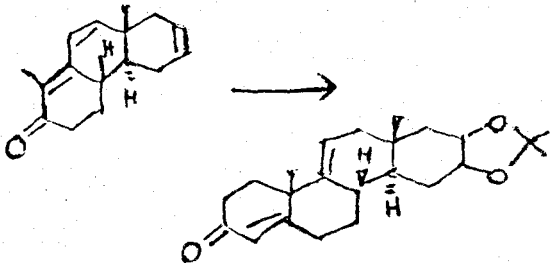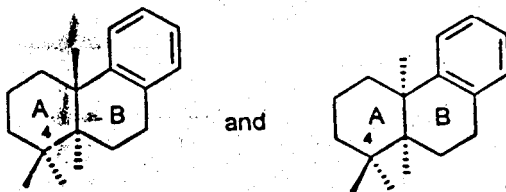(iu)   4

e'
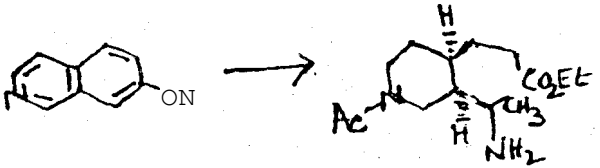
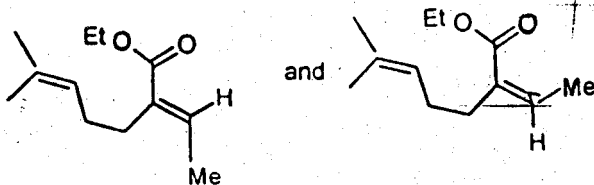*(iv)* Meroquinine   4 1,2-Diethylcyclohexane.   4

GROUP-B

6. (a) How would you distinguish between the following pairs of isomeric compounds from their proton che-**mical shifts** ? **Indicate only the distinguishing feature**(s). Answer any *three:*   **2x3**
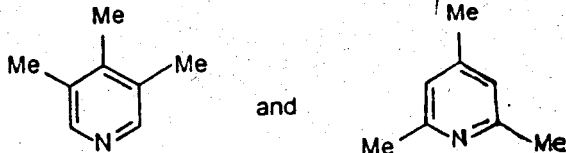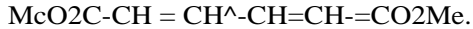
(I)

and

(K)

and

Trans-**stilbene** and cis-**stilbene.**

(*iv*)

and

(b) Draw the possible configurations of the geometrical isomers of demethylmuconate having the general structrural formula

McO2C-CH = CH^-CH=CH-=CO2Me.

Indicate how you would ascertain their stereochemistry from the 'chemical shifts of their olefinic protons. 3

(c) What is Nuclear Overhauser Effect ? Explain the reason for this effect. The chemical shifts (in 6pp,,,) of the vinylic methyl and the olefinic protons of **eitral**-a(1)- and citral=b(2) are shown on their **structural diagrams**. How, would you confirm their indicated stereochemistry and the assignments of the chemical shifts of the vinylic methyl protons at 61.68 , 1.61 and 1.60 by Nuclear Overhauser Effect? 6

1.68 me, H 5.01
1.61 Me H 5.80
2.16 Me CHO

1

1.68 Me H 5.11
1.60 Me CHO
1.98 Me H 5.68

2
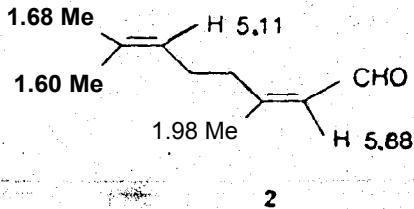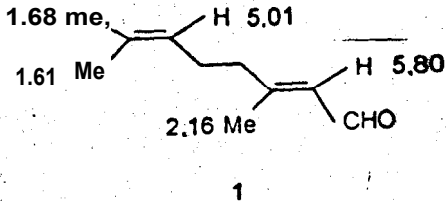
7. (a) What is the relative order of J,,;S, Jga,, and Jtrans of the protons in--a nositbstituted olefin- of the type-.-. R--CH=CH2 ? Give reason for your answer. Indicate the approximate values of J for the two nonequivalent olefinic protons of an isomeric *cis* and *trans* alkenes. **4**

   (b) How does the equatorial proton of a rigid cyclohexane derivative differ from its axial counterpart linked to the same carbon atom ? Give reason for your answer. Cite one specific example. **4**

   (c) Indicate the splitting pattern of the protons of the methylene group attached to the acetoxy function in the compound 3. Give reason for your answer. What changes in the multiplicity of the signals of the above protons would you observe, if the chlorine atom in 3 is replaced by (i) a methyl group and (ii) a hydrogen atom? **3**

$$^\wedge me$$
$$ACO -CHZ C -Et --$$

   (d) Answer *anyone* of the following :

   (i) CompoundA, C,0I41602, gives a dihydro derivative upon catalytic hydrogenation (H2/Pt). Suggest a probable structure for the compound from its following spectral data.

UV: 236nm (log c4-1); IR:Va7,1667 and 1620 cm-' nothing < 5μ (except CH) ; no OH absorption and no bands below 900 cm -'.

'HNMR : 6 0.98 (3H, t, J = 7Hz), 1.0-2.0 (6H, m), 2.35 (3H,s), 3-18(2H, q,J-7Hz), 4.79 (H,,t, J=4Hz) and 6.18 (1H,t,J=3Hz).

(u') Compound B, C8H6 shows two ' H NMR signals at 63-08(s) and 7-4(m) in the ratio o f 1 : 5, while compound C, C H,.. Shows only one 'HNMR signal at 62-2(s). Suggest probable structures for both B and C.

8. (a) Calculate the 6 , values of C- 9 and C-10 of *trans-and* cis-decalins from the given additive parameters and show how the stereochemistry of the ring juncture of the two isomers can be ascertained from the above **6c values.**

[Additive **parameters in ppm** : Base value = 27.7, a-ax-Me = + 1.I, (3-ax-Me = + 5.2, y-ax-Me -5.4, 6-ax-Me=-0-1, a-equat-Me = +5.6, f3-equat-Me = + 8.9, y-equat-Me = 0.0, 6-equat-Me = -03, vic-diequat = - 23 and vic-ax-equat = - 3.1]

(b) **How would you distinguish between the following isomeric compounds** from their **calculated carbon chemical** shifts ? Answer *any three:* 2 x 3

U)
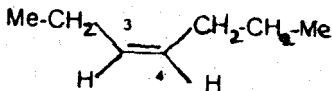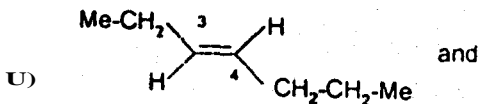
[Calculate <u>the Sc values of</u> only C-3 and C-4. Base value : 1222 ppm ; Additive **parameters. in ppm :** **a-effect** = +11.0, 0°=+6.0, Pn=-7.1, y" 1.9, y° -1.0, S"=+ 1.1, cis-**effect** =-12]

(ii) Me-CH,--CH,--CH.-CH.-OH and Me-CH,-CH (OH)-CH2-Me

[For terminal **alcohol** : Effect on the a-carbon atom: +48-Oppm; Effect on the (3-carbon atom : + 10.0 ppm; Effect on the y-carbon atom : - 5 ppm ; For internal alcohol : Effect on. the a-carbon **atom** : + 41.0 ppm; Effect on the (3-carbon atom: + 8.Oppm; Effect on the -y-carbon atom : - 5 ppm ; a-13-,y-and 8- effects for the parent hydrocarbon have usual values.]

(Continued)

(iii)

Me
       |3 4
Me-CH$_2$-C-CH$_2$-Me   and
       |
      Me

         4   3 2   Met
     Me=CHHCHZC -Me
              \Me

[**Calculate the δc values** of only C-2 and C-3.
Usual additive parameters for α-, β-, γ-effects;
2° (4°) = 7.2 ppm,   4'(2*) = - 8.4 ppm ;
4°(1')=-1.5ppm.

(iv)

[**Calculate only the δc values of the protonated
aromatic carbons of p-anisidine and those of
C-2, C-4 and C- 6 of m-anisidine**. Additive
parameters in ppm : **Base value** = 128.7,
ortho to NH2 = - 12.4, *meta* to N'H2 = + 1.3,
para to NH2 = .9-5, *ortho* to OMe = -15.5,
meta to ,OMe =X7-'0,-Para to OMe =- 8.9]

(c) Draw the DEPT and APT spectra of limonene having the carbon chemical shifts of the individual carbon atoms shown on the structure. What are the full names of DEPT and APT?
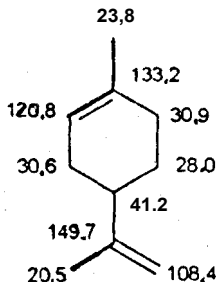
Limonene

9. (a) **What are the full names** of the terms COSY, HMQC **and HMBC in two-dimensional-AMR? Draw the expected** COSY, HMQC and HMBC **spectra of ethyl trans-crotonate having the following** 'H'and'3C NMR spectral data :

'HNMR: 8124 (3H, t, J=7.0 Hz), 1-88(3H, dd, **J, = 6.8 Hz and** J. = 1.7 Hz), 4.13 (2H, q, J = 7.0 Hz), 5.81 (1 H, dq, J, = 16 Hz and J,= IF 7 Hz) and 6.90(1H, dq,J,=16HzandJ2 =**6.8Hz).**

'3C NMR: 8^ 152 and 60.1 (-OEt), 18.1 (Me-CH=), 124.5 and 145.3 (-CH=CH-) and 1680(-C=O)

(b) Compound A, C', AO04, shows the following spectral
    data

    UV : No absorption above 210 nm.

    IR: v,,,ax 1740 cm-' ; no absorption for C=C
and OH.

'HNMR : 510 (3H, t, J=6-5Hz), 13(6H, t,
J=7.OHz), 1.82 (2H, ill-resolved dt), 3.2 (1H, t),
4.2 (4H, q, J = 7.OHz), and 4H, m obscured under
the signal at 61.30.

13C NMR: be 13.8 and 1410 (both q) [intensity of
the signal at S,, 14.10 is about twice that at 6,13.8],
22.4, 28.5 and 29.5 (eacht), 5203 (d), 61.12 (t) and
169-3(s) [For calculation of the 6. values of the
carbon atoms of the compound the additive
parameters for C02R group of terminal ester are :
effect at the a-carbon atom = + 20ppm ; effect at the
(3-carbon atom = + 3 ppm and effect at the y-carbon
atom = - 2 ppm] .

MS : Significant peaks at m/z 216 [M+] (10),
171 (55) and 160 (100).

Suggest a structure for the compound, which is
consistent with its above spectral data.   6

(c) Indicate the important mass spectral fragmentations of the following compound: ┃ 2+1
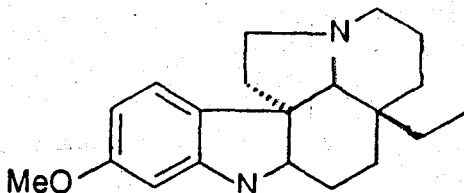
In the mass spectral fragmentations of the above compound if a peak at m/zm2 is assumed to have originated from the peak at m/zm,, where do you expect a metastable peak (m*) in the mass spectrum of the compound?

10. (a) Answer *any one :*

(i) Deduce a relation between We of a positively charged particle of mass m and charge e with the strength of the electrical field V and magnetic **field H, which can be used to make all the positively charged particles traverse the same semicircular path of radius r while recording the mass spectrum of a compound in a single focussing Dempster mass spectrometer.**

(ii) Briefly discuss the basic principle of Chemical **Ionisation** (CI) mass spectrometry.

(b) What is Mc Lafferty rearrangement in the mass **spectral fragmentations of some organic compounds** ?. **Give direct evidence for the mechanism of** this **rearrangement using appropriate deuterium labelled** compound's..

(c) How would you distinguish between the following isomeric compounds from their mass spectral fragmentations? Answer any *twee :*   2x3

(I)   **Me**

and

    Me

and

  OH

and

OH

CO₂Me   CO₂Me
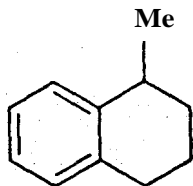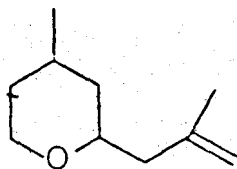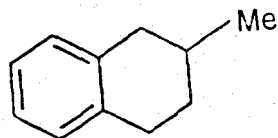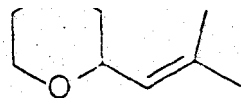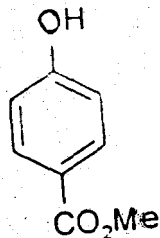
(iv) CH 3-012 CH2-CH2-CH2-CH3   and
CH3-CH2-CH (CH3)-CH2--CH3

(Inorganic Special)

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

GROUP—A

1. *(a) (i)* Why liquid He show superconductivity below
4.2K?   4
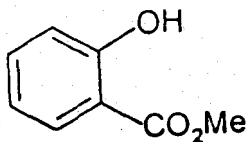
(v) Define soft and hard superconductors.   1

(b) Give brief accounts of semiconductor and exciton: 5+3

(c) What are the differences between Schottky and
Frankel defect ?   2

2. (a) What is distribution ratio and distribution coefficient
in a. solvent extraction method? Establish a relation
between them.   2+1

(b) Depict the basic principle involved in chromato-
graphic separation technique.   3

    (c) **What is differential thermal analysis** ? **What are its physicochemical origins?** **1+2**

    (**d)** **Write the Ilkovic equation for the limiting diffusion current in polarography and state its significance.** **1+2**

    (e) Depict the coulometric **experimental set-up mentioning the significance** of the **supporting** electrolyte. 2+1

3.   (a) What do **you mean by divergent and convergent approach of synthesis of dendrimers** ? Show with **schematic diagram.** $2\frac{1}{2}+2\frac{1}{2}$

    (b) `To synthesize a designed dendrimer– ` complexes using metal‑complexes as ligands ' is one of the best **methz — Explain**, with example. **4**

    (c) How platinum (**III) is stabilized** with **oxalic acid as ligand** **3**

    (d) **1, 4, 7-Triazacyclononane stabilizes Pd (III), draw the probable structure and state the reaction condition.**

4.   **(a) Explain how the nitrification and denitrification occur in seawater? Explain the mechanism of conversion of N03 to nitrogeneous organic compounds**

by phytoplankton.	3+4
(b) Discuss Phosphorous cycle in seawater.	6
(c) Define BOD.	2

        (*Turn Over*)

5. (a) Write down the. fundamental processes that can happen when emr of certain frequency is irradiated **on some inorganic** complex.

Deduce the **following expression** for the above **processes.**

$$\frac{1}{\phi_s} = \frac{1}{\phi_s^a} + \frac{1}{\phi_s^a k_{sv}[Q]}$$

(where symbols have **their usual significance.**)   **2+8**

(b) Write note on ligand field states.   5

GROUP-B

6. **(a) (i) Discuss** the mechanism of the formation of F-centre **with a suitable** example.   4

(i) **Does the F-absorption frequency depends on the interionic distance ?**   **2**

(b) State **the basic assumption** of Drude's theory.   3

(c) **Potassium** crystallizes as a body centered cubic lattice and copper crystallizes as face centred cubic lattice. How would you recognise them in a mixture containing both types of crystals ?

(a) Describe the equilibrium process involved in the extraction of metal chelates ?

   (b) How do strong and weak synthetic ion-exchange resins differ in structure'? Show with examples.   3

   (c) What **are the** different types of thermogravimetric **analysis'? State the principle** applications of thermo-**gravimetric analysis** . Cite examples to show its **application in coordination** chemistry.   1+2+2

   (d) How can you represent the cyclic voltammogram of ferrocene, specify Epa, EpC, ipa, Pc and E12 in the diagram. Comment on the nature of the redox process involved in ferrocene from the volta-mmogram.   2+ /

8. **(a) What** **are** the biological consequences **of Platinum** -DNA bonding?   3

   (b) What are the possible bifunctional binding modes of cis-DDP with DNA.   5

   (c) Discuss the magnetic exchange behaviour of $Fe(SQ)3$ [SQ = semiquinone].   4

   (d) How the unpaired electron on semiquinone species interact with metal cluster and affect EPR signal of the complexes ?   3

9. **(a) What do you mean by** the term 'Corrosion"? How **many types** of corrosions are there ?   2+3

   (b) Discuss **kinetics** of corrosion.   7

   (c) Write note on underground corrosion..   3

10. (a) What do you mean by thexi states and DOSEWCO
     states of inorganic complexes)   21 +21

                                  2   2

   (b) Give a short account on the application of co-
ordination compounds in chemical actinometry
and photochromism. '   5+5

(**Physical Special**)

Answer five questions, taking at least
two from each Group

GROUP-A

1. (a) Write down the energy expression by considering the
effective coupling between vibrational and rotational
motion in the vibration-rotation combined spectrum.
Deduce the expression. of frequency for `P' and `R'
branch of lines in such spectrum.   1+2+2

  (b) Show that in vibration-rotation combined spectrum,
`P' branch lines are at lower frequencies than
expected and `R' branch lines tend to bunch up.

(c) Derive the selection rule for vibrational **transition.**
[Given below the Hermite Polynomial identity i.e.

$$Hv\ (\ )\ vH,\text{-},\ (\ ) + 2\ H,,\ (\ )\ 1.$$ 6

2. (a) Show that the integrated absorption intensity in any spectral transition is proportional to the square of the transition moment integral. 8

(b) How do you account for the broadening in spectral line width'? 7

3. (a) Write short note on Coriolis interaction. 6

(b) What do you mean by Fermi resonance in vibra-**tional** spectra ? 3

(c) Write down the factors responsible for the intensity of spectral lines during electronic transitions.

4. (a) Write an expression for the Hamiltonian operator (H)

of a two spin $(1,=12=2)$ AX system including

spin-spin interaction. 2

(b) Write the possible wavefunctions for the AX system. How will the wavefunctions be modified when A2 system is considered? Explain. 8

(c) Calculate $<$ as I H I as $>$, where symbols have their **usual** significance. 5

5. (a) Explain why not all the vibrations of CO2 molecular system are Raman active.   6

   (b) **Show that the Raman shift in a diatomic molecule is equal to** twice the frequency **of rotation of the molecule.**   4

   (c) Discuss the nature of polarisation of the **Raman signal** for the wreathing vibrations of CC14 and CHC13.   5

6. (a) 3K has nuclear spin $I = 2$ and nuclear g factor is 0.2606.

   (i) Draw a diagram to show all possible orientations of magnetic moment of the **nucleus in magnetic** field.

   (v) **Calculate the transition frequency from one of these orientations to an adjacent one in a field** of 0.1 T (**nuclear magneton** $R_N = 5.0504 \times 10^{-27}$ JT^{-1}.)   6

   (b) **Define chemical shift in nmr spectroscopy. How is it expressed** ? **On what factors the chemical shift depend** ? **The chemical shift of CH3 proton in** CH3CHO is $S = 2.20$ ppm, that of CHO proton it is $o = 9.8$ ppm. **What is the difference in local magnetic field between two regions of the molecule when applied field is 1.5** T ?   2+2+2+3

GROUP-B

7. (a) Write **down the steps involved and the rate of each steps for the unimolecular photophysical processes. Show that**

$$K_{isc} = \frac{1}{ti} \left(1 - \frac{+r}{Vi} \right)$$

where symbols have their **usual** significance. 2+8

(b) Give an outline of TCSPC for **the measurement of excited state** life time of **a fluorophore.** 5

8. (a) What do you mean by static and dynamic quenching **of a fluorophore** ? **How do you obtain the rate constant** for both **static and dynamic quenching of a** fluorophore which undergoes quenching via both static and dynamic quenching mechanism? 2+8

(b) Write down the relation connecting fluorescence intensity (F), fluorescence quantum yield (%%) and absorption intensity (Ia). Hence deduce the relation,

$$F = 2\text{-}303 \; \Phi_f \, \varepsilon \, C \, I$$

where all other symbols have their usual meaning.

Show graphically, how the fluorescence intensity and also fluorescence quantum yield changes with the concentration of fluorophore. 1+2+2

9. (a) Write down the properties of LASER radiation. 3

   (b) Inversion of population can be achieved for a two level system.- Justify or criticize. 7

   (c) A LASER cavity is 1033996 cm long and is operating at a wavelength of 533.6478 nm. How many half wavelength are there along the length of the cavity? By how much would the length have to be changed to increase this number by one? What consequence does this result have for the tuning of such a cavity? 5

10. (a) Discuss the principle involved for the determination of ground as well as excited state acidity constant of phenol. 9

   (b) What do you mean by TICT processes? Give one such example of a fluorophore which shows TICT emission and explain its emission behaviour with the change of polarity of the medium. 2+1+3

11. *Either*

   (a) What are meant by Fourier Transformation and Inverse Fourier Transformation'? 3

   (b) Explain the term, `Fourier pair' in relation to FT NMR giving an example. 3

   (c) What is `Free Induction Decay"? For a liquid sample how is it mathematically expressed? Express graphically its amplitude variation with time. 5

(d) What are the main differences between a conventional NMR and FF NMR ? 4

Or

Discuss the principle of ESR spectroscopy. What do you mean by electron electron double resonance (EEDOR) in ESR spectra? Give, some important application of ESR spectroscopy. 15