2015

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) (i) Round-off the numbers correct to 4-significant figures : 0·35497825, 7·0062.

(ii) Write the approximate value of $\frac{\pi}{4}$ 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 $f(1.5)$ or $f(7.5)$. 2+3

(c) Evaluate $\int_0^1 \left(4x - 3x^2\right) dx$, taking 10 subintervals, by Simpson's 1/3 rule or by Trapezoidal rule. 5

2. (a) Derive the matrix reforesentation of $\hat{L}_+$ and $\hat{L}_-$ operators using basis set Y_{lm} where $l = 1$. 10

(b) Show that the matrix representation of $\hat{L}_+$ and $\hat{L}_-$ operators are adjoint of each other. 2

(c) Prove that $(AB)^{-1} = B^{-1}A^{-1}$ where A, B are two motices. 3

3. (a) Write down the hamiltonion operator of n-electron atom. Why is it not analytically solvable ? 3+2

(b) State and prove Eckart theorem. 8

(c) Define unitary and orthogonal matrices. 2

4. (a) Derive secular determinant as obtained in linear variational problem. 5

(b) Carry out the Huckel calculation of butadiene molecule to find out ground state energy and resonence energy of that molecule. 10

Group—B

5. (a) Find out the eigen value and eigen vector of the following matrix :

$$\begin{bmatrix} 7 & -3\sqrt{3} \\ -3\sqrt{3} & 13 \end{bmatrix}.$$ 8

(b) Show that in Hartree model the total electronic energy of many electron atom is less than the sum of the occupied orbital energies, 7

6. (a) Find the point symmetry group and symmetry operation present for the following molecules : 4

(i) Toluene ; (ii) Ferrocent (staggered) ;

(iii) PCl_5 ; (iv) BCl_3 .

(b) Show that the direct product matrix form a representation of the point group. 4

(c) With the help of group theoretical principle, final the nature of splitting of d-orbitals of a central metal atom when it is placed in an octahedral environment. Following is the character table for 'O' group. 7

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		$(xy,\ yz,\ zx)$

7. (a) How does group theory help in determining the zero and non-zero values of spectroscopic transition moment integral ? 5

(b) Use both cartesian and interval co-ordinate method to obtain the vibrational modes is NH_3. Comment on your results. Predict the 1R and Raman activity of the vibrational modes of NH_3. Following is the Chenader table of C_{3v}. 10

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	1	−1	0	$(x,\ y)\ (R_x,\ R_y)$	$(x^2 - y^2,\ xy)\ (xz,\ yz)$

8. (a) Give the differences between Schottky and Frenkel defects. 2

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

(c) What are F-centres ? Why are solids having F-centres are paramagnetic ? 2+2

(d) How do you explain the production of colour centre in NaCl. 2

(e) What are the successes of Drude-Lorentz classical theory ? 3

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(Organic Special)

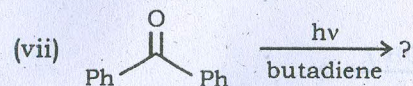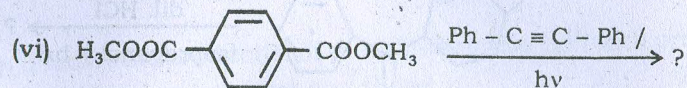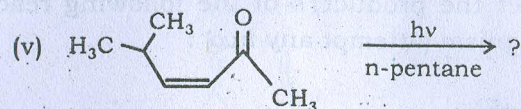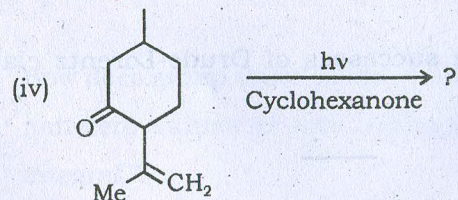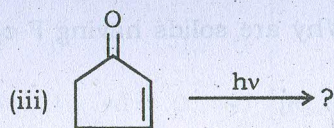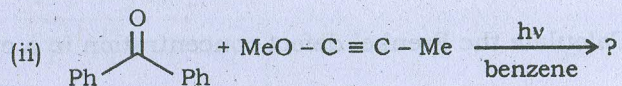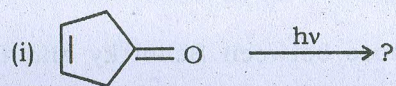Answer any *five* questions taking at least *two* from each group.

Group — A

1. (a) Show various transitions between excited and ground states of organic molecules in a Jablonski diagram and identify their importance in photo chemical reactions.
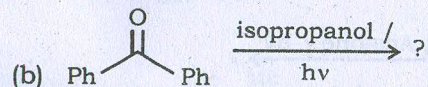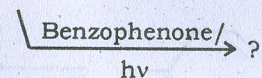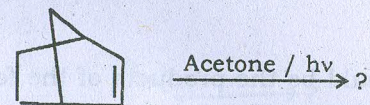
   5

   (b) Predict the product(s) of the following reactions with mechanism (attempt any *five*) :   5×2

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

   (ii) + MeO – C ≡ C – Me $\xrightarrow[\text{benzene}]{h\nu}$?

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

   (iv) $\xrightarrow[\text{Cyclohexanone}]{h\nu}$?

   (v) $\xrightarrow[\text{n-pentane}]{h\nu}$?

   (vi) H_3COOC $COOCH_3$ $\xrightarrow[h\nu]{Ph – C ≡ C – Ph /}$?

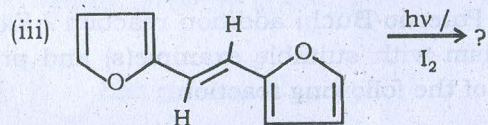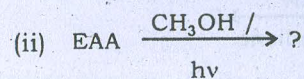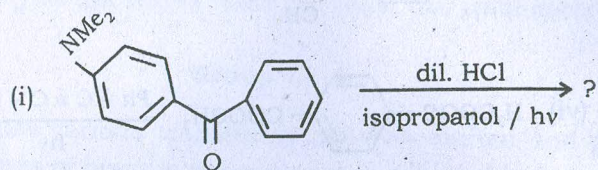   (vii) $\xrightarrow[\text{butadiene}]{h\nu}$?

2. (a) What is Paterno-Buchi addition reaction ? Explain the mechanism with suitable example(s) and predict the product of the following reaction :

    $\xrightarrow{\text{Acetone / } h\nu}$?

   $\xrightarrow[h\nu]{\text{Benzophenone/}}$?

   (b) $\xrightarrow[h\nu]{\text{isopropanol /}}$?

   Quantum yield (φ) for the above reaction was observed '1'. Explain the mechanism of the reaction and establish this observation.   3+2
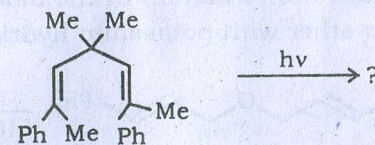
(c) Predict the product/s of the following reaction with mechanism (attempt any *two*) : 2×2

(i)

$$\xrightarrow[\text{isopropanol / h}\nu]{\text{dil. HCl}} \ ?$$

(ii) EAA $\xrightarrow[\text{h}\nu]{\text{CH}_3\text{OH /}} ?$
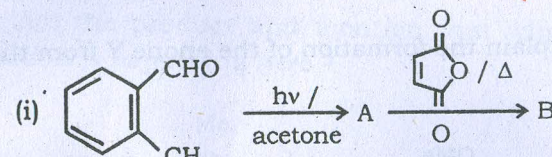
(iii)

$\xrightarrow[\text{I}_2]{\text{h}\nu /} ?$

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

$\xrightarrow[\text{direct irradiation}]{\text{h}\nu} ?$
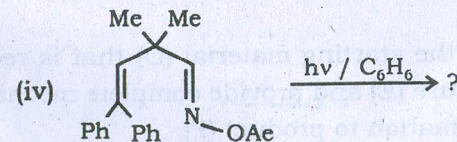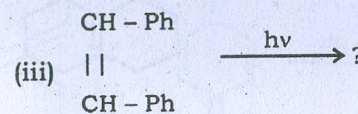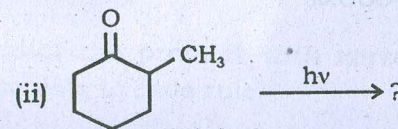
$\xrightarrow{\text{Acetone / h}\nu} ?$
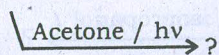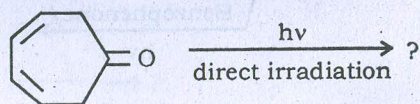
(b) What is di-π-methane rearrangement reaction ? Explain the orbital interactions. Showing symmetry allowed path for the following reaction. 5
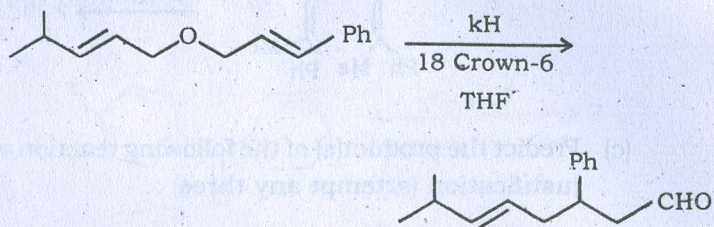

$\xrightarrow{\text{h}\nu} ?$

(c) Predict the product(s) of the following reaction with proper justification (attempt any three) : 2×3

(i)

$\xrightarrow[\text{acetone}]{\text{h}\nu /} A \xrightarrow{O/\Delta} B$

— identify A & B.

(ii)

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

(iii) CH – Ph
      ||
      CH – Ph

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

(iv)

$\xrightarrow{\text{h}\nu / C_6H_6} ?$

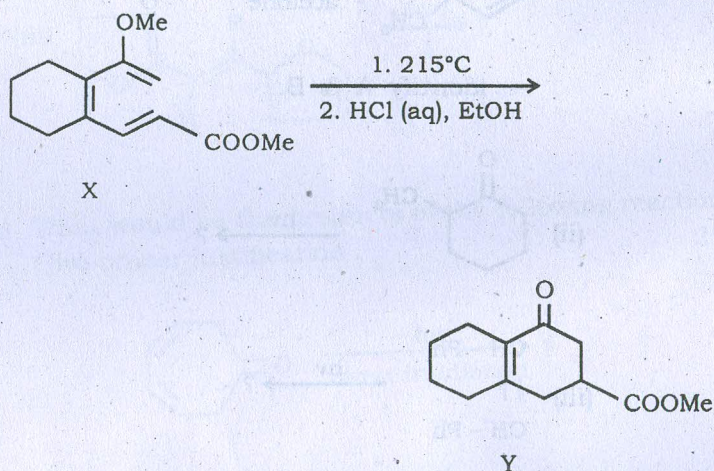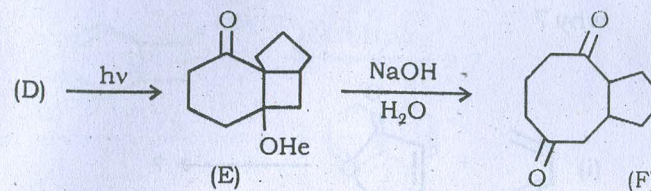**4.** (a) Explain the formation of the aldehyde on treatment of given ether with potassium hydride. 3
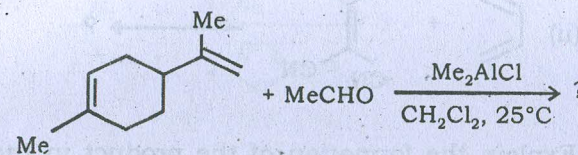

(b) Explain the formation of the enone Y from the triene X. 3

X

Y

(c) Determine the starting material (D) that is required to form structure (E) and provide complete mechanism for its transformation to product (F). 3

(Continued)

(D) $\xrightarrow{hv}$ (E) $\xrightarrow[H_2O]{NaOH}$ (F)

(d) Predict the product and mention that what kind of reaction is happening here? 3

+ MeCHO $\xrightarrow[CH_2Cl_2, 25°C]{Me_2AlCl}$?

(e) Predict the product with correct stereo-chemistry according to endo rule. 3

(i)

+ $\xrightarrow{Ph\ H}$?

(ii)

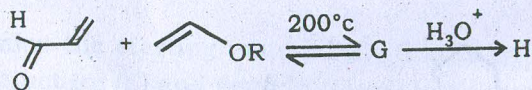$\xrightarrow{\Delta}$?

(Turn Over)
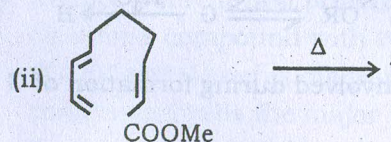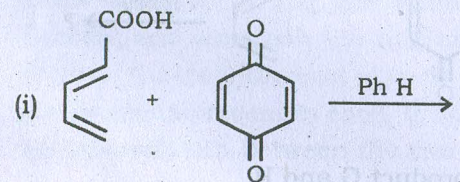
5. (a) Which cycloaddition reaction will occur at faster rate and why ?

(i) + ⟶ ?

(ii) + ⟶ ?
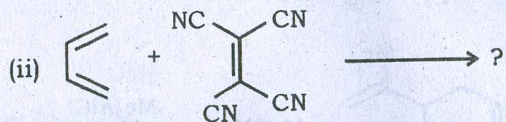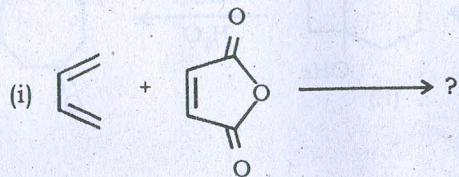
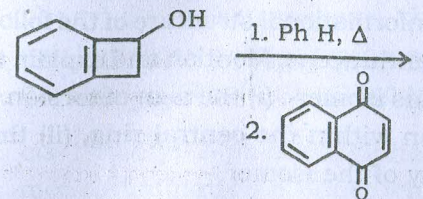(b) Explain the formation of the product in the following reaction : 3

 + —100°c→ ?
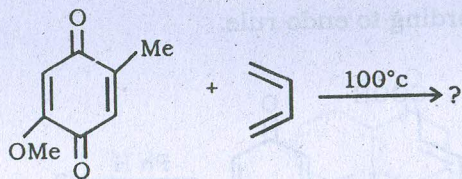
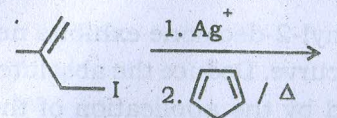(c) Identify the product G and H. 3

 + —200°c⇌ G —H₃O⁺→ H

Which reaction is involved during formation of G ?

(d) Explain the formation of the product : 3

 —1. Ph H, Δ → ? 2.

(e) Indicate FMO interaction to predict product :

 —1. Ag⁺ 2. / Δ → ?

Group — B

6. Answer the following :

(a) Draw the steroidal and non-steroidal conformers of *cis*-decalin, and ascertain the sign of torsin angles on both sides of the ring junction of each. Delineate the symmetry elements present in each. What is the type of stereoisomeric relation between the two conformers ?

2+2+2+2

(b) Deduce from the first principle the Curtin-Hammett principle for a compound with two conformers with the help of a potential energy diagram where the more populated conformer yields the major product. Mention the conditions under which the principle is valid. 5+2

7. (a) How many stereoisomers of perhydroanthracene are possible ? How many of them are achiral ? Draw the conformational structure of the following isomer of perhydroanthracene. Mention and explain the following regarding this isomer : (i) the sign of torsion angle at the ring junction within the central ring, (ii) the symmetry and chirality of the isomer. 2+1+2+2
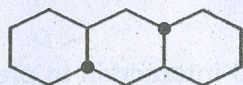
(b) (-)-*trans*-10-Methyl-2-decalone exhibits negative Cotton effect in its ORD curve. Deduce the absolute configuration of the compound by the application of the octant rule. Specify the absolute configurations of the stereocenters in *R, S* notation. 5+3

8. (a) Predict the sign of Cotton effect that the anacomeric form (1a) of the following 2-decalone derivative (1) and its axial 1-bromoderivative will exhibit in their ORD curves. Name the compound (1). Explain why (1a) is anacomeric ?

$$4\tfrac{1}{2}+1\tfrac{1}{2}+1\tfrac{1}{2}$$

(1)   (1a)
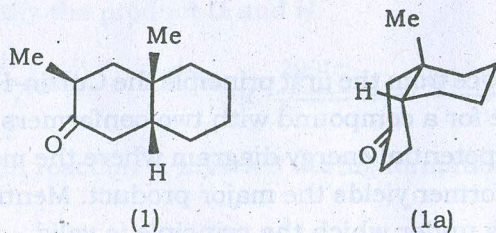
(b) (i) Explain why in a base catalysed equilibrium 2-phenyl-6-nitrocyclohexene, the conformer having axial nitro group predominates over the conformer having equatorial nitro group ? 3

(ii) *cis*-1-Acetyl-2-phenylcyclohexane furnishes a monobromination product when subjected to acid catalysed bromination, but the corresponding *trans* isomer fails to do so under the same condition. Explain with reason(s).

$$4\tfrac{1}{2}$$

9. (a) Write down the planar projection formula and the flipped conformers of 9, 10-dimethyl *cis* – decalin. Comment on its point group and optical activity. Determine the torsion angle signs at both sides of the ring junction of each conformer and hence identify the steroidal and nonsteroidal conformers. Why are they named so ? 9

(b) Comment on the optical activity and relative stability of the conformer of : 3×2

 (i) Cyclohexene ;

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

 (iii) 1, 4, 6-trimethyl cyclohexene.

10. (a) Explain the term periselectivity in pericyclic reaction.

3

(b) Explain the product/s of the following reactions :

6×2

(i) + MeOOC – C ≡ C – COOMe $\xrightarrow{\Delta}$?

(ii) $\xrightarrow{\Delta}$

(iii) $\xrightarrow{\Delta}$

(iv) + $\xrightarrow{\Delta}$

(v) + $\xrightarrow{H_2O}$

(vi) + MeOOC – C ≡ C – COOMe $\xrightarrow{170-190°c}$?