PG/IIIS/CH-301/14

M.Sc. 3rd Semester Examination, 2014

CHEMISTRY

PAPER—CEM - 301

The figures in the right-hand margin indicate marks

(*Organic Special*)

[*Marks* : 40]

Time : 2 hours

Answer any **five** questions

1. (*a*) How many chiral centers are there in 9, 10-dimethyl decalins ? Write 3d structures of those conformers and show in them the *gauche-butane* interactions. 4

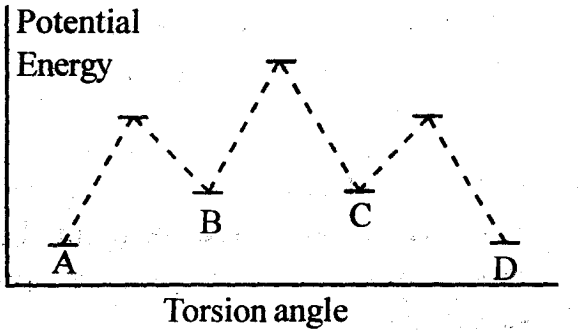
(*b*) Draw the 3d structures for the following conformers and show in them different steric interactions and comment on their chiralities : 4

(*i*) cis-transoid-cis perhydroanthracene

(*ii*) trans-cisoid-cis perhydrophenanthrene.

2. (*a*) The observed rotation of a 0·3 g of cholesterol in 15 ml of $CHCl_3$ contained in 10 cm long polarimeter tube is $-0{\cdot}78°$. Calculate specific rotation of cholesterol. When (+)-cholesterol was mixed to the above (–)-cholesterol, the mixture had a specific rotation of 13°. What is the fraction of the (+)-cholesterol ? 4

(*b*) The following is the energy profile drawing of 1, 1-dibromo-2-methylpropane, draw the appropriate Newman conformations of A, B and C. 4



(*Continued*)

3. Write in brief about the following terms (any *four*) : 2 × 4

   (*i*) ORD

   (*ii*) CD

   (*iii*)Cotton Effect (CE)

   (*iv*)Predict the CE as positive or negative of 9-Methyl-deca-3-ones

   (*v*) Cieplak Model.

4. Write all the possible streoisomers of perhydrophenanthrenes and correlate them with perhydrodiphenic acids by epimerization protocols. 8

5. Draw the 3d structures for the following conformers and show in them different steric interactions : 2 × 4

   (*i*) *cis*-Decalin

   (*ii*) *trans*-Decalin

   (*iii*) *cis*-1, 2 dihydroxy Cyclohexane

   (*iv*) *trans-transoid-trans*-Perhydroanthracene.

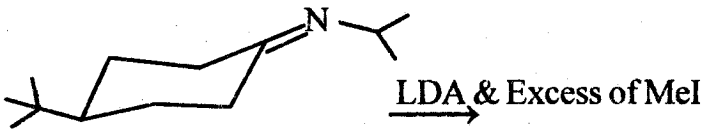
6. Answer the following : 2 × 4

(*a*) What is a symmetry forbidden reaction ? Explain by taking the example of ethene under thermal as well as photochemical conditions.

(*b*) How can you account for the opposite stereochemistry in the photochemical cyclization of a 1, 3-butadiene to a cyclobutene than the thermal reaction ?

(*c*) Why thermal [1, 3] sigmatropic migrations of hydrogen are unknown ?

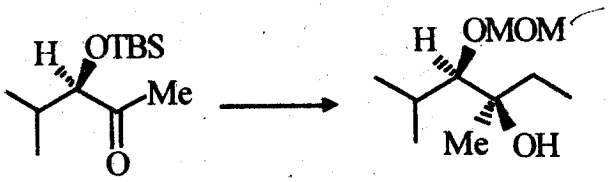
(*d*) Predict the product(s) with appropriate reasoning :



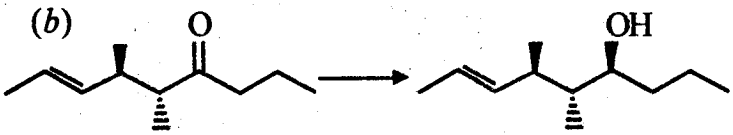
7. For each of the following transformations, clearly explain the basis for the observed selectivity. For full credit, show reagents, key

conformations, transition states, and/or reactive intermediates to support your agruments. Be specific : 2 × 4

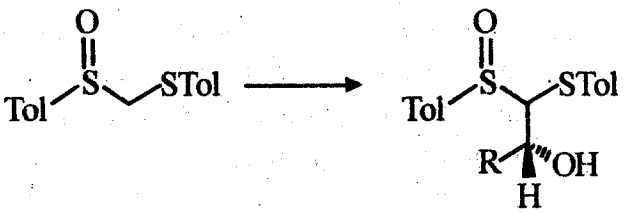
(*a*)



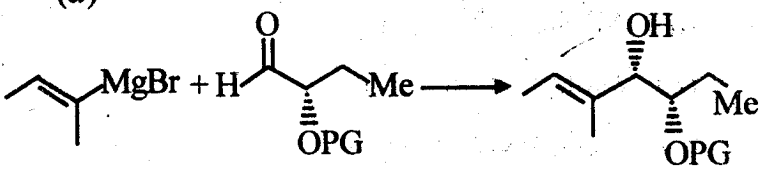
(*b*)



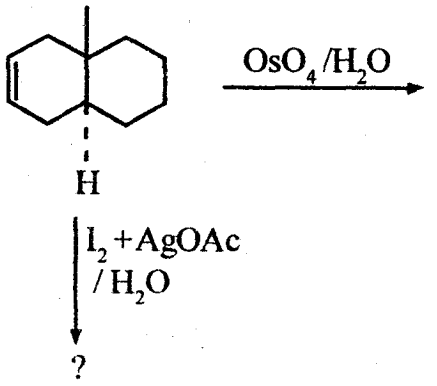
(*c*)



(*d*)



8. (*a*) Predict the product(s) with plausible mechanism : 4



(*b*) Write all the possible conformational structures for 2, 2, 3, 3 tetramethyl *n*-butane and draw the energy profile diagram showing the rotation between $C_2 - C_3$ bond in Newman Projection structures. 4

9. Write in brief with one example in each case : 8

(*a*) Allylic 1, 2-strain

(*b*) 2-alkylketone effect

(*c*) 3-alkylketone effect

(*d*) Allylic 1, 3 strain.

(*Inorganic Special*)

[*Marks* : 40]

Time : 2 hours

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

GROUP – A

1. Applying group theory justify that electrocyclic reaction of *cis*-butadiene must occur via conrotatory mechanism under thermal condition but disrotatory mechanism under photochemical condition. (Given below the character table and correlation table). 8

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{2v}	C_2	$\sigma(xz)$ C_s	$\sigma(yz)$ C_s
A_1	A	A'	A'
A_2	A	A''	A''
B_1	B	A'	A''
B_2	B	A''	A'

2. Find out the effect of polarization of incident radiation in the electronic transition of $[Cr(C_2O_4)_3]^{3-}$. (Given below the character table and correlation table). 8

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

O_h	D_3
A_{2g}	A_2 (ground state)
T_{1g}	$A_2 + E$
T_{2g}	$A_1 + E$

3. With the help of group theory determine the symmetries of the group of orbitals of hydrogen atoms which are effective for σ–bond formation in H_2O molecule. Constract a qualitative σ–bonding molecular orbital energy level diagram for H_2O molecule. Show that for water only one $n \rightarrow \sigma^*$ electronic transition is possible. Find out the polarization of incident radiation for this transition. (Use the character table of C_{2v} point group given in *Question No.* 1). 2 + 2 + 2 + 2

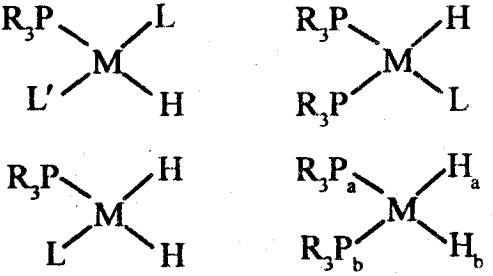
4. (*a*) Use group theoretical principle to determine the symmetry of vibrational mode of mer-$[ML_3X_3]$ molecule using cartesian coordination method. Identify the symmetry of IR and Raman active mode in this molecule. (Use the character table of C_{2v} point group given in *Question No.* 1). 4

   (*b*) Why do the configurations d^n and d^{10-n} give identical ligand field terms in any given field symmetry ? 2

(*c*) Show that the d-orbital whose angular wave function is constant times ($\sin^2\theta \cos 2\phi$) is $d_{x^2-y^2}$ orbital. 2

GROUP – B

5. (*a*) Draw ^{1}H NMR spectra for the square planar metal complexes given below. (M, L and L' are non magnetic.) 3



(*b*) What is the solvent effect on chemical shift in NMR-spectroscopy for main group hydrides ? 2

(*c*) How many types ^{1}H NMR signal are found for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$? What is the temperature effect on ^{1}H NMR spectra of trimethylaluminium dimer ? 1 + 2

6. (*a*) Draw ^{19}F NMR spectrum for IF_5 and ^{31}P NMR spectrum for $[H_2P_2O_5]^{2-}$ ion, indicating stick diagram for each. 2

(*b*) Two peaks at 1·8 and 2·8 ppm in proton NMR spectra are recorded in 400 MHz spectrometer. What is the peak to peak separation in Hz ? Draw ^{31}P NMR spectrum for $[Rh(PR_3)_5]^+$ indicating stick diagram. 1 + 2

(*c*) Discuss the ^1H NMR spectra of $NaBH_4$. 3

7. (*a*) Explain the ^1H NMR spectra of terminal and bridging protons in $^{11}B_2H_6$. 3

(*b*) ^{11}B NMR spectra of $B_{10}H_{14}$ consist of four different peak. Assign the peaks. 2

(*c*) Predict the ^{11}B NMR spectra of B_5H_9. 3

8. (*a*) Write down the number of signals obtained from ^{19}F NMR of BF_4^- in D_2O with proper explanation. 3

(*b*) Show the ^1H NMR spectra of mer-$IrCl_3(PMe_2Ph)_3$. 3

(*c*) Show the ^1H NMR spectra of $Na_2[HV(CO)_5]$. 2

(*Physical Special*)

[*Marks* : 40]

Time : 2 hours

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

GROUP – A

1. (*a*) Define Absolute error, Relative error and Percentage error. Round-off the numbers correct to 4-significant figures : 0·34026, 2·5555. 3 + 2

   (*b*) Evaluate

$$\int_0^1 (4x - 3x^2)dx,$$

   taking 10 intervals, by Trapezoidal rule. 5

2. (*a*) What is meant by matrix representation of operators ? Show with examples. 5

(*b*) Derive the matrix representation of Schrödinger equation. 5

3. Derive the matrix representation of $\hat{S}_x$ and $\hat{S}_y$ operators. 5 + 5

4. Describe Hartree SCF method and show the expression of the total energy in terms of Hartree orbital energy. 10

GROUP – B

5. Derive Hartree-FUCK equations and convert it to the Pseudoeigenvalue form. 7 + 3

6. (*a*) Find the normalisation constant for a 2N electronic system considering a Slater determinantal representation. 5

(*b*) Write notes on K_{ii}. 5

7. Write a short note on projection operator. Use projection operator to obtain the SALC of hydrogen 1S orbital of NH_3 which can be used as

approximate solution to bond with nitrogen atomic orbital.

Following is the character table of C_{3v} point group. 10

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

8. (*a*) Show that each non-degenerate MO of a molecule belonging to a particular point group serves as a basis for one dimensional IR of the point group.

(*b*) How does group theory help in determining zero and non-zero value of Integrals ? 10