M.Sc. 3rd Semester Examination, 2013

CHEMISTRY

PAPER—CEM-301

The figures in the right-hand margin indicate marks
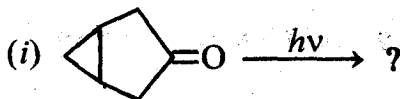
(*Organic Special*)

[*Marks* : 40]

Time : 2 hours

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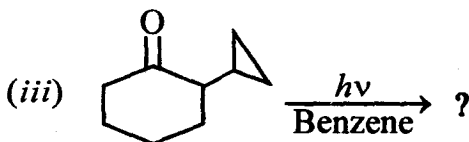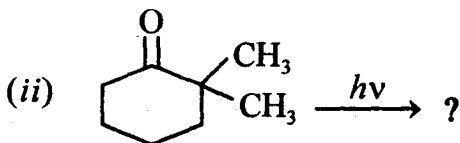**two** from each Group

GROUP — A

1. (*a*) What are Norrish type-I and type-II reactions.
   Explain with suitable examples in each case.   4

   (*b*) Predict the products of the reactions with
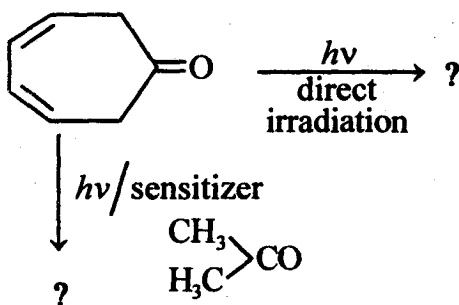   suitable mechanism (attempt any *two*) :   2 × 2
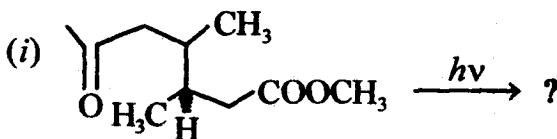
   (*i*) $\xrightarrow{h\nu}$?

(2)

(ii) $\xrightarrow{h\nu}$?

(iii) $\xrightarrow[\text{Benzene}]{h\nu}$?

2. (a) What would be the products of the following reactions. Give proper justification :   2 + 2

 $\xrightarrow[\substack{\text{direct} \\ \text{irradiation}}]{h\nu}$?

$\downarrow h\nu/\text{sensitizer}$
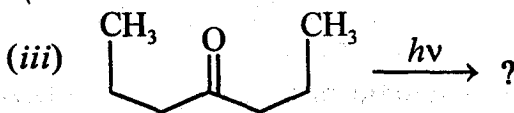
? $\underset{H_3C}{\overset{CH_3}{>}}CO$

(b) Predict the products of the reactions with mechanism (attempt any two) :   2 × 2

(i) $\xrightarrow{h\nu}$?

(ii)

$$\xrightarrow[\text{acetone}]{hv/} [A] \xrightarrow{\Delta} [B]$$

Identify 'A' and (B)

(iii)

$$\xrightarrow{hv} \quad ?$$
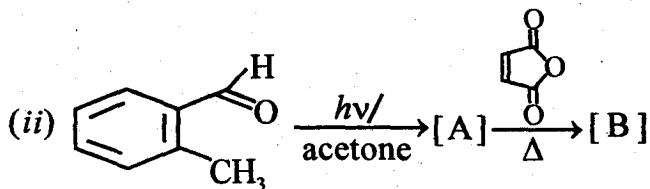
3. Predict the products of the following reaction with proper justification :   4 + 2 + 2

(i)

$$\xrightarrow[\text{cyclohexane}]{hv} \quad ?$$

(ii) H_3C

$CH_3 + (CH_3)_2C(OH) \xrightarrow{C_6H_6/hv} ?$

Or

$$C_6H_5 \, CO \, COOC_2H_5 + CH_3 - \underset{\underset{OH}{|}}{CH} - C_2H_5 \xrightarrow{hv} ?$$

(iii)

$$\xrightarrow[\text{(CH)}_2\text{CH OH}]{hv/\text{div HCl}} \quad ?$$
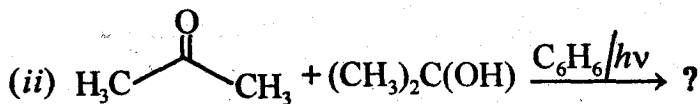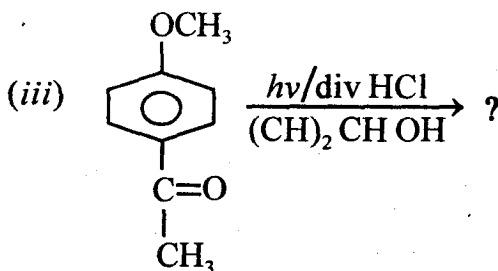
4. (a) Michler's ketone does not undergo photo reduction under the same condition at which benzophenone absorbs." — Explain the statement with justification.   4

(b) What would be the products of the following reactions :   4

$$\xrightarrow[\text{(CH}_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \text{CH}_3)]{\begin{array}{c} hv \\ \text{Acetone} \end{array}} \quad ?$$

$$hv / \bigg| \; \text{Ph} - \overset{\overset{\displaystyle O}{\|}}{C} - \text{Ph}$$

?

(Continued)
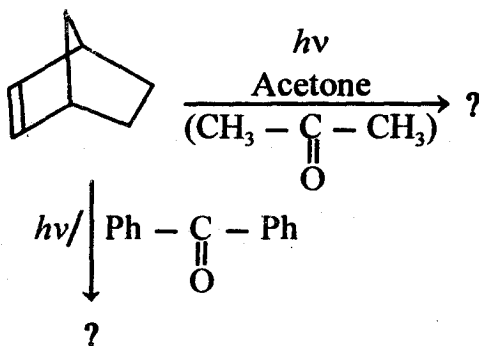
GROUP – B
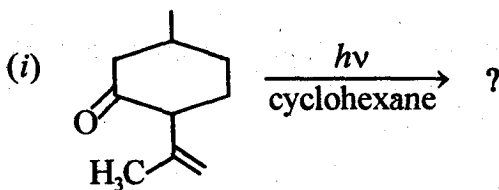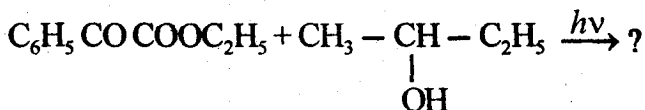
5. Predict the products of the following reactions with mechanism (attempt any *four*) :   2 × 4

(i) $+$ $\xrightarrow{h\nu}$?

(ii) $+ \ Ph - C \equiv C - Ph \xrightarrow{h\nu}$?

(iii) $\xrightarrow{h\nu}$?

(iv) 2 $\xrightarrow{h\nu}$?

(v) $\begin{array}{l} CH - Ph \\ \| \\ CH - Ph \end{array} \xrightarrow{h\nu}$?
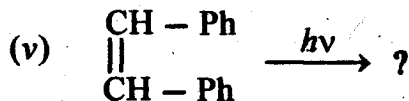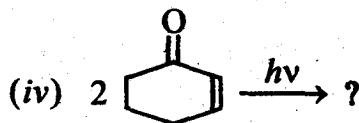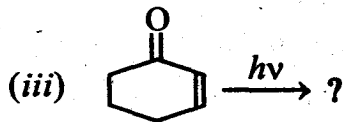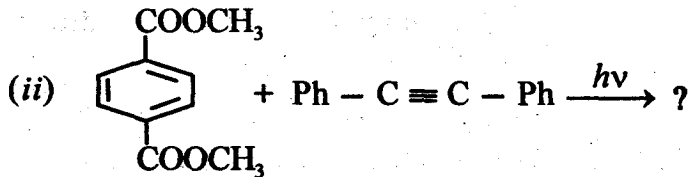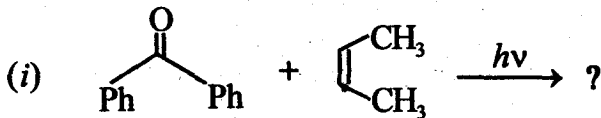
(6)

6. Draw the 3d structures for the following conformers and show in them different steric interactions including their optical properties : 8

   (i) cis-transoid-cis perhydroanthracene

   (ii) trans-cisoid-cis perhydrophenanthrene

   (iii) 9, 10-dimethyl cis decalin

   (iv) trans-hydrindane

7. Give the products of the following reactions. Where more than one product is likely to be formed in significant yield, indicate which will be the major product and also predict the mechanism of the reaction involved. 8

(a)

(b)

(c)

NaOEt

(d)

LDA & Excess of MeI
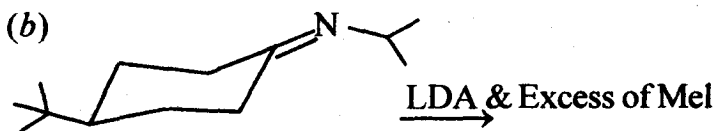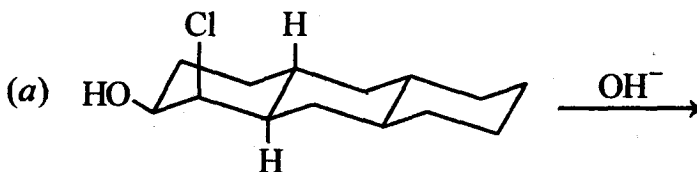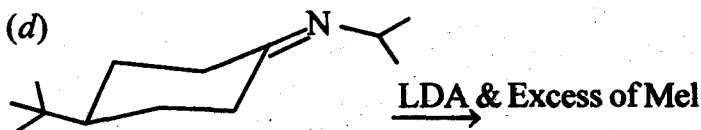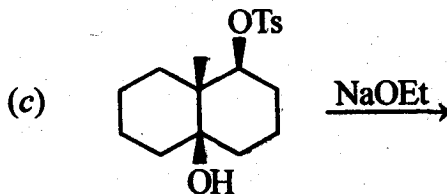
8. Write in brief with *one* example in each case : 8

(a) Allylic 1, 2-strain

(b) 2-alkylketone effect

(c) α and β -strains

(d) Curtin-Hammett principle.

9. What is (i, g) sigmatropic shift ? Illustrate with examples and also predict the product of the following reactions with frontier orbital interactions (attempt any *three*) : $2 + (3 \times 2)$

(i)

$\xrightarrow{\Delta}$?

(Turn Over)

(ii)

$\xrightarrow{\Delta}$?

(iii)

$\xrightarrow{\Delta}$?

(iv)

$\xrightarrow{190\,^\circ C}$?
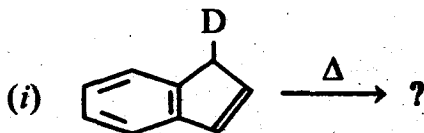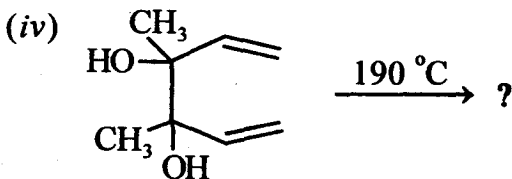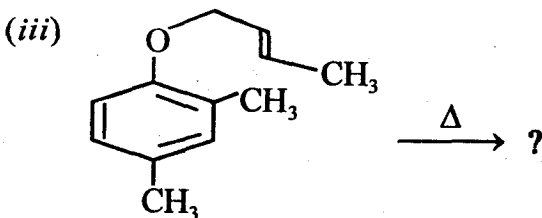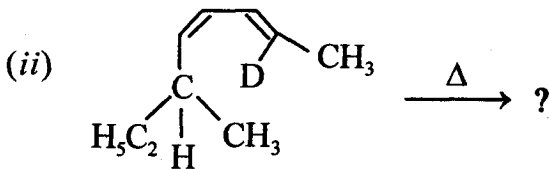
10. Predict the products of the following reaction indecation F.O.I (attempt any *four*) : 8

(a)

 $+ EtOOC - C \equiv C - COOEt \xrightarrow{h\nu}$?

(b)

 $+$ $\xrightarrow{\Delta}$?

(*Continued*)

(c)

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

(d)

$+ \;\; \underset{\underset{CO_2CH_3 \;\; CO_2CH_3}{}}{C \equiv C} \;\; \xrightarrow{\Delta} ?$

(e)

$+ \;\; \underset{N \diagdown COOCH_3}{\overset{N \diagup COOCH_3}{\|}} \;\; \xrightarrow{\Delta} ?$
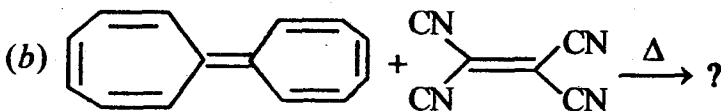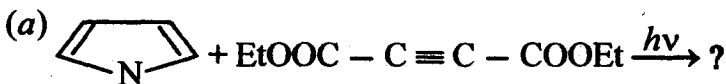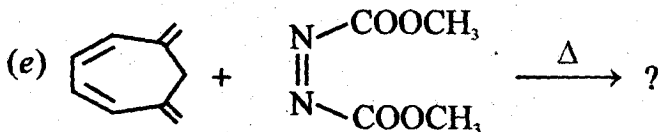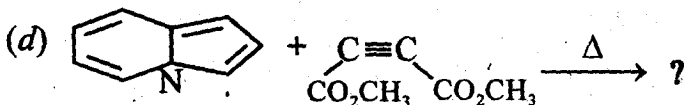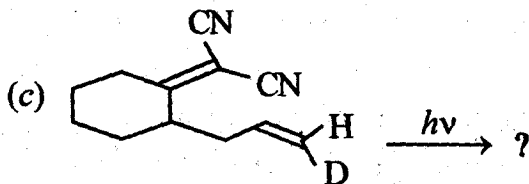
(*Inorganic Special*)

[*Marks* : 40]

Time : 2 hours

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

GROUP – A

1. In $[Co(NH_3)_6]^{3+}$, the ground state belongs $^1A_{1g}$ representation and two excited states belong to

(*Turn Over*)

$^1T_{1g}$ and $^1T_{2g}$ representation. Show that the electronic transition from the ground state to these excited states will be vibronically allowed. (Given below the character table for O_h point group). 8

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)	
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		

2. (a) Using group theory how can you explain the allowedness of d-d transitions in octahedral complexes ? 3

(b) Find out the effect of polarization of incident radiation in the electronic transition of

$[Cr(C_2O_4)_3]^{3-}$. (Given below the corresponding correlation table and character table).   5

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	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

3. (a) With the help of group theory determine the symmetries of possible combinations of atomic orbitals of oxygen atoms which are effective for Π-bond formation in carbonate anion. Using projection operator method find out the appropriate SALCs for these symmetries. Construct qualitative Π-molecular orbital energy level diagram

for the carbonate anion. (Given below the character table for D_{3h} point group).   6

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

4. With the help of group theory determine the symmetries of the ligand grounp of orbitals which are effective for σ and Π-bond formation in octahedral ML_6 molecule. Construct a qualitative molecular orbital energy level diagram (considering both σ and Π-bond formation) for this molecule. (Use the character table of O_h point group given in Q. No. 1)   8

(*Continued*)

GROUP – B

5. (a) Explain ^1H, ^{19}F, ^{31}P nmr spectrum (with stick diagram) for $HP(O)F_2$. Where $^1J_{PH} = 880$ Hz, $^1J_{FH} = 115$Hz.   3

   (b) An A-X system gave four peaks (quartet) recorded on a 200 MHz NMR spectrometer, are observed at 1·2, 1·4, 1·6 and 1·8 ppm. What is the chemical shift value and coupling constant (J_{AX} in Hz).   3

   (c) How can you differentiate αP_4S_4 and βP_4S_4 by ^{31} P NMR spectroscopy ?   2

6. (a) Explain the ^1H nmr spectra for $^{11}B_2H_6$. Comment on the intensity. (including stick diagram).   3

   (b) Predict ^{19}F nmr spectra of difluromethane. Comment on the proton environment in CH_2F_2 and $C_2H_2F_2$.   2

   (c) What will be ^{31}P nmr spectrum of $[Rh(PR_3)]^+$ at very low temperature and room temperature. Give stick diagram.   3

7. Use group theoretical principle to determine the symmetry of vibrational modes of ClF_3 molecule using cartesian coordinate method and internal coordinate method. Comment on the results. Determine the missing modes in internal coordinate method. Identify the symmetry of IR and Raman active mode in this molecule. (Given below the character table for C_{2v} point group). $2 + 2 + 1 + 2 + 1$

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

8. (a) What do you mean by "Exclusion rule" ? Justify this rule using $trans-N_2F_2$ as an example. (Given below the character table for C_{2h} point group).   5

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	zx, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

(b) The complex $K_4[Ni(NO_2)_6]$ shows bands at 1387, 1347, 1325 and 1206 cm^{-1}. What does this suggest about the binding mode of the NO_2 ligand.   3

(*Physical Special*)

[*Marks* : 40]

Time : 2 hours

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

GROUP – A

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

   45·1235845, 0·4350782, 0·005820   3

(b) Define (i) absolute error, (ii) relative error (iii) percentage error in connection with the approximate value of $\Pi = \frac{22}{7} = 3·14$ 3

(c) Evaluate

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

taking 10 subintervals by Simpson's 1/3 rule. 4

2. (a) If the matrices obey the rule $ABC = D$, then show that

$$d_{ij} = \sum_k \sum_l a_{ik}\, b_{kl}\, c_{lj} \qquad 4$$

(b) Find out the inverse of the following matrix :

$$A = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} \qquad 6$$

3. Derive the matrix representation of $\hat{L}_z$ and $\hat{L}^2$ using the basis Y_{lm} with $l = 1$. 10

4. Calculate the ground state energy of the atom and Li-atom using independent particle model approximation. Critically comments on the result. 8 + 2

(Continued)

GROUP – B

5. Discuss some experiments which lead to the postulate that electrons should posses intrinsic spin angular momentum. **10**

6. Show the essential steps to derive the Hartree-Fock equations. **10**

7. (a) What is meant by linear function space ? Illustrate with an example. **2 + 2**

   (b) Show that the set of n-degenerate molecular orbital serve as basis for the representation of an n-dimensional IR of the point group. **6**

8. (a) Obtain the transformation matrix which transform the n-dimensional base vectors, $(e_1, e_2, e_3 \ldots e_n)$ into its prime set, $(e_1', e_2', e_3' \ldots e_n')$. **4**

   (b) What do you mean by (i) Hermitian, (ii) orthogonal and (iii) unitary matrix. Show that eigenvector matrix that diagonalises a Hermitian matrix is unitary·in nature. **3 + 3**