M.Sc. 3rd Semester Examination, 2012

CHEMISTRY

PAPER—301

The figures in the right-hand margin indicate marks

(*Organic Special*)

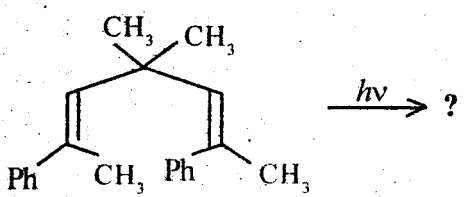
[*Marks* : 40]

Time : 2 hours

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

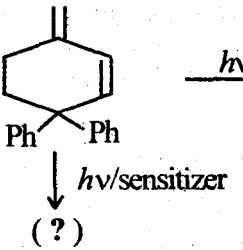
GROUP – A

1. (a) **What is Di-π methane rearrangement reaction ? Predict the product of the following reaction showing mechanistic path with F.O.I. (Frontier-Orbital interaction) :** 4



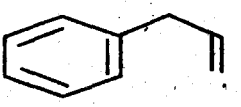
(*b*) What happens when treated as follows :

(*i*)



2

(*ii*)



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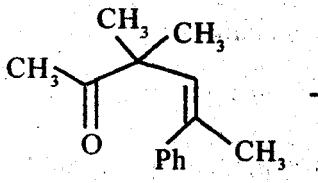
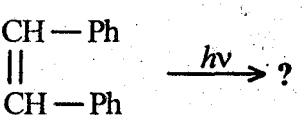
(*iii*)



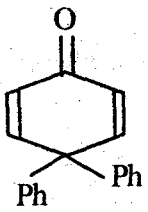
1

2. Predict the product/s of the following reactions showing mechanism in each case (attempt any *two*) and explain the path way : 4 × 2

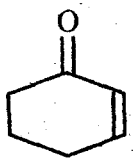
(*i*)



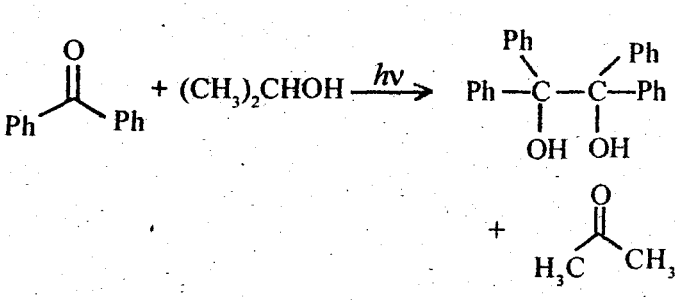
(*ii*)



(*iii*)



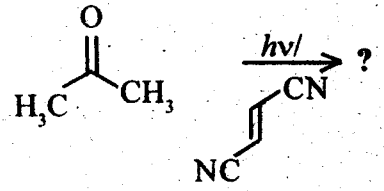
3. (*a*) The following reaction undergoes as follows :



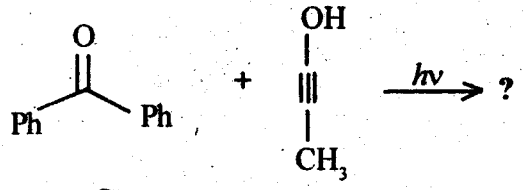
with the quantum yield, $\phi = 1$. Explain the mechanistic path validating this observation. 4

(*b*) Predict the product/s of the following reaction indicating plausible mechanism (attempt any *two*): 2 × 2

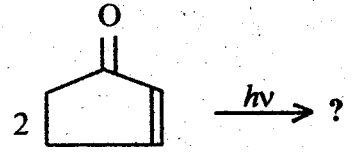
(*i*)



(*ii*)

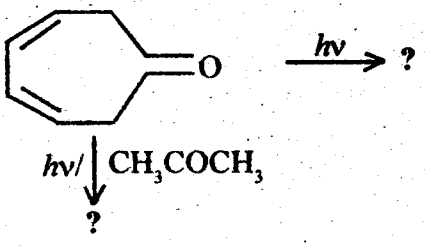


(*iii*)



4. Predict the product/s of the following reaction indicating probable mechanistic pathway:

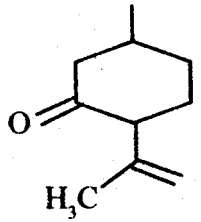
(*i*)



3

(*Continued*)

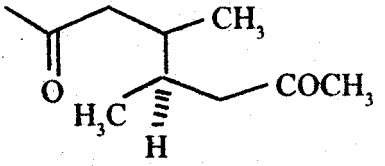
(*ii*)



$\xrightarrow{h\nu/}$?
cyclohexanone

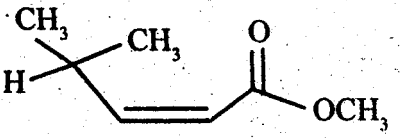
3

(*iii*)



$\xrightarrow{h\nu}$ 2

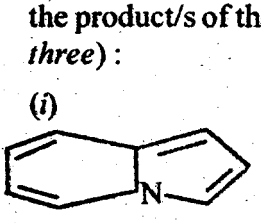
Or



$\xrightarrow{h\nu/n\text{-pentane}}$?

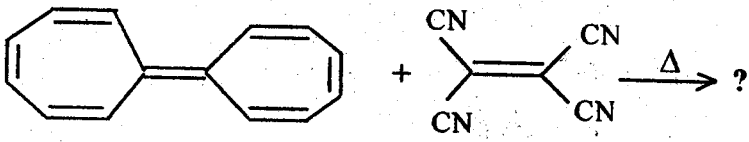
5. What are supra and antara additions in cycloaddition reaction ? Explain with examples and hence predict the product/s of the following reactions (attempt any *three*) : 2 + 2 × 3

(*i*)

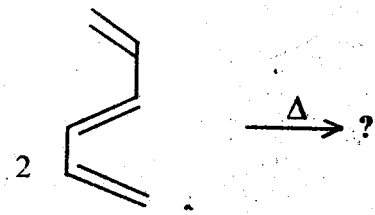


$+ H_3CO_2C{\equiv}{-}CO_2CH_3 \xrightarrow{\Delta}$?

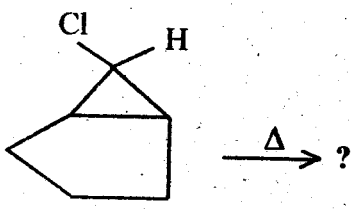
(*ii*)



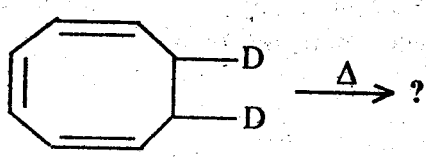
(*iii*)



(*iv*)



(*v*)



(*Continued*)

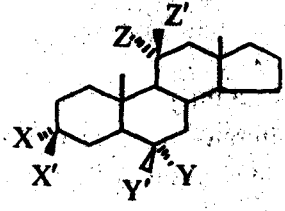
GROUP – B

6. 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

7. (a) Write down the conformers of 9(*s*), 10(*R*) 9-methyl *cis*-2-decalone, give the sign of torsion angles of ring junction in both rings, and mention the steroidal and nonsteroidal conformer. 5

(b) Comment on the symmetry and chirality of *cis*-decalin. 3

8. (a) Predict the relative rates of chromic acid oxidation of the following steroidal alcohols and justify your prediction : 4



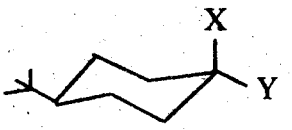
(I) : X = Y = Y′ = Z = Z′ = H; X′ = OH

(II) : X = X′ = Y = Z = Z′ = H; Y′ = OH

(III) : X = X′ = Y = Y′ = Z = H; Y′ = OH

(IV) : X = X′ = Y = Y′ = Z′ = H; Z′ = OH

(*b*) Compare relative rates of saponification of the following esters : (*A*) vs (*A'*), and (*B*) vs (*B'*). Comment on the relative ratio of rate constants $k_A/k_{A'}$ and $k_B/k_{B'}$ 4



(A) : X = H; Y = $-CO_2Ph$

(A') : X = CO_2Ph ; Y = H

(B) : X = H ; Y = –OCOPh

(B') : X = –OCOPh ; Y = H

9. (*a*) Write the two conformers of (*s*)-enantiomer of $\Delta^{1,9}$-octalin. Draw Newman projection showing torsion angle of ring junction (both sides) in each conformer. 4

(*b*) *Trans*-2-decalone has a tendency to enolise to give 2, 3-double bond whereas *cis*-2-decalone prefers enolisation to give 1,2-double bond. Explain this observation. 4

10. (*a*) *cis* and *trans*-isomers of 4-*test* butyl-2-nitro-1-phenyl cyclohexene are equilibrated in presence of base. Which one predominates and why ? 2

(*b*) Convert *cis*-2, 4-dimethylcyclohexane into *trans*-1, 3-dimethylcyclohexane. Explain the reactions involved. 3

(*c*) Draw two conformers of each of the *anti* and *syn*-isomers of 2-methyl cyclohexylidene acetic acid. State which conformer is state in each case, and explain your answer. 3

(*Inorganic Special*)

[*Marks* : 40]

Time : 2 hours

Answer any *four* questions

1. With the help of group theory determine the symmetries of possible combinations of atomic orbitals of carbon atoms which one effective for π-bond formation in cyclobutadiene. Using projection operator method find out the appropriate SALCs for these symmetries. Construct qualitative π-molecular orbital energy level diagram for cyclobutadiene molecule and explain why it is an extremly unstable molecule. Although cyclobutadiene is unstable, (cyclobutadiene) $Fe(CO)_3$ is a stable molecule – explain. (Given below the character table and correlation table).

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Correlation table

D_{4h}	C_{4v}
A_{2u}	A_1
B_{2u}	B_1
E_g	E

2 + 3 + 2 + 3

2. (*a*) Using group theoretical principle construct qualitative 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. (Given below the character table for C_{2v} point group) 2 + 3 + 1

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*) Determine the symmetry of vibrational mode of *cis*-1,2 dichloroethylene molecule using cartesian coordinate method. Identify the symmetry of IR and Raman active mode in this molecule. 3 + 1

3. Applying group theory justify that electrocycle reaction of *cis*-butadiene must occur via conrotatory mechanism under thermal condition but disrotatory mechanism under photochemical condition. (Use the character table of C_{2v} point group given in *Question No. 2*. Given below the correlation table). 10

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

4. (*a*) Establish the relation

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

where the term have usual significance. Use group theoretical principle to obtain the splitting of *d*-orbitals of a transition metal ion in a square planar environment. Following is the character table for rotational subgroup "D_4". 5 + 3

D_4	E	$2C_4$	$C_2(=C_4^2)$	$2C'_2$	$2C''_2$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	z, R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

(*b*) Show that the *d*-orbital whose angular wave function is constant times $(3\cos^2\theta - 1)$ is d_{z^2} orbital. 2

5. (*a*) Two peaks in a proton NMR spectrum recorded at 100 MHz occur at 4·1 and 4·2 ppm. What is their separation in Hertz ? 2

(*b*) What would be the splitting pattern of IF_5 in ^{19}F NMR spectrum ? Give reason. 3

(*c*) What would be the appearence of the ^{31}P NMR of $[H_2P_2O_5]^{2-}$ ion. 3

(*d*) Explain the proton NMR of $^{11}BH_4^-$ and $^{10}BH_4^-$ ions. 2

6. (*a*) Show the splitting pattern of $HP(O)F_2$ in ^1H, ^{19}F and ^{31}P NMR spectrum. Given that $^1J_{PH} = 880$ Hz, $^1J_{PF} = 1110$Hz and $^2J_{FH} = 115$ Hz. 3

(*b*) Using ^1H, ^{19}F and ^{31}P spectra write down the structure of HOP(O)FH. Given

$^1J_{PH} = 780$ Hz, $^1J_{PF} = 1030$ Hz and $^2J_{FH} = 115$ Hz. 3

(*c*) Which of the following molecule would show (*i*) microwave (rotational) spectrum (*ii*) an infrared (vibrational) spectrum ?

$$Br_2,\ HBr,\ CS_2,\ \text{and}\ CO_2$$

Justify your answer with proper explanation. 4

7. (*a*) Define with suitable example, (*i*) Symmetric top molecule and (*ii*) Asymmetric top molecule. 2

(*b*) The rotational constant (*B*) for $H^{35}Cl$ is observed to be 10·5909 cm^{-1}. What are the values of *B* for $H^{37}Cl$ and for $^2D^{35}Cl$. 3

(*c*) The vibrational wave numbers of the following molecules in their $v = 0$ (ground states) are : HCl 2885 cm^{-1}; DCl 1990 cm^{-1}; D_2 2990 cm^{-1} and HD 3627 cm^{-1}. Calculate the energy change in KJ mol^{-1} of the reaction. Determine whether energy is liberated or adsorbed

$$HCl + D_2 \longrightarrow DCl + HD$$ 5

(*Physical Special*)

[*Marks* : 40]

Time : 2 hours

Answer any *four* questions taking *two* from each Group

GROUP – A

1. (*a*) Round off the number to correct upto 4 significant figures.

55·143833, 0·335082. 2

(*b*) Write down the approximate value of 1/3 and hence find 3

(*i*) Absolute error

(*ii*) Relative error

(*iii*) Percentage error.

(*c*) Calculate $f(1{\cdot}2)$ 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*) What is meant by matrix representation of operators ? 5

(*b*) Derive the matrix representation of $\hat{S}_z$ operator. 5

Or

Show that a nondegenerate Hermitian matrix can be diagonalized by the matrix of its eigen vector. 10

3. Derive the expression for the total electronic energy of a many electron system in terms of orbital energy at the Hartree SCF level. 10

4. Show the essential steps to derive the expression for total electronic energy of a 2N electron system in a closed shell configuration. 10

GROUP – B

5. (*a*) State and describe antisymmetric principle. 5

(*b*) Write a note on projection operator. 5

6. Using two non-degenerate orthonormal space orbitals ϕ_1, ϕ_2 construct all possible wavefunctions and convert them to slater determinants (show each step). 10

7. (*a*) What do you mean by Linear subspace and Linear product space ? 2 + 2

(*b*) Show that the direct product matrices of a point group also form a representation of that point group. 6

8. What is accidental degeneracy ? Obtain the symmetry of the splitted *d*-orbital of a transition metal ion when it is placed in an octahedral environment.

Character table for '*O*' group is given below. 2 + 8

O	*E*	$6C_4$	$3C'_2$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	-1	1	1	-1		
E	2	0	2	-1	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	1	-1	0	-1	(R_x, R_y, R_z); (x, y, z)	
T_2	3	-1	-1	0	1		(xy, yz, zx)