OLD & NEW

2016

M.Sc. Part–II Examination

CHEMISTRY

PAPER—V

Full Marks : 75 / 100

Time : 3 / 4 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*)

Old Syllabus

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and answer *five* questions from group C.

(Turn Over)

Group—A

1. (a) (i) Round-off the following numbers correct to 4-significant figures : 0.21337145, 1.011500, 0.000421685, 0.56985875

   (ii) Write the approximate value of $^1/_3$ and hence find the absolute error (E_A), relative error (E_r) and relative percentage error (E_P).   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 $\int_0^1 \left(4x - 3x^2\right) dx$, taking 10 sub-intervals.   5

   Or

   (a) What is electrical potential ? What is the unit of capacitance ?   3+1

   (b) Derive Debye Equation for molar polarization.   6

   (c) For SO_2 gas at 273(K) and 1 atm pressure, dielectric constant is 1.00993. This molecule has a parmanent

dipole moment of 1.63D. Assuming that SO_2 behaves as an ideal gas calculate per mole of — (i) total (ii) orientation and (iii) distortion polarizability.   3

(d) What is magnetic domains ?   2

2. (a) Derive the matrix representation of $\hat{L}_+$ operator using Y_{lm} as set of basis functions where $l = 2$.   7

   (b) Calculate inverse of the following matrix :

   $$\begin{bmatrix} 2 & 3 \\ 4 & 5 \end{bmatrix}.$$
                                                              3

3. (a) Discuss the Hartee's Self Consistent Field (SCF) method to derive one elector wave function in many electron system.   8

   (b) Using Hartee's one electron wave function find out the energy expression for n-electron system.   7

Group—B

4. Using Huckel approximation find out the energy and π-molecular orbitals for allyl radical : $CH_2 - CH - CH_2$.
                                                              8+7

5. (a) Prove that the representation of a direct product, Γ_{AB}, will contain the totally symmetric representation if the irreducible Γ_A = the irreducible Γ_B. **5**

(b) Find out the vibrational modes of water molecule using group theory. Character table for C_{2v} is given below : **5**

C_{2v}	E	C_2	σ_{xz}	σ_{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

(c) Why no polarization effect is observed for cubic c or higher symmetry groups ? **2**

(d) Write the three simple equations for G.O.T. **3**

6. (a) State the spectral transition selection rules. **2**

(b) Find out the σ ligand group orbital (LGO) involved for the construction of SALC in BF_3 molecule. Character Table for D_{3h} is given below : **8**

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
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)

(c) What is projection operator and draw the M-O picture of water molecule is using projection operator technique ? **1+4**

7. (a) Prove $\sigma = \dfrac{Ne^2\tau}{2m}$ where σ = conductivity, N = number of electrons, τ = relaxation time or mean free time, m = mass of electron. **4**

(b) Define f_j and F_{hkl} and also prove that

$$F_{hkl} = \sum_{j=1}^{n} f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

f_j = atomic scattering factor for the jth atom ; u_j, v_j and w_j are the indices of the jth atom. **2+4**

(c) Derive Bragg's law from Laue equation. **4**

(d) Define V-centre. **1**

8. (a) Explain with reason the effect of bias on depletion width in a p-n junction. 4

(b) Calculate the Schottky defect concentration in an ionic crystal of MX type. 4

(c) Colour centre is due to lattice defect which absorbs light. Explain the mechanism of absorption process. 3

(d) Cerium crystallizes as a face centred cubic lattice and the length of the unit cell is 516 pm. Given that density of Cerium is 6.773 gcm^{-3}. Calculate the Avogadro Constant. 4

Group—C

9. Answer any *five* of the following : 5×5

(i) State and Proof Eckart's theorem.

(ii) Use variational principle to obtain the energy of the MO's of ethylene.

(iii) Write down Hartree-Fock equation and the explicit form of Hamiltonian for 2N electron system. "Hartree-Fock equation is called Integro-differential equation" — Explain.

(iv) Use time independent non-degenerate perturbation theory to obtain first order correction to energy.

(v) What is a projection operator ? Show that it is idempotent.

(vi) What is Faraday ?

(vii) What is polarizability ?

(Continued)

(*Organic Special*)

Old Syllabus

F.M. – 75 Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. – 100 Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B)
and also group C.

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

Group — A

1. (a) 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

(b) Write down the structure of product(s) with stereo-chemistry of the following reactions.

(i)
$$\xrightarrow[\text{ii. } Ac_2O]{\text{i. } PhMgBr} \, ?$$

(Turn Over)

(ii) $\xrightarrow[\text{ii. Br}_2]{\text{i. AcOH}}$?

(iii) $\longrightarrow$?
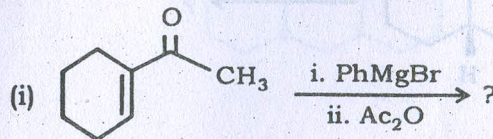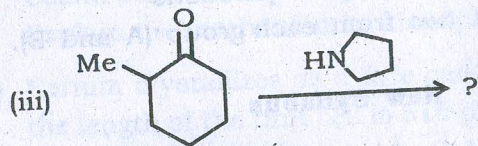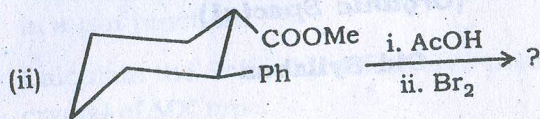
(c) Write down the preferred conformations of (Z)-2-methylcyclohexylideneacetic acid.　　(2+2+2)+1

2. (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 sterodial and nonsteroidal conformer.　5

(b) Comment on the symmetry, chirality and optical activity of cis-decalin.　3

(c) Write down the structure of product(s) of the following reactions.

(i) $\xrightarrow{\text{base}}$?

(ii) $\xrightarrow{\text{NaOAc}}$?
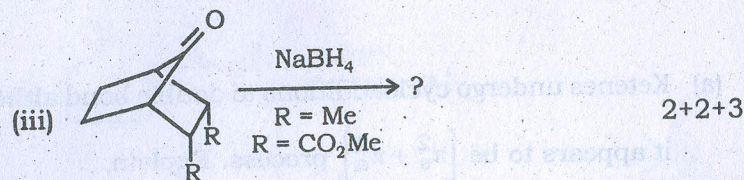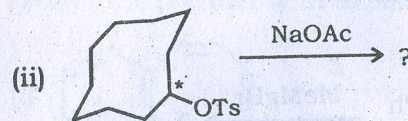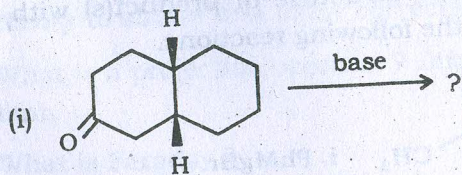
(iii) $\xrightarrow[\substack{R = Me \\ R = CO_2Me}]{\text{NaBH}_4}$?　　2+2+3

3. (a) Predict the sign of the cotton effect that the steroid form of 9(s), 10(R)-9-methyl-cis-2-decalone would exhibit.　6

(b) 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.
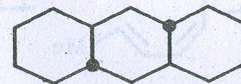
2+1+2+2

(c) Write the major product

$\xrightarrow{\text{MeMgBr}}$?   2
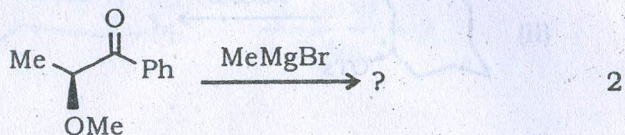
4. (a) Ketenes undergo cycloadditions to double bond although it appears to be $\left[\pi_s^2 + \pi_a^2\right]$ process. Explain.   2

(b) What is Cycloreversion reaction ? Give an example.   1

(c) Explain the following observations :   3+3

(i)
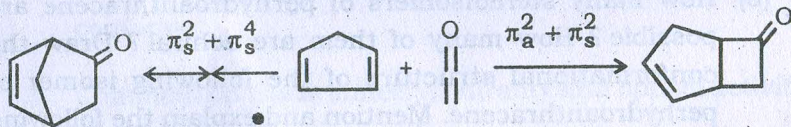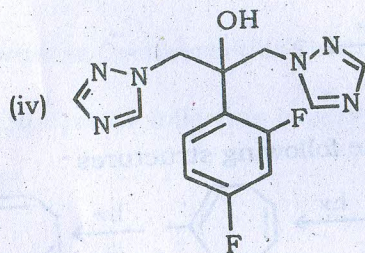

(ii)
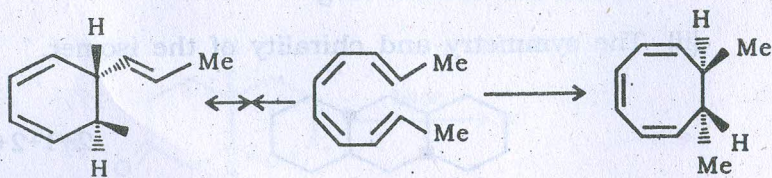
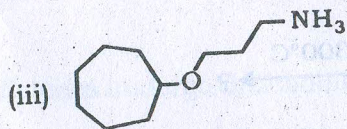(d) Predict the product with explaination.   3×1

(i)

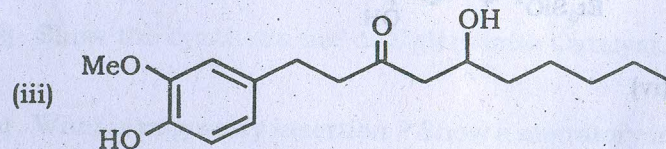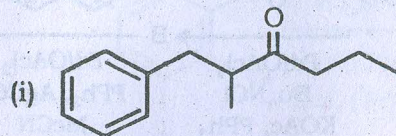(ii)

(iii)
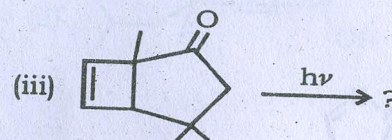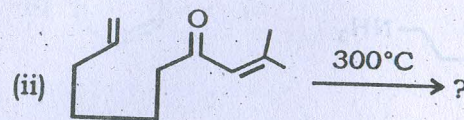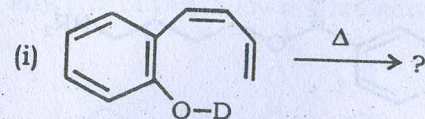
(e) Explain formation of the following structures :   3
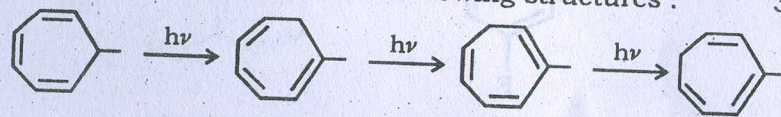
5. (a) Define FGI and Synthon with example.   3

(b) Show the retrosynthesis of any *four* of the following molecules :   4×2

(i)

(ii)

(iii)

(iv)

(v)

(vi)
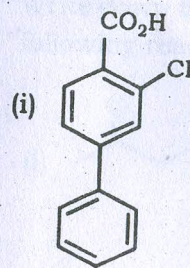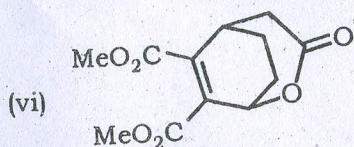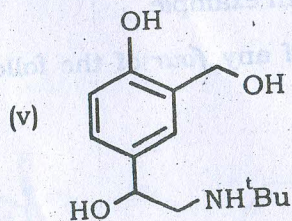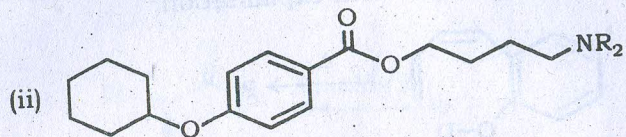
(c) Draw the retrosynthesis as well as forward reactions of any *one* of the following molecules. 4
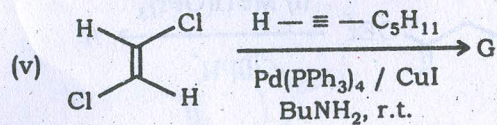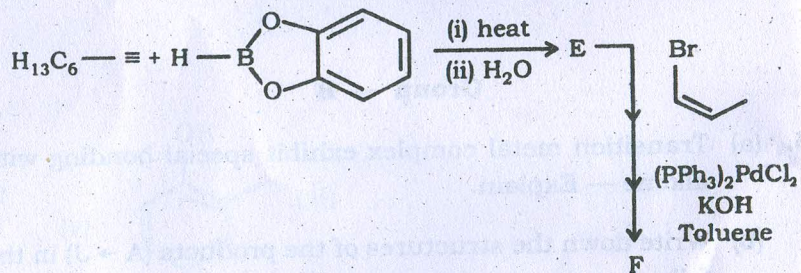
(i)

(ii)

(iii)

Group — B

6. (a) Transition metal complex exhibit special bonding with alkene — Explain. 2

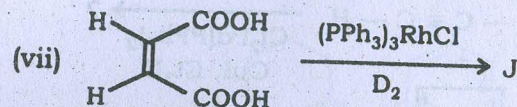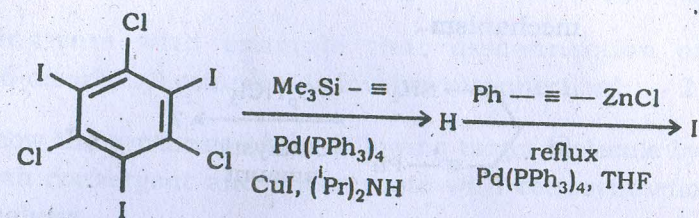(b) Write down the structures of the products (A → J) in the following reactions : 10×1

(i)

(ii)

(iii)

(iv)

(v)

(vi)
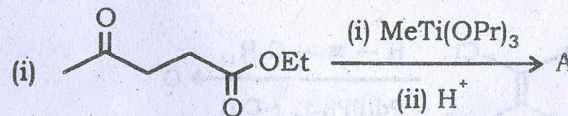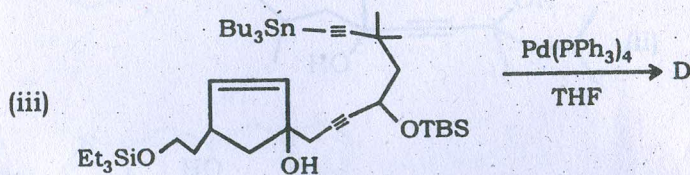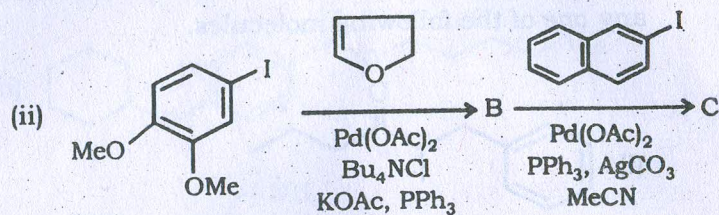
(vii)

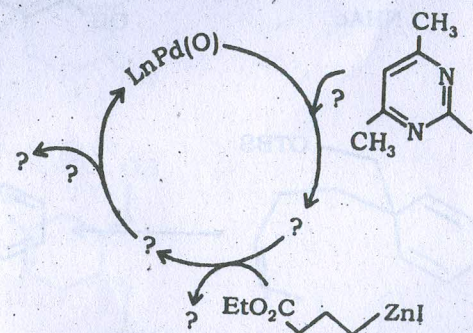
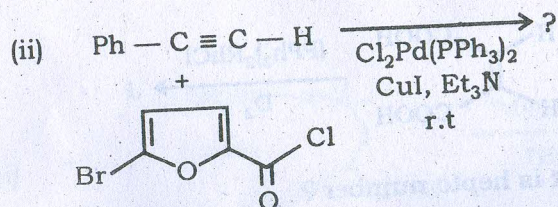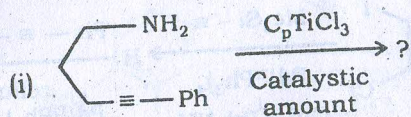(c) What is hepto number ?   1

(d) Show the synthetic use of Zigler Natta Catalyst.   2

7. (a) What is migratory insertion ? Show a migratory insertion
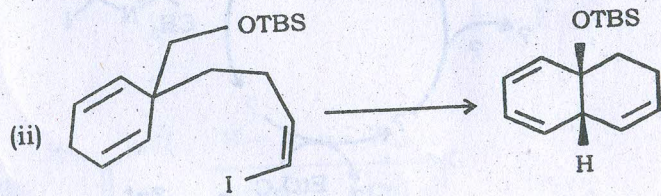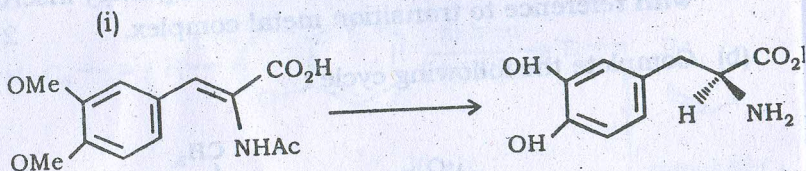   with reference to transition metal complex.   2+3

   (b) Complete the following cycle :   4

(c) Predict the product of the following reactions with mechanism : 2×2

(i)

(ii) Ph — C ≡ C — H

+

$\xrightarrow{\text{Cl}_2\text{Pd(PPh}_3)_2}$?
CuI, Et$_3$N
r.t

(d) Indicate appropriate reagents in each of the following transformation : 1+1

(i)

(ii)

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8. (a) What is 'Functional Group Interconversion'? 1

(b) Illustrate with example that disconnection of 1,6-dicarbonyl compounds involve 'reconnection'. 2

(c) Show the synthesis of the following target molecule by both convergent and linear route with retrosynthetic analysis. 3
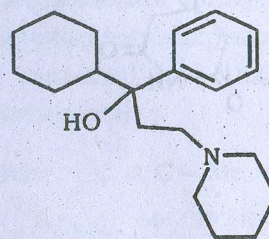
(d) Describe the synthesis of the following compounds with proper retrosynthetic analysis (any *three*) : 3×3

(i)

(ii)

(iii)

(iv)
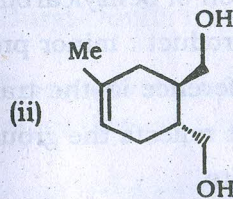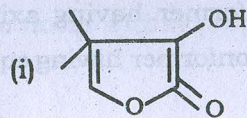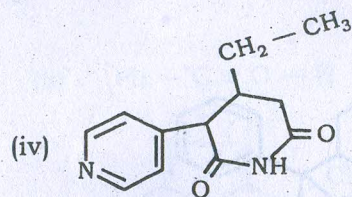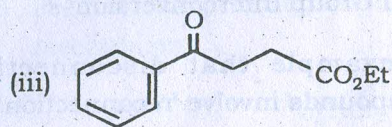
9. (a) Derive Curtin-Hammett principle and state the conditions under which the principle is valid. 4+2

(b) Explain why in a base catalyzed equilibrium of 2-phenyl-6-nitrocyclohexene, the conformer having axial nitro group predominant over the conformer having equatorial nitro group ? 3

(c) In the base catalyzed elimination of benzylcarbinyl-2,4,6-triethylbenzoate the major product : minor product - 100:1, find out the energy difference in the transition states, and comment on how it reflects the group state energy difference of the products. 6

10. (a) (–)-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 configuration of the stereoisomers in R, S notations. 5+2

(b) Explain the following reaction sequence with mechanism showing the involvement of the π-orbitals in the second step. Designate the absolute configuration of (B) which was found to be levototatory. Explain the sign of rotation of the starting material and the final product by application of relevant rules. 8
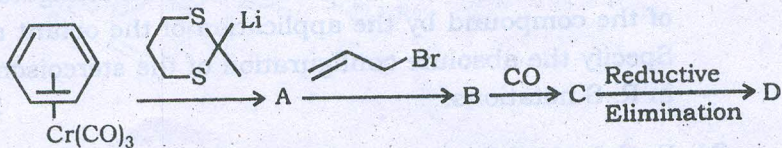
(Polarizability Order : $-C \equiv C - Me > Me > OH$)

$$(R)(+)-Me-CHOH-C \equiv C-Me \xrightarrow{Me_2CHCHO} (A) \xrightarrow{SiO_2} (-)(B)$$
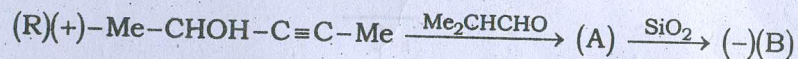
Group—C

1. Write notes within proper example & reasoning : (any *three*) 5×3

(a) Ciepak Model.

(b) Burgi-Dunitz trajectory.

(c) Trans annular intractions and their effect on properties of medium ring cycloalkanes.

(d) Axial Haloketone Rule.

2. Identify A, B, C and D.   **4**

3. Show the catalytic cycle of Suzuki coupling with oxidation state of the metal properly marked.   **4**

4. What is Tebbe's reagent ? Show its usefulness in organic synthesis.   **2**