M.Sc. 3rd Semester Examination, 2011

CHEMISTRY

PAPER—CEM-301.

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Organic Special*)

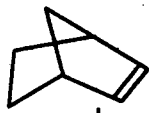
Answer any **five** questions taking at least **two** from each Group

GROUP – A

1. (*a*) Show various transitions between excited and ground states of organic molecules in a Jablouski diagram and identify their importance in photochemical reactions. 6

(*b*) Predict the product/s of the following reactions with mechanism (attempt *one* only) : 2 × 1

(*i*)

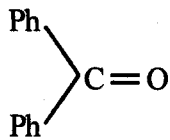


$h\nu$/benzophenone → ?

$h\nu$/acetone

?

(*ii*)

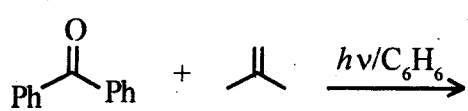


$h\nu$/ trans-butene/ cis-butene → ?

2. What is Paterno-Büchi addition reaction ? Explain the mechanism of the reaction with suitable example and also predict the products of the following reactions with mechanism (attempt any *two*) : 4

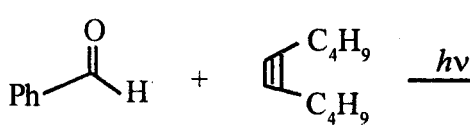
(*i*) $(CH_3)_2CO + CH(CN)=CH(CN) \longrightarrow$ 2

(*ii*) (*a*)

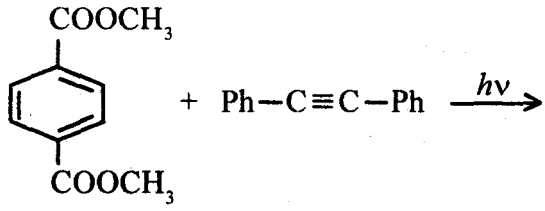


1

(*b*)

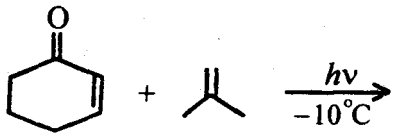


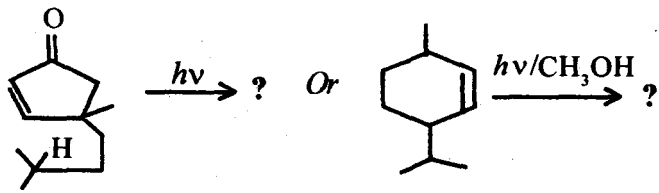
1

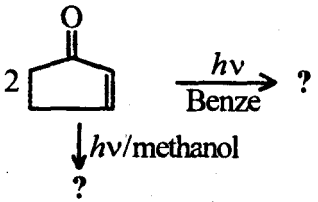
(*iii*) 

2

3. Predict the product of the following reactions with plausible mechanism: 3 + 2 + 3

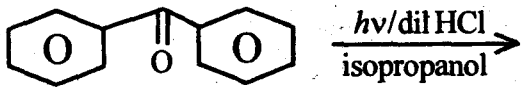
(*i*) 

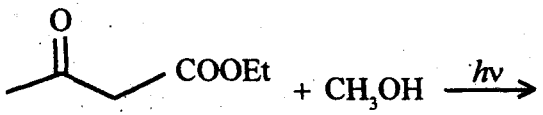
(*ii*) 

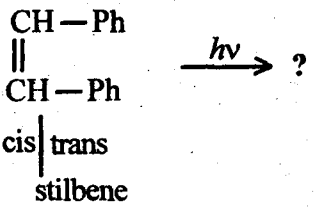
(*iii*) 

4. (*a*) Mischler's ketone does not undergoes photo-reduction under the same condition at which benzophone absorbs. Explain. 4

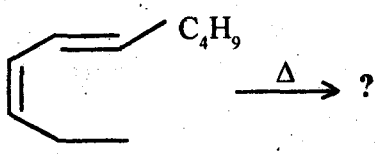
(*b*) Predict the product/s with mechanism (attempt any *two*) : 4

(*i*) 

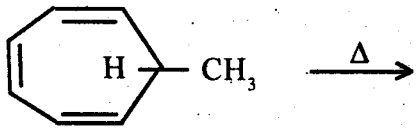
(*ii*) 

(*iii*) 

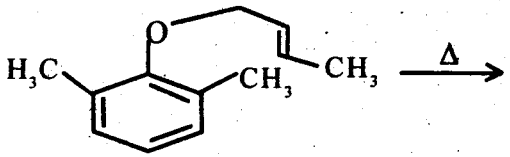
5. What is (*i, g*) sigmatrofic shifts ? Explain with examples end hence predict the product/s of the following reactions with mechanism (attempt any *three*) : 2 + 3 × 2

(*i*) 

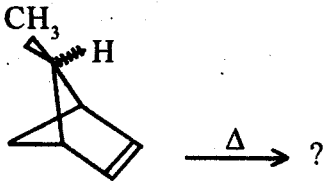
(*ii*)



(*iii*)

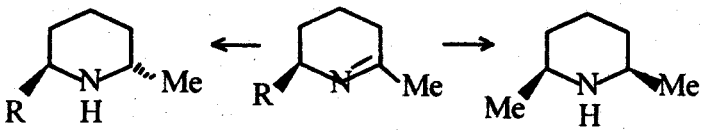


(*iv*)



GROUP – B

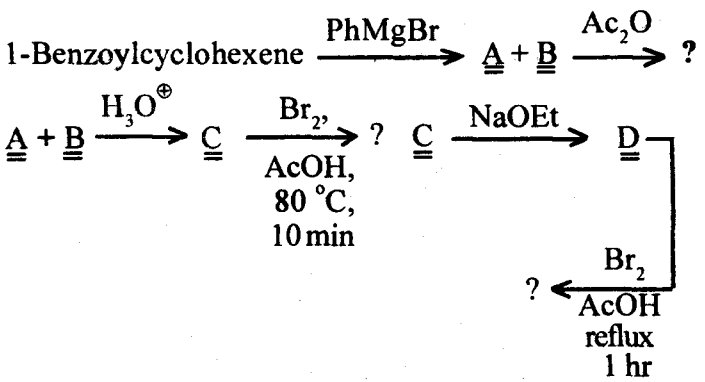
6. (*a*) How can you effect the following conversions ? Explain in terms of steric and stereoelectronic effects involved. Indicate and name the natural product. 4



R = n–$C_{11}H_{23}$

(*b*) How can you convert the more stable diastereomer of ethyl-4-*t*-butylcyclohexanone completely into the less stable one ? Explain the reactions involved. 4

7. Complete the following reaction sequence explaining in terms of stereoelectronic and steric effects, wherever necessary : 8



8. (*a*) Deduce the Eliel equation showing the relationship between equilibrium constant and different specific rate constants of a mobile system. How can you derive Winstein-Holness equation from the first principle and also from the Eliel equation ? 6

(*b*) Comment on the optical activity of *cis*-decalin and its 1- or 2- substituted derivative. 2

9. (*a*) Delineate the symmetry elements of *cis*-decalin and *trans*-decalin and write their point groups. 3

(*b*) Write down the conformers of both enantiomers of *cis*-1-decalone-, indicate the torsion angle signs at the ring junction (both sides) of each and hence label each conformer of each enantiomer as in steroidal or non-steroidal form. 5

10. (*a*) *cis*-2-Decalone upon bromination with bromine in acetic acid forms predominantly the axial-1-bromo derivative. Explain the fact in terms of mechanism, steric and stereoelectronic factors involved. 4

(*b*) (S)-Methylethynyl-*t*-butylcarbinol when treated with $SOCl_2$ in dry ether in *presence or absence of pyridine* produces the same product, though following different mechanisms. Show the mechanisms involving the π-orbitals, and name the product specifying its absolute configuration. 4

(*Inorganic Special*)

Answer any **four** questions

1. (*a*) With the help of group theory determine the symmetries of the group of orbitals of *F* atoms which are effective for σ-bond formation in PF_5 molecule. Construct a qualitative σ-bonding molecular orbital energy level diagram for PF_5 molecule. From this molecular orbital energy level diagram comment about the π-acid nature of PF_5 molecule. (Given below the character table for D_{3h} point group). 8

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$2\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	-2	1	0	(R_x, R_y)	(xz, yz)

(*b*) Show that the *f*-orbital whose angular wave function is constant times $(\sin^2\theta \cos\theta \sin 2\phi)$ is f_{xyz} orbital. 2

(*Continued*)

2. (*a*) Find out the effect of polarization of incident radiation in the electronic transition of $[Cr(C_2O_4)_3]^{3-}$. (Given below the correlation table and character table). 7

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

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

(*b*) With the help of group theory find out the hybridization of carbon atom in CH_4 molecule. (Given below the character table for T_d point group.) 3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma'_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

3. (*a*) Why NMR experiment is generally carried out at very low temperature ? 2

(*b*) Calculate the angular momentum and magnetic moment values for a proton. (Given : $g = 5{\cdot}585$, $h = 6{\cdot}626 \times 10^{-34}$ J.s., $m_p = 1{\cdot}673 \times 10^{-27}$ kg). 3

(*c*) Express the energy of an spin half nucleus in presence of a magnetic field. Explain why the energy of α-spin $\left(m_S = +\frac{1}{2}\right)$ of nucleus decreases linearly whereas that of β-spin $\left(m_S = -\frac{1}{2}\right)$ increases with the increase in the external magnetic field. 5

4. (*a*) Use group theoretical principle to determine the symmetry of vibrational mode of cis-N_2F_2 molecule using Cartesian coordinate method. Identify the symmetry of IR and Raman active

mode in this molecule. (Given below the character table for C_{2v} point group). 5

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

(*b*) Establish the relation 5

$$\chi(\alpha) = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin \alpha/2}$$

where the term have usual significance.

5. Establish a correlation diagram for a d^2 ion in an octahedral environment. (Given below the character table for O_h point group). 10

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

6. (*a*) What type of structural information we can predict from NQR spectra ? Explain the NQR spectra of phosphorous pentachloride. 2 + 2

(*b*) Draw and explain IR spectrum of $(C_5H_5)_2Fe_2(CO)_4$ molecule. 3

(*c*) Justify the IR frequencies of the following silver cyanide complexes. 3

$[Ag(CN)_4]^{3-}$ 2135 cm^{-1}

$[Ag(CN)_3]^{2-}$ 2105 cm^{-1}

$[Ag(CN)_2]^{-}$ 2092 cm^{-1}

7. (*a*) Draw the UV-PE spectra of crystalline MnF_2 and FeF_2 and explain the characteristics features. 2 + 2

(*b*) How many fundamental vibrations you will expect for CO_2 molecule ? Draw all the vibrational modes. 2

(*c*) Why IR frequencies of Platinum carbonyl complexes decrease in the order. 2

$$\text{cis-}[\,Pt(CO)_2Cl_2] > [\,Pt(CO)_4]$$

(*d*) Explain why IR frequency of $C \equiv N$ bond of $[Mn(CO)_3(NC-CH_2-CH_2-CN)\,Cl\,]$ is at 2068 cm^{-1} whereas the IR frequency for the same bond in free succinonitrile is at 2257 cm^{-1}. 2

(*Physical Special*)

GROUP – A

Answer any *two* of the following

1. (*a*) Round off the following numbers correct upto 4-significant figures : 2

(*i*) 56·243827

(*ii*) 0·235082

(*b*) Write down the approximate value of $\pi/4$ correct upto 4-significant figure and then find 3

(*i*) Absolute error
(*ii*) Relative error
(*iii*) Relative percentage error.

(*c*) Calculate $f(1{\cdot}6)$ where 5

x	1·0	1·5	2·0	2·5	3·0
y	0·11246	0·14032	0·16800	0·19547	0·22270

2. (*a*) Define: 5

(*i*) Nilpotent matrix
(*ii*) Idempotent matrix
(*iii*) Inverse of a matrix
(*iv*) Trace of a matrix
(*v*) Diagonal matrix.

(*b*) Derive the matrix representation of $\hat{L}^2$ using Y_{lm} as the basis function with $l = 1$. 5

3. (*a*) Calculate the ground state electronic energy of He and Li atom using independent particle model. 5

(*b*) Show that Koopman's theorem is valid for Hartru self-consistent theory. 5

(*Continued*)

4. Describe few experiments which need to introduce the hypothesis of electronic spin. 10

GROUP – B

Answer any *two* of the following

5. (*a*) What do you mean by linear function space ? Illustrate with an example. Obtain the transformation matrix which transform the *n*-dim base vectors $(e_1, e_2 \ldots e_n)$ into its prime set $(e_1', e_2' \ldots e_n')$. 3 + 4

   (*b*) What do you understand by linear subspace and linear product space ? 3

6. (*a*) Eigen vector matrix that diagonalism a Hermitian matrix is unitary in nature. Explain.

   (*b*) Show that the set of *n*-degenerate orbitals form a bais for the representation of an *n*-dimensional IR of the point group to which the molecule belongs. What do you understand by accidental degeneracy ? 3 + 5 + 2

7. (*a*) Find out the value of S_α and $S^2\alpha$ using their matrix representation. 5

   (*b*) For a given space orbital φ_1 construct an anti-symmetric two electron wavefunction and show that it is an eigenfunction $\hat{S}_z$ operator. 5

8. Derive the Hartru-Fock self consistent field (SCF) equations. 10