PG/IVS/CEM-401/14

M.Sc. 4th Semester Examination, 2014

CHEMISTRY

PAPER – CEM - 401

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Organic*)

Answer any **five** questions

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

   (*i*) 9, 10-dimethyl-*cis*-Decalin

   (*ii*) 9, 10-dimethyl-*trans*-Decalin

   (*iii*) *Cis*-1, 2 dihydroxy Cyclohexane.

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

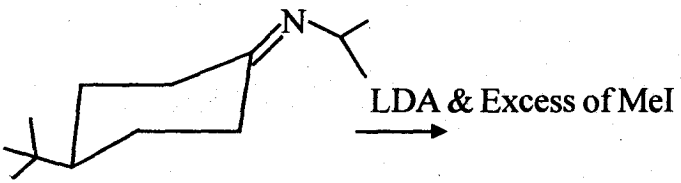
2. Answer the following : 2 × 4

(*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 ?

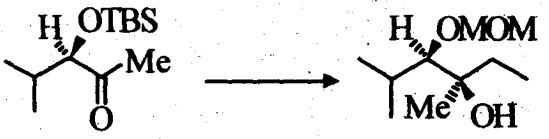
(*d*) Predict the product(s) with appropriate reasoning :



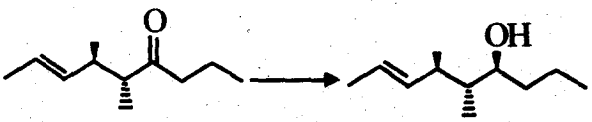
3. For each of the following transformations, clearly explain the basis for the observed selectivity. For

full credit, show reagents, key conformations, transition states, and/or reactive intermediates to support your arguments. Be specific. 2 × 4

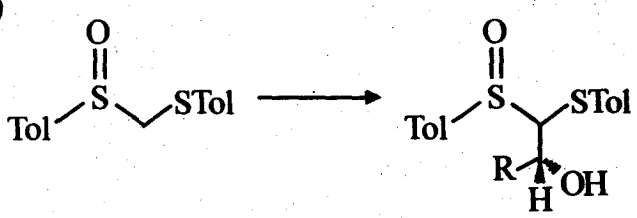
(*a*)



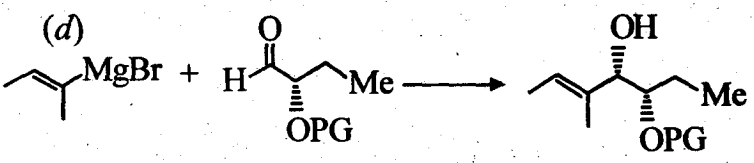
(*b*)



(*c*)



(*d*)



4. Write in brief about the following terms : 2 × 4

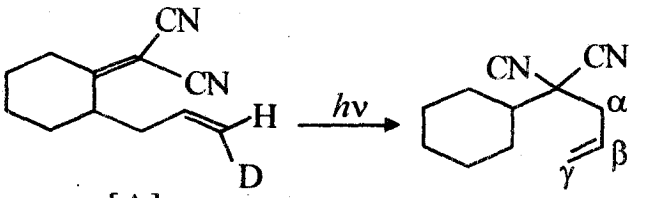
(*i*) ORD

(*ii*) CD

(*iii*)Cotton Effect(CE)

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

5. (*a*) The following transformation gives the product as : 4

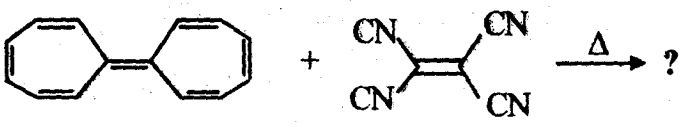


[A] [B]

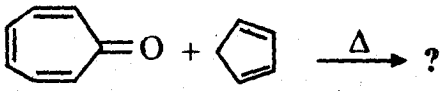
Designate the expected position of the D in the product 'B'. Do you expect 'D' would be found at α or γ position or both. Explain with mechanisms.

(*b*) Predict the product of the following reaction with F.O.I. in each case(attempt any *two*) : 2 × 2

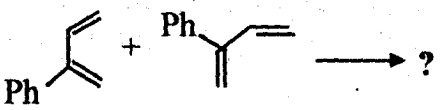
(*i*)



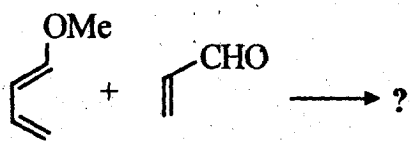
(*ii*)



(*iii*)

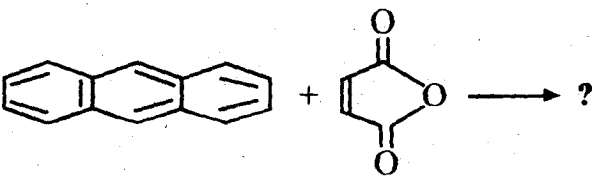


6. (*a*) Define Regioselectivity and hence predict the product/s of the following reaction indicating reavon behind it 2

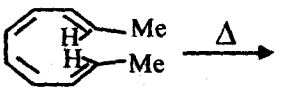


(*b*) Differentiate between 'periselectivity' and 'site selectivity' and hence the predict the product of the following reactions : 2 + 2 + 2

(*i*)

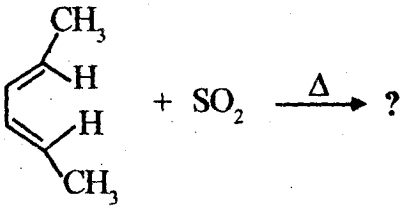


(*ii*)



7. (*a*) What is chelotropic reaction ? Explain the mechanism of the reaction with proper example. 2

(*b*) (*i*) Predict the product/s of the reaction with proper explanation indicating Frontier orbital interaction (F.O.I) (Attempt any *three*) : 2 × 3



PG/IVS/CEM-401/14

M.Sc. 4th Semester Examination, 2014

CHEMISTRY

PAPER – CEM - 401

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Organic*)

Answer any **five** questions

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

   (*i*) 9, 10-dimethyl-*cis*-Decalin

   (*ii*) 9, 10-dimethyl-*trans*-Decalin

   (*iii*)*Cis*-1, 2 dihydroxy Cyclohexane.

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

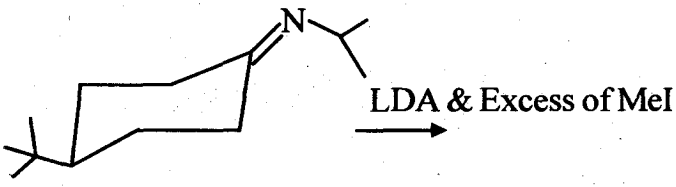
2. Answer the following : 2 × 4

(*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 ?

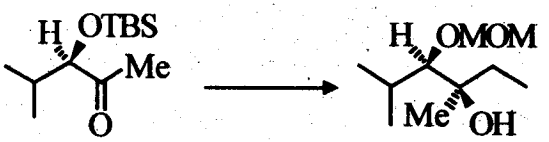
(*d*) Predict the product(s) with appropriate reasoning :



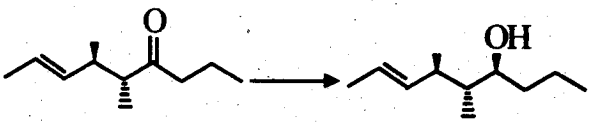
3. For each of the following transformations, clearly explain the basis for the observed selectivity. For

full credit, show reagents, key conformations, transition states, and/or reactive intermediates to support your arguments. Be specific. 2 × 4

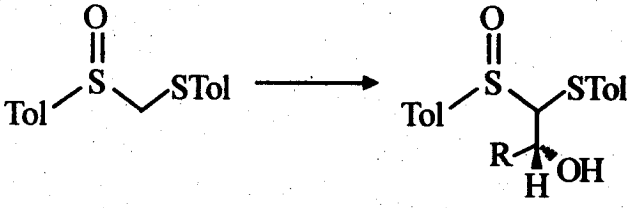
(*a*)



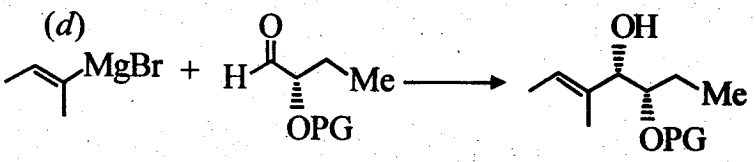
(*b*)



(*c*)



(*d*)



4. Write in brief about the following terms : 2 × 4

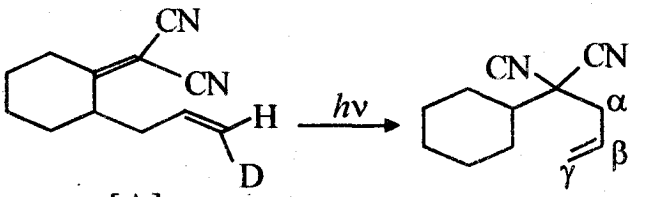
(*i*) ORD

(*ii*) CD

(*iii*)Cotton Effect(CE)

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

5. (*a*) The following transformation gives the product as : 4

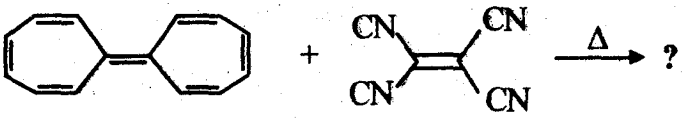


[A] [B]

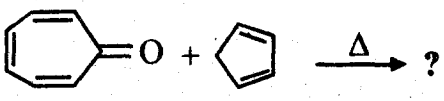
Designate the expected position of the D in the product 'B'. Do you expect 'D' would be found at α or γ position or both. Explain with mechanisms.

(*b*) Predict the product of the following reaction with F.O.I. in each case(attempt any *two*) : 2 × 2

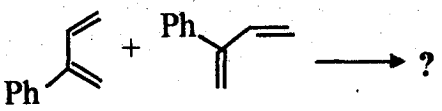
(*i*)



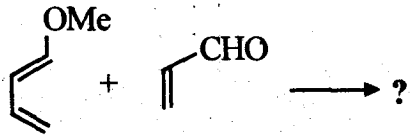
(*ii*)



(*iii*)

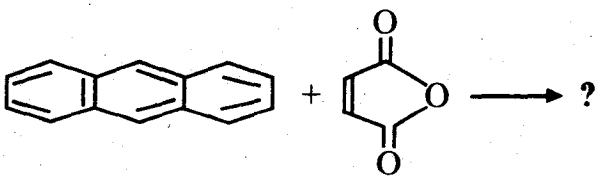


6. (*a*) Define Regioselectivity and hence predict the product/s of the following reaction indicating reavon behind it 2

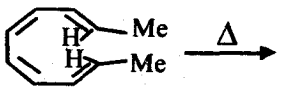


(*b*) Differentiate between 'periselectivity' and 'site selectivity' and hence the predict the product of the following reactions : 2 + 2 + 2

(*i*)

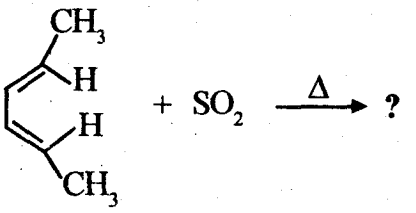


(*ii*)



7. (*a*) What is chelotropic reaction ? Explain the mechanism of the reaction with proper example. 2

(*b*) (*i*) Predict the product/s of the reaction with proper explanation indicating Frontier orbital interaction (F.O.I) (Attempt any *three*) : 2 × 3



(*b*) Chromium crystallizes as bodycentered cubic structure with a density of 7·20 gcm^{-3} at 20°C. Calculate the length of a unit cell and the distance between successive (111) planes. 3

6. (*a*) What is critical magnetic field for a superconductor ? 2

(*b*) How does Hg become a superconductor below 4·2 K ? 5

(*c*) Define Hall angle and Hall mobility. 3

7. (*a*) Define geometrical structure factor and find out it's value for NaCl crystal. 5

(*b*) Europium, which crystallizes as a body -centered cubic lattice, has a density of 5·243gcm^{-3} at 20°C. Calculate the crystallographic radius of europium atom at 20°C. 3

(*c*) What is the advantage of quantum theory over classical theory of free electron ? 2

8. (*a*) Write down the steps for the determination of vibrational modes of linear molecule using group theoretical principle. 2

(*b*) Use subgroup method to determine the symmetry species of vibrational modes of acetylene. Following in the character table of D_{2h} point group. 8

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_{1g}	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_{1u}	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_3u	1	−1	−1	1	−1	1	1	−1	x	

hydrolysis is given below. Rationalize the trends observed. 3

Complex	$\Delta V^{\neq}$(cm^3/mol)
$[Co(NH_3)_5(OHC(NMe_2)]^{3+}$	+ 43·2
$[Co(NH_2Me)_5Cl]^{2+}$	+ 32·7
$[Co(NH_2Et)_5Cl]^{2+}$	+ 31·1
trans – $[Co(en_2)Cl_2]^+$	+ 24·8
Cis – $[Co(en_2)Cl_2]^+$	+ 27·9

(*Physical Special*)

GROUP – A

Answer any **two** questions

1. (*a*) State the essential features of extended Hückel theory. 8

(*b*) Can molecular geometry be known from the theory ? Discuss. 2

2. Calculate the ground state energy of H-atom using variational principle. 10

3. Find out the CO polarity of the formaldehyde molecule in its doubly excited state (Π^{*2}) by Huckel theory. 10

4. (*a*) Discuss the basic difference of variational principle and perturbation theory. 2

   (*b*) Show that $(2n + 1)$ th order perturbation energy can be calculated from *n*th order perturbation wave function only calculate the ground state energy of H-atom using variational principle. 8

Or

Calculate the ground state energy of He atom using first order perturbation method. 10

GROUP – B

Answer any **two** questions

5. (*a*) What is 'V_2' centre ? Discuss the mechanism of formation of 'V_2' centre with a suitable example. 7