

2007**CHEMISTRY****PAPER-V***FullMarks : 75**Time : 3 hours*

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

The figures in the right -hand margin indicate marks

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

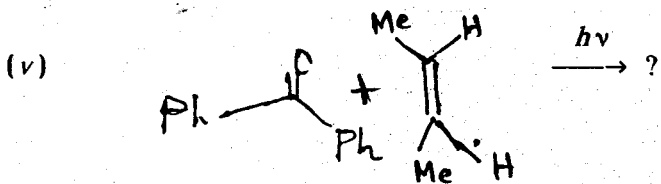
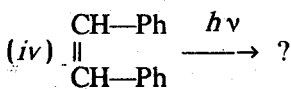
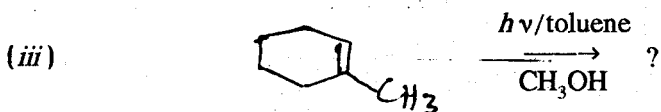
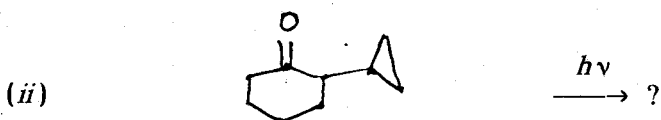
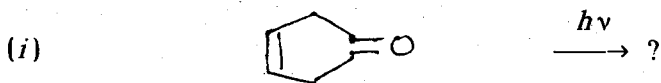
Write the answers to questions of each Group **in separate books**

GROUP-A*(Organic)*

1. (a) What is Jablowski diagram? Show various transitions between ground and excited states initiated through photochemical radiation and explain their significance stating major events occurring on those states. 6
- (b) Predict **the product(s)** of the following **reactipns with mechanism** (attempt any *four*) :

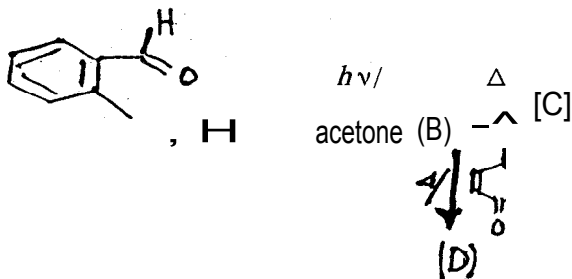
$$\begin{array}{l} 11 \times 4 \\ 2 \end{array}$$
(Turn Over)

(2)



(c) Complete the following transformation :

3



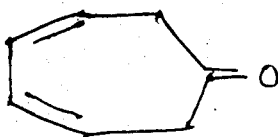
Identify (B), (C) and (D).

2. (a) Explain Norrish type-I and type-II reaction with suitable example.

4

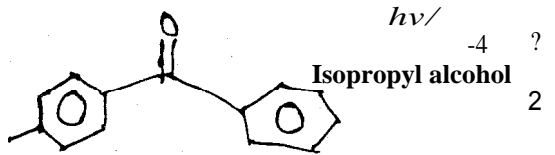
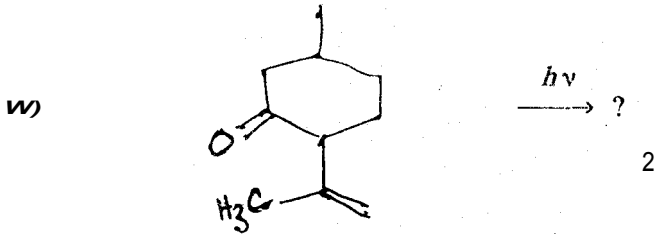
(b) Predict the product(s) of the following reactions with mechanism :

(i)



2

$h\nu$ Sensitizer/ acetone

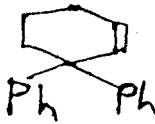


(iv) ? - $h\nu/$
sensitizer



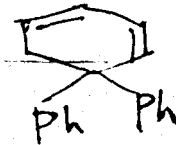
$h\nu/$
direct irradiation
2

(v)

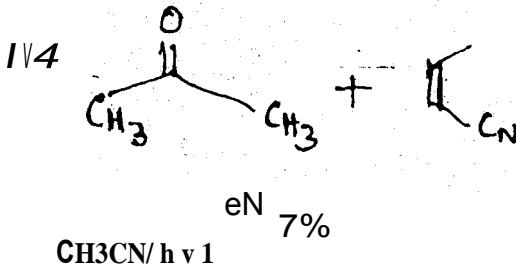


$\xrightarrow{h\nu / \text{sensitizer}}$?
1

Or



by
sensitizer



hν/CH₃CN

3. (a) **How does the curved Hammett plot obtained by plotting logarithms of rate constants of solvolysis of 3-aryl-2-butylbrosylates in acetic acid, obtained by titrating the p-bromobenzene sulfonic acid formed, against the ρ -values of the substituents on the aromatic ring establish the formation of a phenonium ion intermediate.**

(b) **Explain why the Hammett plot obtained in the formation of arylaldehyde semicarbazone in strong acid is linear (with a positive slope) while a curved Hammett plot is obtained when the same reaction is carried out at pH 4.**

5.

(c) **Explain why a Hammett plot with a positive slope indicates that the reaction is accelerated upon electron withdrawal from the reaction centre.**

4. (a) **Discuss the conceptual basis of Yukawa-Tsuno equation and Taft's (30 scale). What are the difficulties encountered in the application of the latter ?**

(b) **In the dediazonation of aromatic diazonium salts the analysis of the reaction rate by the Dual Substituent Parameter treatment leads to the following equation :**

For meta - substituents : $\log k/k_0 = -4.5 \rho + 1.8 \sigma$

For para-substituents : $\log k/k_0 = 3.7 \rho + 2.4 \sigma$

Show how these data indicate that the reaction follows a S_N1 mechanism.

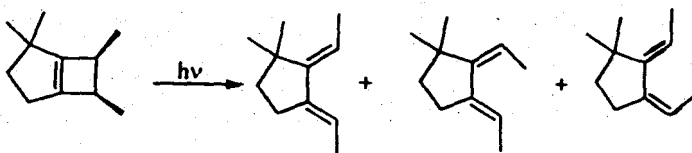
5

- (c) Explain why the Hammett plot for the saponification of methyl benzoate in 60% aq. acetone at 25 °C is linear with a large positive ρ , while the hydrolysis of the ester in 99% H₂SO₄ gives a curved Hammett plot (concave upwards).

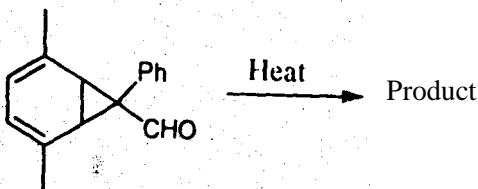
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- S. ('a) In the following electrocyclic ring opening reactions, three isomers are formed *via* allowed processes. Identify the processes.

6



- (b) The product from the following reaction showed the following peaks in ¹H-nmr spectrum : δ 1-43 (s, 3W, 1.52 (t, J1.5Hz, 3H), 3-76 (m, 1H), 5.71 (m, 1H), 5.73. (dd, J10 and 1.5 Hz, 1H), 5.79 (d, J10 Hz, 1 H) , 6-74 (s, 1H). No carbonyl group and cyclopropyl group were present in the product. Give the structure of the product with expected stereochemistry.



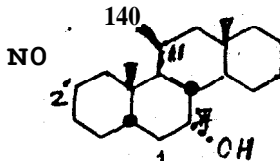
- (c) Using (meso)-3-4-dimethylhexa-1, 5-diene how would you derive at the preferred transition state geometry in Cope rearrangement? 4

GROUP-B

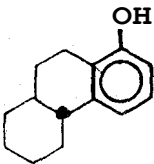
6. Answer any *two*

71 x2
2

- (a) Discuss briefly the relative rates of (i) *acetylation* as well as (ii) *chromic acid oxidation* of the hydroxyl groups present at different positions of the following **compound 1**:



- (b) Complete the following reaction sequence. Justify the relative rates $k_L > k_3$, and different behavior of the ketones 4 and 5 toward base in terms of their conformations.



tat. Y7, Dr
AcON

2 + 3

k2)K3

CyO3
kL

← Base

↓ CrO3
k3
Base
5

(c) (i) Deduce Eyring equation displaying the relationship between equilibrium, constant and specific rate constants of a mobile system. How can you derive it from Winstein-Hoiness equation ?

(ii) The specific reaction rates of *cis-4- t-butyl* cyclohexanol *trans-4- t-butyl*cyclohexanol and *cis-4-methyl*cyclohexanol in their acetylation with Ac₂O/Py at 27 °C are 2.89, 1065 and 3.76 units. (the unit being 10⁻⁵ L mol⁻¹ sec⁻¹). Find out the conformational equilibrium constant of 4-methylcyclohexanol and hence calculate ΔG^\ddagger for its two conformers.

7. (a) (i) Deduce Curtin-Hammett principle from first principles for a case where the more stable conformer gives rise to the predominant product. Explain with an energy diagram. Briefly state the conditions for validity of the C-H principle. 6

(ii) In the base catalyzed elimination of benzyl-phenylcarbinyl 2, 4, 6-triethylbenzoate, PhCH₂CH(Ph).OCOC₆H₂(2, 4, 6-triethyl), the major product : minor product = 100: 1. Find out the energy difference in the transition states and comment on how it reflects the ground state energy difference of the products. 3

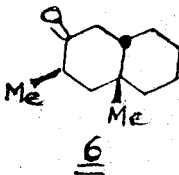
- (b) Draw the molecular conformations of *trans-transoid-trans* and *trans-cisoid,trans* diastereomers of perhydrophenanthrene, and hence comment on their ΔH° (relative enthalpy), relative stability and torsion angle signs at both sides of the ring junctions. Draw the conformation of the enantiomer of the resolvable diastereomer.

6

8. Attempt any *three* :

- (a) Name the compound **6** given below, including absolute-configuration. Predict the sign of the cotton effect that its anomeric conformation will display, by application of the octant projection diagram. What charges will you observe in the ORD curve of its 1-axial bromo derivative? Draw qualitative ORD curves for both and indicate the position of the λ_{max} in each case.

5



- (b) Complete the following reaction sequence and rationalize mechanistically, showing involvement of

the z_c -orbitals in the second step, Designate the absolute configuration of



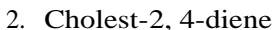
H+

SiO₂

A

(c) Predict the sign of the optical rotation and of the Cotton effect that the following compounds will display by application of relevant rules. Name the rules you apply. Attempt any *two*

5



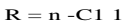
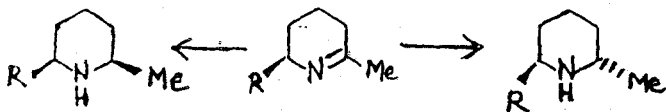
(d) Predict the sign of the Cotton effect that the steroids will exhibit in their CD spectra. Name the rule you have applied and show the nature of the CD curve, the units of the x-axis and the y-axis and the position of the λ_{max} in each case.

(i)	2a, 3(3-dibenzoyloxycholestane
(ii)	613, 7(3-di-p- dimethylaminobenzoyloxy-cholestane.

5

9. Answer any *three* :

- (a) How were the following conversions effected?
Explain in terms of steric and stereoelectronic effects.
Indicate the natural product and **its name**.

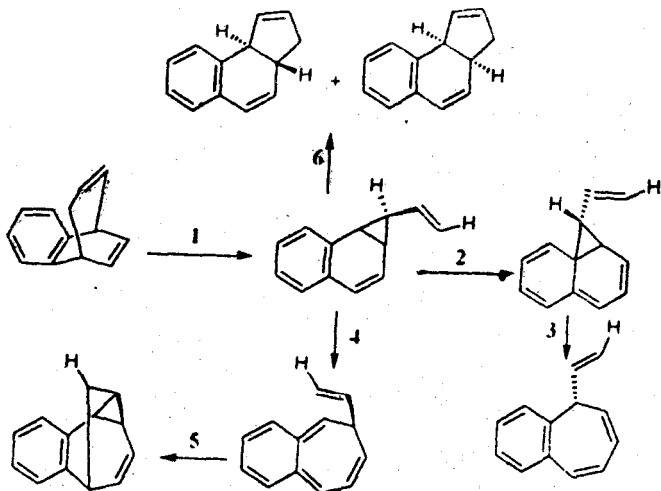


- (b) Comment on the relative rates of saponification of the p-nitrobenzoate esters of *cis*-2-*cis*-decalol and *cis*-2-*trans*-decalol, using Winstein-Holness equation. 5
- (c) Predict and designate the absolute configuration of (-)-*trans*-9-methyl-2-decalone showing negative Cotton effect, by application of the octant rule. Comment on the changes in the ORD curves displayed by its epimeric 1-bromo derivatives.
- (d) *trans*-2-Decalone forms predominantly **the axial** 3-bromo derivative, whereas *cis*-2-decalone forms predominantly the axial I-bromo derivative upon kinetically controlled bromination with Br₂ in acetic acid.

Explain in terms of torsion angle/steric strain
 -whichever is applicable.

10. (a) Identify the thermal reactions involved in steps 1 to 6 in the given example showing clearly the nos. of electrons involved in each step.

13

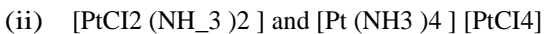
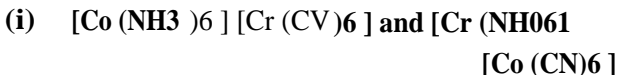


- (b) Although Pericyclic reactions are not supposed to be catalyzed by any chemical reagent yet, use of Lewis acid is known to accelerate the rate of Diels-Alder reaction. Explain the possible reason. 2

Ir³⁺ complex: Snel.1a1) .

GROUP- A

1. (a) What is dpph? Why is it used as a standard in esr studies'? 2+2
- (b) Comment on the number of expected lines in the esr spectra of
- (i) methyl radical
- (ii) [VO (acac)₂] 3+3
- (c) Ni²⁺ is usually esr inactive, while Ni³⁺ is always esr active-Explain. 5
2. (a) Explain whether there will be any orbital contribution to magnetic moment in the following cases-
- (i) d² tetrahedral
- (ii) d⁷ octahedral (high spin) 2+2
- (b) Give a brief account on the magnetic properties of the lanthanides. 6
- (c) Write a short note on spin cross-over region. 5
3. (a) Which type of isomerism is present in the following complexes 3



(b) Cite examples-

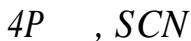
2 x 3

(i) Purely inorganic optically active complex

(ii) Tetrahedral optically active complex

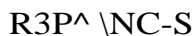
(iii) Square planar optically active complex.

(c)



is less stable but

Pt



is stable—~~Explain.~~

(d) How free macrocycles are obtained from their metal complexes?

4. (a) State the general features of Marcus theory.

(b) How would you account 'energy variation' in transition state during an electron transfer in homonuclear redox system ?

5

(c) Write notes on (any one):

5

(i) Metal ion catalysed reaction

(ii) Effect of π bonding ligand on the rate of **dissociation** of a complex:

5. (a) Using symmetry principle, obtain the state of hybridization and the hybrid orbitals for the central metal ion in $[\text{PtCl}_4]$

(b) Find the sigma ligand group orbitals (LGO) involved for the construction of SALC in the above complex. (Character table for the appropriate point Group will be supplied).

7

GROUP-B

6. (a) What is meant by anisotropic esr spectra ? Show, with appropriate diagrams, the types of anisotropic spectra that are observed for transition metal complexes. Why very low temperature is necessary to observe anisotropic spectrum ?

3+4+2

(b) State with proper reasoning, the type of anisotropic esr spectrum expected for

(i) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and

(ii) $\text{mer-}[\text{Fe}(\text{NO})_3]$.

3+3

7. (a) Comment on the structure of $\text{HPO}(\text{OH})_2$ and $\text{H}_2\text{PO}(\text{OH})$ with reference to NMR spectra.

2

- (b) 'In P_4S_3 molecule one phosphorous is unique'-
Explain. 2
- (c) What are the factors that affect the chemical shift values in photoelectron spectroscopy? 2
- (d) $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ are **isoelectronic and their IR-observed carbonyl absorption are 1860, 2000 and 2095 cm^{-1} respectively** Explain. 2
- (e) The configuration of $I_2Br_2C_{14}$ has been derived from the structure of I_2C_{16} . Explain with the help of **Mossbauer** spectroscopy. 6

8. (a) **What is electric field gradient?**

- (b) What is the condition for a molecule to have electric field gradient? 2
- (c) Why, the nucleus with $I=3/2$, will split into two energy levels corresponding to $m = f/2$, $m = t/2$ 2
- (d) The compound PFC_{14} can **exist in two** different **isomeric forms**. Comment on the ^{35}Cl NQR spectroscopy of those isomeric forms. 4

How quadrupole moment affects Mossbauer spectroscopy?

9. (a) Base hydrolysis, a well known reaction of octahedral complexes, is generally 10⁶ times faster than acid hydrolysis. What can you say about the existence and importance, if any, of a special mechanism for base hydrolysis.

9

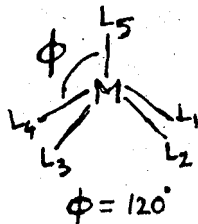
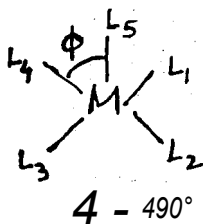
(b) **Starting** from PtCl₄²⁻, how would you prepare **various isomeric forms** of [PtClBr (NH₃) Py] ?

10. (a) Find the ligand group orbitals and their symmetries in [Co (NH₃)₆]³⁺. Obtain the bonding, **antibonding**, **non-bonding** MO and the **qualitative** MO energy level diagram of the above complex. (Character table for the appropriate point group will be supplied.) 5+3+2

(b) Using appropriate character table, depict the **orbital correlation diagram** for the following conversion.

$$\frac{1}{2} \times 2$$

(I) ML₆ (O_h) → 4 ML₅ (C_{4v})



(Physical Special)

GROUP -A

1. (a) **Establish the Newton 's forward difference interpolation formula in modified form. When is it used?** 4+1

(b) Compute

$$\int_0^2 \sin x \, dx$$

using Simpson's one third rule taking $h = 1/4$. 5

- (c) **Find the root of the nonlinear equation $X^3 + X - 5 = 0$ by Bisection method.** 5

Or

Solve by Gauss elimination method

$$\begin{aligned} x_1 - x_2 - x_3 &= 1 \\ 2x_1 - 3x_2 + x_3 &= 1 \\ 3x_1 + x_2 - x_3 &= 2 \end{aligned} \quad 5$$

2. (a) **Derive Hartree-Fock. equations mentioning the essential steps in its derivation.** 10

b) How Hartree-Fock equations can be converted to pseudo eigenvalue form'? Show briefly. 5

3. (a) Show that $|01\ 02\rangle$ and $|1\ 01\ 02\rangle$ are not eigenfunctions of SZ operator but the combination $\frac{1}{\sqrt{2}}(|01\ 02\rangle \pm |1\ 01\ 02\rangle)$ are eigenfunctions of the same operator where $|01\ 02\rangle$ etc represents two particle wavefunction. 10
- (b) Write a note on branching diagram. 5
4. From the consideration of the time dependent perturbation theory show that the probability of finding the system in a state m is proportional to the square of the Fourier transform of the perturbation. 15
5. (a) Show that a non-degenerate hermitian matrix can be diagonalised by the matrix of its eigenvectors. 9
- (b) The Mulliken molecular orbital coefficients for butadiene molecule are given by

$$C_{11} = C_{22} = C_{33} = 0.37,$$

$$C_{12} = C_{13} = C_{24} = -0.60$$

Calculate the electron density q_r , the bond orders R_2 and P_{23} and the free valence indices P and F_2 .

GROUP -B

Either

6. (a) What do you mean by direct product representation of a group ?
Show that the product functions of the bases of IR r and r' can serve as a base function for the direct product representation of the group. 2+8
- (b) What do you mean by linear space. Illustrate with two different examples. 2+3

Or

Find out the symmetry of the normal modes of vibration of H₂O using a basis set of nine Cartesian displacement vectors. Comment on the infrared activity of the normal modes.

(Character table for the appropriate point group is given). 15

7. (a) **Write down the steps involved to find out the symmetry species of the vibrational modes of a non-linear molecule.**
- (b) **Obtain the symmetry species of the vibrational mode of BF₃ .**
(Character table for the appropriate point group will be supplied).

- (c) Using group theoretical principle, obtain the symmetry species of the vibrational mode of CO₂.

(Character table for the appropriate point group will be supplied).

15

8. (a) Prove that

$$F_{hkl} = \sum_{i=1}^N f_i e^{2\pi i (hu_i + kv_i + lw_i)}$$

where the symbols have their usual meanings.

- (b) Justify the phenomena :

(i) A decrease in quantum yield of the reaction $2F \rightarrow F_2$ in the beginning of the irradiation with F light is observed at temperatures below 140 K.

(ii) When KBr is heated in Br₂ vapour, new absorption band is appeared in the UV-region.

- (c) How would you identify a face-centered cubic lattice by calculating geometrical structure factor. $4 + (3+3) + 5$

9. (a) Find out the conditions for occurring maximum diffraction according to the theory of Von Laue.

(b) Write short note on exciton.

- (c) Potassium crystallizes as a body centered cubic lattice, and the length of a unit cell is 533.3 pm. Given that the density of potassium is 0.8560 g cm^{-3} , calculate the Avogadro constants 9+3+3

10. (a) Show that a fcc lattice is the reciprocal lattice of the bcc lattice. 4
- (b) Find the equation involving reciprocal lattice vectors G to show the condition for diffraction and hence find the usual form of the Bragg law from this. 8
- (c) Using Ewald construction explain the diffraction **condition is three dimensions.** 3

PG/II/CHEM/V/07

Relevant Character Tables

Q,P E	2C4	C2	2C3	2C2	I	2S4	all	2a _g	2a _u
A	1	1	1	1	1	1	1	1	1
<i>A_g</i>	1	1	1	-1	-1	1	1	-1	-1
BS	1	-1	1	1	-1	1	-1	1	-1
<i>B=0</i>	1	-1	1	-1	1	1	-1	-1	1
Be	2	0	-2	0	0	2	0	2	0
Ali	1	1	1	1	1	-1	1	-1	-1
<i>A_{1w}</i>	1	1	1	-1	-1	-1	-1	1	1
DIU	1	-1	1	1	-1	-1	1	-1	1
B3	1	-1	1	-1	1	-1	1	1	-1
Br	2	0	-2	0	0	-2	0	2	0

Z,+YZ; z!

1:=

x[^]- y=

xy

(xzc yZ)

(x, y)

