2014

M.Sc. Part–II Examination

CHEMISTRY

PAPER—V

Full Marks : 75

Time : 3 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) Define inverse of a matrix.

Show that two matrices A, B, obey the following relation :

$$(AB)^{-1} = B^{-1}A^{-1}.$$ 2+3

(b) Derive the matrix representation of $\hat{L}_+$ and $\hat{L}_-$ operators using the basis set Y_{lm}, where $l = 2$. 10

2. (a) State and prove the Eekart's theorem for the ground state of a system. 5

(b) With the help of Huckel theory find out the energies of π-MO of butadiene. Also express the total energy of the system in terms of bond order and charge density. 6+4

3. (a) Discuss the basic concept of perturbation theory. 3

(b) Derive an n-th order perturbation equation. Also find out the expression of mixing co-efficient of two un-perturbed orbitals in 1st order approximation. 6+6

4. (a) Write down the Hamiltonian for N-electrons systems. Why is it not exactly solvable ? 5

(b) Discuss the Hartee's 'Self Consistent Field' method to obtain the one electron wave function from many electron system. 10

5. (a) Show that the transpose of the product of two matrices A & B obey the following rule : 6

$$\bar{AB} = \tilde{B}.\tilde{A}$$

(b) Considering the orbital energy ϵ_i for one electron wave function i in Hartee's 'Self Consistant Field' method, calculate the total energy of the N-electron system. 9

Group—B

6. (a) (i) Round-off the numbers correct to 4-significant figures :

0.24468145, 2.011500, 0.000421685, 0.56985875.

(ii) Write the approximate value of $\frac{1}{3}$ and hence find the absolute error, relative error and relative percentage error. 2+3

(b) Given :

x	:	1	2	3	4	5	6	7	8
f(x)	:	1	8	27	64	125	216	343	512

Construct the difference table and hence find f(1.5). 2+3

(c) Evaluate $\int_0^1 (4x - 3x^2)dx$, taking 10 subintervals, by Simpson's $\frac{1}{3}$ rule. 5

7. (a) How can you determine crystal structure using Bragg's law? 5

(b) State and prove Laue equation. 6

(c) Discuss Hall Effect in metal or n-type semiconductor. 4

8. (a) Calculate the Frenkel defect concentration in a crystal. 4

(b) Calculate the geometrical structure factor (F_{hkl}) for bcc lattice. 4

(c) Mention the reasons due to which a potential barrier is developed across a p–n junction. 4

(d) How does conductivity of a semiconductor depend on temperature and why? 3

9. (a) Define linear space. Show that the direct product matrix form a representation of the point group. 1+3

(b) Find the point symmetry group and the symmetry operation present for the following molecules : 4

(i) H_3BO_3, (ii) SO_2, (iii) CH_2Cl_2, (iv) NH_3.

(c) Use the group theoretical principle to obtain the state of hybridisation of the central atom in CH_4. Use the following characters table for CH_4 : 7

	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)

10. (a) With the help of group theoretical principle, find the nature of splitting of α-orbitals of a central metal atom when it is placed in an octahedral environment. Following is the character table for 'O' group : 8

	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)

(b) Use group theoretical principle to obtain the symmetry of vibrational modes in water molecule. Given below the character table for water molecule : 7

	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

(*Organic Special*)

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

Group — A

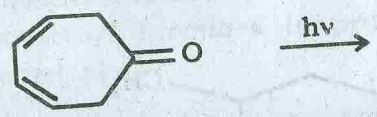
1. (a) What is Jablonski Diagram? Show different transitions between ground and excited states initiated through photochemical excitation stating major events occurring on those states. 6

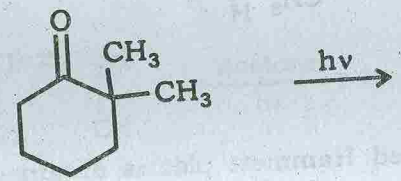
   (b) How 'energy transfer' occurs in excited state molecules? Explain with example. Define 'Intersystem Crossing' with proper example. 3+2

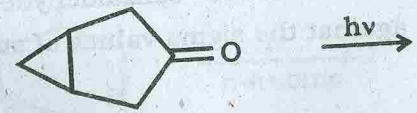
   (c) Explain with example the phenomenon of 'quencing' and 'sensitization' in photochemical reactions. 2+2

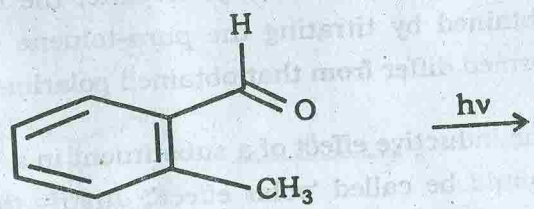
2. (a) Explain Norrish type–I and type–II reaction with suitable examples and also illustrate them with mechanism. 3+4

   (b) Predict the product/s of the following reactions with mechanism (attempt any *four*) : 2×4

(i) 

(ii) 

(iii) 

(iv) 

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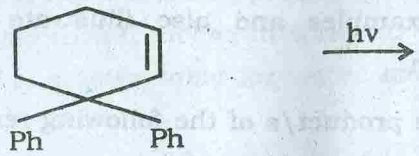

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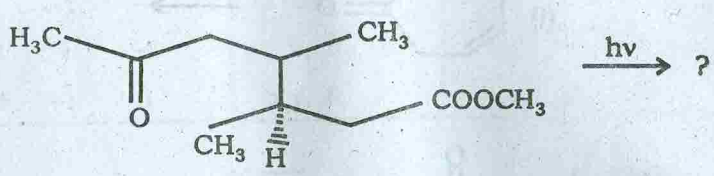


3. (a) Why a curved Hammett plot is obtained when the logarithms of rate constants in semicarbazone formation of substituted benzaldehydes at pH 4, are plotted against the sigma values of substituents ? 7

(b) How can you explain that is the acetolysis of *erythro*–3–phenyl–2–butyl tosylate, the rate constant obtained by titrating the *para*–toluene sulfonic acid formed differ from that obtained polarimetrically ? 8

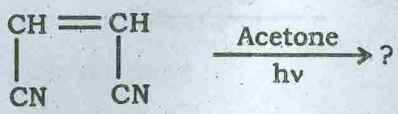
4. (a) The inductive effect of a substituent in a benzene ring should be called 'polar effect'. Justify the statement with proper reasoning. 3

(b) Discuss the conceptual basis of the separation of Polar and Mesomeric effects in Taft's Dual Substituted Parameter equation. How does this differ from separation of these effects in extended Hammet approach ? 6

(c) Account for the necessity of using sigma minus values of substituents in base induced dehydrobromination of arylethyl bromides in order to have a linear Hammet plot. 6

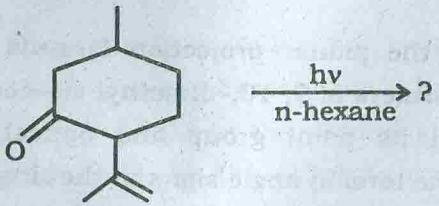
5. Predict the product(s) of the following reactions with mechanism (attempt any *five*) : 5×3

(i)

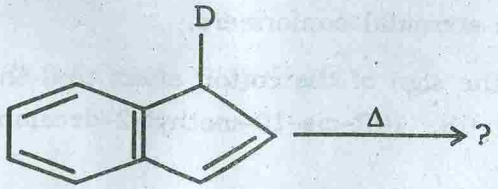


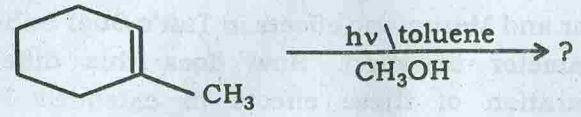
(cis & trans both)

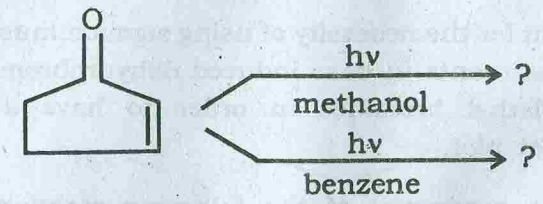
(ii)

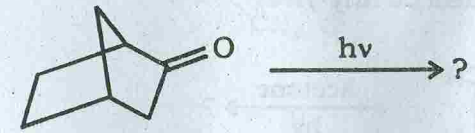


(iii)



(iv) 

(v) 

(vi) 

Group—B

6. (a) Write down the planar projection formula and the flipped conformers of 9, 10,–dimethyl cis–decalin and comment on its point group and optical activity. Determine the torsion angle signs at the ring junction (both side) of each conformer and name the steroidal and non-steroidal conformers. 9

(b) Predict the sign of the cotton effect that the steroid form of 9S, 10R–cis–10–methyl–2–decalone would exhibit. 6

7. (a) Write down the conformers of both enantiomers of trans-1-decalone and cis-1-decalone and label each conformer as steroidal and non-steroidal conformers. 5

(b) Elucidate the absolute configuration of the following compounds with application of the relevant Rules. Name the rules you would apply :

(i) (–)-2-Bromopropionic acid ;

(ii) (–)-1-Bromo-1-chloro-3-methylallene. 5

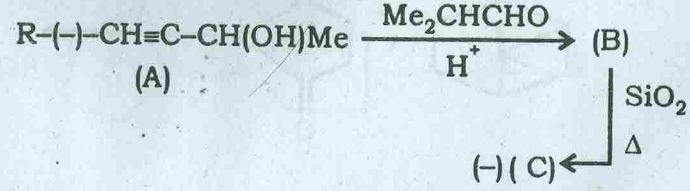
(c) Comment on the optical activity and relative stability of the conformers of

(i) cyclohexane ;

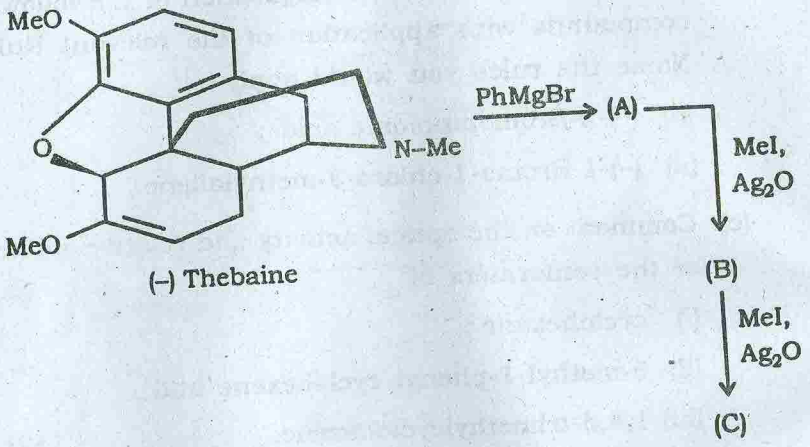
(ii) 6-methyl-1-phenyl cyclohexene and

(iii) 1,4,6-trimethylcyclohexene. 1+2+2

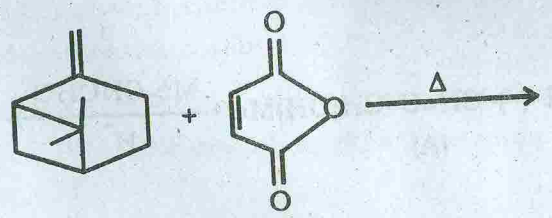
8. (a) Complete the following reaction sequence and rationalize mechanistically. Show the involvement of the π-orbitals in the second step. Name (A) and (C) and designate the absolute configuration of (C) : 8



(b) Explain the following reaction sequence with mechanism, designate the absolute configuration of a final product (C). Specify the absolute configurations of the chiral centers of (–) thebaine : 7



9. (a) What is ene reaction? Explain the product of the following reaction on the basis of FMO interaction : 2+3



(b) Explain the following terms with an example : 3

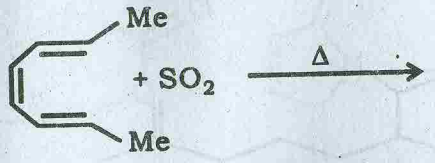
(i) 'Superficial' and 'Antrafacial' mode of addition in cycloaddition reaction ;

(ii) Cycloreversion reaction.

(c) Using an experiment prove that (1, 5)-hydrogen migration is allowed but (1, 3)-hydrogen migration is forbidden under thermal condition. 3

(d) Predict the product of the following reaction indicating Frontier Orbital Interaction (any *two*) : 2+2

(i)



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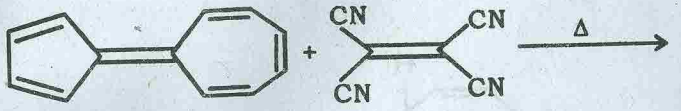

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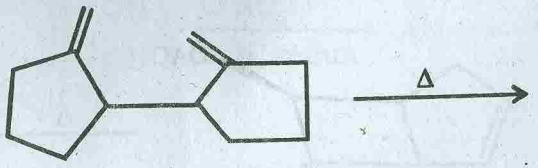
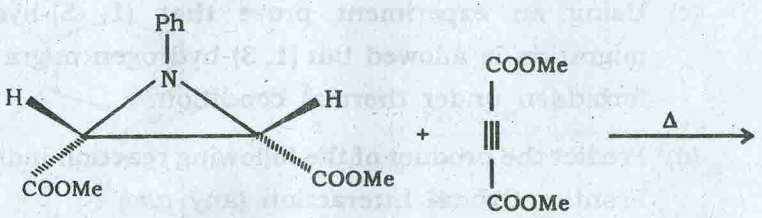


10. (a) Predict the product of the following reaction indicating Frontier Orbital Interaction.

Answer any *four* : $2\frac{1}{2} \times 4$

(i)



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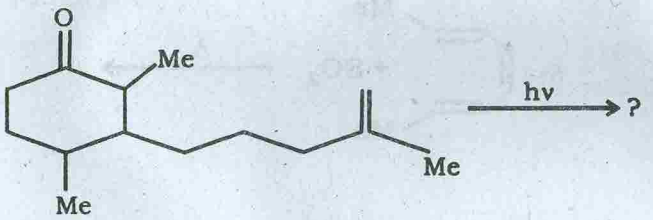

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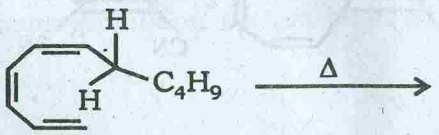

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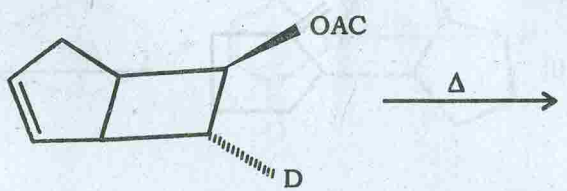

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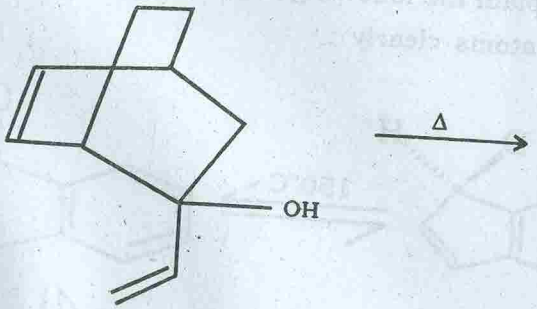

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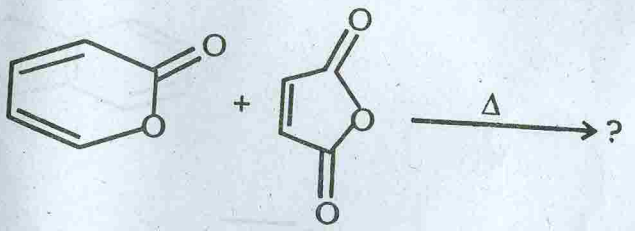
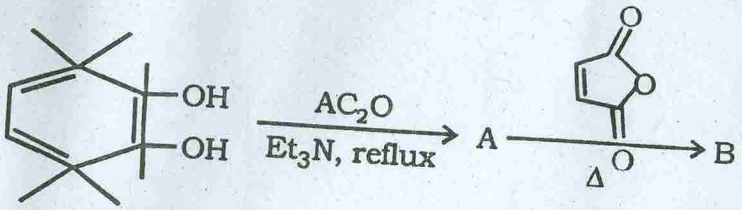


(b) Write the product A and B : 2



(c) Explain the following reaction by indicating migration of atoms clearly : 3