Ro	ll No	Total Pages : 03
		LMDQ/D-23 6531
	IN	ORGANIC CHEMISTRY (GENERAL)
		CHEM-301
		(CBCS-LOCF)
Tin	ne : T	Three Hours] [Maximum Marks : 45
No	te :	Attempt Five questions in all, selecting at least one
		question from each Unit. Q. No. 1 is compulsory. All
		questions carry equal marks.
		(Compulsory Question)
1.	(a)	Explain the structure and function of Hemerythrin.
		3
	(b)	Write and explain the ilkovic equation. 2
	(c)	What is the interference of $O_2$ in the determination
		of Metal ion in polarography?
	(d)	Define the terms vertical and adiabatic ionization. 2
		Unit I
2.	(a)	Describe the basic structural features of hemoglobin
		and myoglobin and explain their biological functions.
		5
	(b)	Explain that cytochrome p-450 is a monooxygenase.
		4
(5-12	2/3) L	-6531 P.T.O.

P.T.O.

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- 3. (a) What are the electron carriers? Describe the role of iron-Sulphur proteins as electron carrier in biological system.
  - (b) Write a short note on model synthetic complexes of cobalt.

#### **Unit II**

- **4.** (a) Explain the determination of coordination number of complexes with the help of  $E_{1/2}$ .
  - (b) Describe the term hydrogen voltage and explain itsvolume, Erdy and Gruss theory.5
- 5. (a) Determine and depict the IR active modes of  $SF_4$  (AX<sub>4</sub> type) by using group theoretic approach. 5
  - (b) On the basis of IR spectroscopy, explain the coordination behavior of  $\beta$ -diketones with transition metal ions.

#### Unit III

6. (a) Explain the term isomer shift and quadrupole splitting in Mossbauer.

L-6531

(b) Define photoelectric effect. Draw and explain the possible peaks for  $N_2$  molecule in photoelectron spectrum.  ${\bf 5}$ 

2

- 7. (a) Give the principle of ESCA. What chemical information is obtained from ESCA?

  5
  - (b) Explain the adiabatic and vibrational ionization energies in PES by using vibrational structure for a molecule.

(5-12/4) L-6531 3

- (b) Discuss the Mc-Connell equation and its application by taking suitable example.
- (c) Discuss the hyperfine structure in ESR spectra of an electron interacting with two non-equivalent protons. [Hint: Use 'stick diagram' and take  $a_1 > a_2$ ]
- (d) List the factors which determine the suitability of a nucleus for investigation by NMR spectroscopy.

3,2,2,2

#### **Section C**

- **6.** (a) Draw stereogram corresponding to the following combination of symmetry elements:
  - (i)  $\overline{3}$  m
  - (ii)  $\overline{4}+i$
  - (iii)  $\frac{3}{m}$
  - (iv) 3m.

Also state for each case, which point group is generated?

- (b) Draw space group diagram for Pm. Specify the coordinates of general positions.
- (c) Why is  $2_1$  called a neutral axis? 5,2,2

Roll No. .....

**Total Pages: 05** 

## LMDQ/D-23

6532

# PHYSICAL CHEMISTRY GENERAL CHEM-302

Time : Three Hours]

[Maximum Marks: 45

**Note**: Attempt *Five* questions in all, selecting *one* question from each Section. Q. No. 1 is compulsory. All questions carry equal marks.

- 1. This question is compulsory:
  - (i) What is the basic criteria for a molecule to be IR active ?
  - (ii) Why is there no translational spectroscopy?
  - (iii) Express in eV, the thermal energy of a gaseous molecule at 298 K.
  - (iv) Why is NQR observed in solid state?
  - (v) A NMR frequency is approximately equal to 60 MHz. Calculate the corresponding energy in kJ/mol.
  - (vi) Why are ESR signals plotted in first-derivative mode?

- (vii) In tetragonal crystal system, A-centred lattice does not exist. Why ?
- (viii) Prove  $\vec{a}^* \cdot \vec{a} = 1$  and  $\vec{b}^* \cdot \vec{b} \cdot = 0$
- (ix) What is the index used to determine the accuracy of a structure after refinement? Give corresponding expression.

  1×9=9

#### **Section A**

- 2. (a) Show that for a diatomic rigid rotor, the moment of inertia is given by  $I = \mu r^2$ , where symbols have their usual meaning. Discuss how are molecules classified based on their principal moments of inertia? Give one example for each group.
  - (b) The rotational spectra of  $^{79}Br^{19}F$  shows a series of equidistant lines 0.71433 cm<sup>-1</sup>. Determine the energy of  $J = 9 \rightarrow J = 10$  transition.
  - (c) What are the degeneracies of the following diatomic rotational energy levels: 5,2,2

2

- (i) 0
- (ii)  $\frac{6\hbar^2}{I}$

- 3. (a) The fundamental vibrational frequency of  $H^{35}Cl$  is  $2890 \text{ cm}^{-1}$ . Calculate the force constant of a molecule in  $Nm^{-1}$ .
  - (b) Discuss the quantum theory of Raman scattering.
  - (c) Elaborate with an example, the concept of 'zero-point energy'. 4,3,2

#### **Section B**

- **4.** (a) Explain with energy level diagram, the operating principle of NMR spectroscopy. Based on this diagram, justify why do nuclei such as <sup>12</sup>C, <sup>16</sup>O do not show NMR spectra.
  - (b) Explain the following terms:
    - (i) Chemical shift
    - (ii) Spin-spin coupling constant
    - (iii) Spin-Lattice relaxation.

4,5

5. (a) Calculate number of ESR lines in the following free radicals:

- (i) Pyrazine
- (ii) n-propyl
- (iii)  $^{13}CF_2D$ .

- 7. (a) Using reciprocal lattice concept, derive expression for interplanar spacing in case of cubic crystal system and determine the ratio  $\frac{d_{112}}{d_{321}}$ ?
  - (b) Write down expression of structure factor for bodycentered lattice and derive the corresponding condition for systematic absences. Justify here which hkl reflection will be observed at smallest value of  $\theta$ ?
  - (c) Powder XRD pattern of cubic crystal gives the following three peaks:

 $2\theta$ : 43.16; 50.30; 73.99

Index these reflections.

3,3,3

- 7. (a) Using reciprocal lattice concept, derive expression for interplanar spacing in case of cubic crystal system and determine the ratio  $\frac{d_{112}}{d_{321}}$ ?
  - (b) Write down expression of structure factor for body-centered lattice and derive the corresponding condition for systematic absences. Justify here which hkl reflection will be observed at smallest value of  $\theta$ ?
  - (c) Powder XRD pattern of cubic crystal gives the following three peaks:

 $2\theta$ : 43.16; 50.30; 73.99

Index these reflections.

3,3,3

- (a) How is UV-Visible spectroscopy helpful in detectionof functional group in organic compounds?
  - (b) Discuss the different ionisation techniques being used in mass spectrometry, highlighting the advantages and disadvantages of each.6

- 4. (a) [18] Annulene shows two signals in its <sup>1</sup>H-NMR spectrum, one at 9.25 ppm and other upfield at -2.88 ppm. What hydrogens are responsible for each of the signals? Also discuss about the factor responsible for these chemical shift values.
  - (b) How the  $^{1}$ H-NMR spectra of four isomeric forms of compounds with molecular formula  $C_{3}H_{6}Br_{2}$  differ ?
  - (c) How many signals will you get in the <sup>1</sup>H-NMR of the following compounds and mention the expected multiplicity for each proton?

Roll No. ..... Total Pages: 06

## LMDQ/D-23

6533

# ORGANIC CHEMISTRY GENERAL CHEM-303

Time : Three Hours] [Maximum Marks : 45

Note: Attempt *Five* questions in all, selecting at least *one* question from each Section. Q. No. 1 is compulsory.

All questions carry equal marks.

### (Compulsory Question)

- 1. (a) Why is an O-H stretch more intense than N-H stretch in IR?
  - (b) How an increase in solvent polarity shift  $n-\pi^*$  and  $n-\sigma^*$  absorption bands?
  - (c) Arrange the following compounds in order of decreasing frequency of carbonyl absorption in theirIR spectra:

(3-18/7) L-6533 P.T.O.

- (d) Primary alcohols have a strong peak at m/z = 31. What fragment is responsible for this peak?
- (e) What m/z value would you predict for the base peak in the mass spectrum of 3-methyl pentane?

1

- (f) A signal has been reported to occur at 120 Hz downfield from TMS in an NMR spectrometer with a 300-MHz operating frequency. Then:
  - (i) What is its chemical shift?
  - (ii) What would its chemical shift be in an instrument operating at 100 MHz?
  - (iii) How many Hz downfield from TMS would the signal be in an 100 MHz spectrometer?

2

(g) Compound A, with molecular formula C<sub>4</sub>H<sub>9</sub>Cl, shows two signals in its <sup>13</sup>C-NMR spectrum.
 Compound B, an isomer of compound A, shows four signals and in the spin coupled mode, the signal most downfield is doublet. Identify compounds A and B.

#### Section A

2. (a) Using Woodward and Fisher's rule, calculate the expected is  $\lambda_{max}$  for the given compounds : 3

- (b) Discuss the fragmentation pattern of 4-n-butyltoluene involving (i) benzylic fission, (ii) the McLafferty rearrangement. Label the ions formed as cations or radical cations along with their masses.
- (c) What identifying characteristics would be present in the mass spectrum of a compound having single halogen atom or more halogens of same kind or different kinds?

  3

3

(3-18/8) L-6533

- 7. (a) Briefly introduce the terms (i) Fermi resonance and(ii) Overtones, used in IR spectroscopy with suitable examples.
  - (b) Deduce the structure of a compound of molecular formula  $C_3H_7NO$  with the following spectral data : 6 M.F.  $C_3H_7NO$

UV :  $\lambda_{max}$  238 nm,  $\epsilon_{max}$  10500

IR:  $v_{\text{max}}$  cm<sup>-1</sup> 3428, 2941-2857, 1681 and 1452  $^{1}$ H NMR:  $\delta$  1.9 (3H, s), 2.7(3H, s) and 8.13 (1H, s)  $^{13}$ C-NMR (off resonance decoupled): Two quartets and one singlet.

The singlet at  $\delta$  176.

- 5. Briefly discuss the following:
  - (a) Virtual coupling

3

(b) Nuclear Overhauser effect

- 3
- (c) Simplification of complex NMR spectra through chemical methods.

#### **Section C**

- 6. (a) How proton noise decoupled <sup>13</sup>C-NMR spectroscopy be used to distinguish the following: 3
  - (i) 1,2-, 1,3-, and 1,4-dinitrobenzenes
  - (ii) 1-Methylcyclohexene and 1-Methylenecyclohexne
  - (iii) Acetone and Methylacetate
  - (b) Compare the sensitivity and chemical shifts values of <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy. **3**
  - (c) How is IR spectroscopy used to differentiate the following:

(iii) 
$$\bigcirc$$
 and  $\bigcirc$  o

Roll No Total Pages: 03					
LMDQ/D-23 6534					
INORGANIC CHEMISTRY SPECIAL–I CHEM-304					
Time : Three Hours] [Maximum Marks : 60					
Note: Attempt <i>Five</i> questions in all, selecting at least <i>one</i> question from each Section. All questions carry equal marks.					
Section A					
<ol> <li>(a) Comments on the lability or inertness of the following complexes with justification: 6</li> <li>(i) [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup></li> <li>(ii) [Cr(CN)<sub>6</sub>]<sup>4-</sup></li> <li>(b) Discuss in brief about the theories of trans effect. 6</li> <li>(a) Discuss the stereochemical changes in the acid</li> </ol>					
hydrolysis of Co(III)-ammine Complexes. <b>6</b> (b) Write down the mechanism of preparation of nitrito derivative of [Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> with explanation. <b>6</b>					
Section B					
3. (a) Explain the following:  (i) Mixed valance complexes and their electron transfer processes  (ii) Non-complimentary redox reactions.					
(5-19/2) L-6534 P.T.O.					

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- (b) Discuss the mechanism of electron transfer reactionwith reference to inner sphere reactions.6
- 4. (a) What are cross-reactions? Give two examples of such reactions and explain the evaluation of their rate constants with good degree of accuracy.6
  - (b) The electron transfer between  $[Co(CN)_6]^{4-}$  +  $[IrCl_6]^{2-}$  is relatively fast. Although both Cl<sup>-</sup> and CN<sup>-</sup> are good bridging ligands.

#### Section C

- 5. (a) Discuss the base hydrolysis reaction of coordinated nitriles and its bonding with transition metals.
  - (b) Give a brief account of redistribution reactions involving exchange of ligands between two molecules of the same type.6
- 6. (a) Discuss the nucleophilic substitution reactions of coordinated hydrocarbons.6
  - (b) What is fluxional isomerism? Explain fluxional behaviour in allylic and cyclopentadienyl organometallic complexes. 6

#### **Section D**

- 7. (a) Give preparation and properties of silicone elastomers. 6
  - (b) Discuss the structure and bonding in polyphosphazenes. Give its chemical reactions with water and ammonia.

- 8. (a) Acetic acid is a weak acid and nitric acid is a strong acid in aqueous solution, but both behave as base in sulfuric acid. Explain.6
  - (b) What is the aprotic solvent system concept of acids and bases? Ferric chloride exhibits acidic behaviour in phosphoryl chloride solvent. Explain.6

(5-19/3) L-6534 3 100

Rol	ll No.	<b>Total Pages: 03</b>	
		LMDQ/D-23	6535
	INC	ORGANIC CHEMISTRY	SPECIAL-II
		CHEM-305	
Tin	ne : Tl	nree Hours] [	Maximum Marks : 60
Not	C	Attempt <i>Five</i> questions in all, squestion from each Section. All marks.	•
		Section A	
	(a)	Explain the synthesis of σ-be compounds by metal alkene n and elimination reactions.	· ·
	(b)		the fluxionality in
2.	(a)	Write the reactions of organ with $\alpha$ , $\beta$ -unsaturated carbony mechanism.	
	(b)	Explain the β-hydrogen elimi	nation decomposition
		pathway in σ-bonded organon	netallic compounds. 4
		Section B	
3.	(a)	Discuss the structure and bon	ding in Schrock type
		carbene complexes.	6
5-32	2/8) I/	6E2E	РТО

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- (b) Give any *three* methods of preparation of metal hydrides.
- 4. (a) Differentiate between Fischer and Schrock type carbene compounds.6
  - (b) Give any *three* methods of preparation of Fischer carbene complexes.

#### **Section C**

- 5. (a) Complete the following reactions: 6
  - (i)  $\operatorname{Mn}\left(\eta^{5} C_{5}H_{5}\right)_{2} \xrightarrow{3CO} \rightarrow$
  - (ii)  $\operatorname{Mn}\left(\eta^{5} C_{5}H_{5}\right)_{2} \xrightarrow{2H_{2}O} \rightarrow$
  - (iii)  $\operatorname{Ni}\left(\eta^3 C_3H_5\right)_2 \xrightarrow{\operatorname{CO}_2}$ .
  - (b) Give any *three* methods for the synthesis of transition metal cyclopentadienyls. 6
- 6. (a) Give any *two* methods of preparation of  $\eta^2$ -alkene metal complexes.
  - (b) Write *three* reactions of  $\eta^2$ -alkyne metal complexes with electrophiles. 6

#### **Section D**

7. (a) Explain the mechanism of hydrogenation of alkene using Wilkinson catalyst.6

2

(b) Discuss the hydroformylation of alkene by using Rhodium catalyst. 6

- 8. (a) Write a brief note on the activation of C.H bond. 6
  - (b) Give the mechanism of polymerization of propylene using Zeigler-Natta catalyst.6

(5-32/9) L-6535

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Roll No. ..... Total Pages : 03

## LMDQ/D-23

6536

# PHYSICAL CHEMISTRY (Special-I) CHEM-304 (CBCS-LOCF)

Fime: Three Hours] [Maximum Marks: 60

**Note**: Attempt *Five* questions in all selecting at least *one* question from each Section. All questions carry equal marks.

#### Section A

- 1. (a) Describe the general procedure to obtain the energy and the eigenfunction of a system up to first order correction by perturbation method.
  - (b) What is Born-Oppenheimer approximation? Under what condition is this approximation applicable? 3
  - (c) The trial function,  $\varphi(x) = x(a x)$ . At the boundaries,  $\varphi(0) = 0$  and  $\varphi(a) = x(a a) = 0$ . Thus,  $\varphi$  satisfies these boundary conditions. Justify.
- 2. (a) What are symmetric and antisymmetric solution of hydrogen molecule ion  $(H_2^+)$ ?

(7-16/3) L-6536 P.T.O.

- (b) Write a note on "spin-orbit coupling". 2
- (c) Write the term symbol for the electronic configuration:
  - (i)  $1s^22s^22p^4$
  - (ii) Term symbol for the ground state of nitrogen atom. 3

- (a) Compare the molecular orbital and valence bond treatments of hydrogen molecule in the ground state.
  - (b) Discuss the molecular orbital treatment of heteronuclear diatomic molecules with examples. 6
- 4. (a) What are hybrid orbitals? Describe the quantum mechanical treatment for bond formation in ethylene molecule.
  - (b) With the help of Hückel's rule, show that cyclopropenyl cation is more stable than its anion or radical 6

#### **Section C**

5. (a) Neatly draw Jablonsky diagram and label it with its various transitions that can occur after a molecule has been excited photochemically. With the diagram, explain why phosphorescence life time is much longer than fluorescence.

- (b) How do you correlate selection rules and transition moment integral? Explain. 4
- 6. (a) What is oscillator strength in spectroscopy?How is absorption intensity related to oscillator strength?
  - (b) Discuss about Einstein's coefficient of absorption and emission phenomenon.
  - (c) Write a note on "Probability of Induced Emission and its Application to Lasers". 3

#### Section D

- 7. (a) What is a surface active agents? Discuss the different types of surface active agents with examples.6
  - (b) Explain the terms 'Micellization' and 'Critical micellar concentration'. How the mass action model can be used to discuss micellization?
- 8. (a) Discuss briefly the different types of intermolecular forces in liquids.5
  - (b) What is the physical interpretation of internal pressure? Discuss the significance of internal pressure in liquids.
  - (c) Give a brief account about 'Liquids as disordered solids'.

(7-16/4) L-6536

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# LMDQ/D-23

6537

# PHYSICAL CHEMISTRY SPECIAL-II CHEM-305

Fime: Three Hours] [Maximum Marks: 60

**Note**: Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks. Calculator is allowed for solving numerical only.

#### **Section A**

- (a) What do you mean by phase space, representative point and ensembles?
  - (b) Using Lagrange's method of undetermined multipliers derive an expression for Maxwell-Boltzmann Statistics.
- (a) Differentiate microcanonical, canonical and grand canonical ensembles.
  - (b) Derive a relation for Maxwell distribution law of velocities from Boltzmann distribution expression. 7
  - (c) Particles to be distinguished in 2 boxes such that box 1 contains 30 particles and box 2 contains 26 particles. Find the number of ways of distribution. 2

(7-23/2) L-6537 P.T.O.

- (a) Derive and expression for B.E statistics showing its deviation from ideal gas when B > 1.
  - (b) Why is He more degenerate than Hydrogen for B.E statistics ? 3
  - (c) Describe the case of degeneration for Fermi Dirac system when  $\alpha$  of  $e^{\alpha}$  is positive.
- 4. (a) Illustrate thermionic emission of electron from metals for F.D statistics.9
  - (b) Comment on the degeneracy of classical and quantum mechanical objects. 3

#### Section C

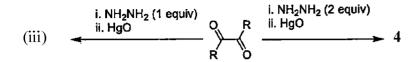
- 5. (a) Derive an expression for translational partition function of gas and also derive Sackur Tetrode equation.8
  - (b) The rotational constant of gaseous HCl, determined from microwave spectroscopy is 10 cm<sup>-1</sup>. Calculate rotational partition function of HCl at 25°C. **2**
  - (c) What do you understand by characteristic vibrational temperature? 2
- 6. (a) Derive an expression of relationship of internal energy of system in terms of partition function and absolute temperature.6

- (b) What are the postulates of statistical thermodynamics? What is significance of Boltzmann constant?
- (c) The vibrational frequency of a homonuclear diatomic molecule is v. Calculate the temperature at which the population of the first excited state will be half that of the ground state.

#### Section D

- 7. (a) Derive a relationship between Partition function and equilibrium constant. How is this relationship helpful in understanding Activated complex theory? 5
  - (b) Determine pre exponential and steric factor for the system:
     Atom + Linear molecule ⇒ Linear molecule
     Linear molecule + Linear molecule ⇒ Nonlinear molecule
- 8. (a) What are the forces and fluxes in irreversible Thermodynamics? How are they related? Explain with examples.
  - (b) Derive an expression for :
    - (i) Entropy production in matter flow.
    - (ii) Entropy production in current flow. 6
  - (c) What is Onsager Reciprocal Relationship? 3

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**6.** Rationalize the following transformation with a suitable mechanism:

(ii) 
$$\frac{1.\text{TI}(\text{NO}_3)_3, \text{MeOH}}{2. \text{H}_2\text{SO}_4}$$

(iii) 
$$\frac{1. O_3}{2. Zn}$$

#### Section D

7. Write the product and mechanism of the following reactions:

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**Roll No. ...... Total Pages : 05** 

## LMDA/D-23

6538

# ORGANIC CHEMISTRY SPECIAL-I CHEM-304

Time: Three Hours] [Maximum Marks: 60

**Note**: Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks.

#### Section A

1. Write product of the following transformations and propose a mechanism for each transformation to explain the observed regionselectivity and stereochemistry.

(i) 
$$\frac{\text{i. CO}_2}{\text{ii. H}_3\text{O}^+}$$
  $\frac{\text{i. 2 equv MeLi}}{\text{ii. H}_3\text{O}^+}$  3

(2-13/11)L-6538 P.T.O.

2. Complete the following organic reactions and propose a mechanism for each transformation to explain the observed regioselectivity and stereochemistry.

(i) 
$$\begin{array}{c|c} & \text{i. } \text{CH}_2\text{=CH}_2\\ \hline \text{ii. } \text{CH}_3\text{CH=CH}_2\\ \hline & \text{ii. } \text{(CF}_3\text{CO)}_2\text{O}\\ \hline & \text{iii. } \text{NaOH, } \text{H}_2\text{O}_2\\ \end{array} \qquad 3$$

(ii) 
$$R_1$$
  $SiMe_3$   $PhCOCI$  AlCl<sub>3</sub>

#### Section B

**3.** Complete the following chemical conversion with suitable mechanism:

2

L-6538

(ii) Br 
$$\stackrel{OMe}{\longrightarrow}$$
  $\stackrel{Ni(CO)_4}{\longrightarrow}$   $X + \stackrel{O}{\longrightarrow}$   $\stackrel{(i)}{\longrightarrow}$   $\stackrel{(i)}{\longrightarrow}$   $\stackrel{(ii)}{\longrightarrow}$   $\stackrel{V}{\longrightarrow}$   $\stackrel{V}{\longrightarrow}$   $\stackrel{V}{\longrightarrow}$ 

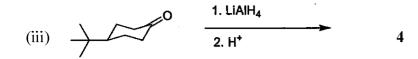
(iii) 
$$R = R + CH_3 = Co_2(CO)_8$$

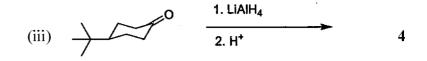
**4.** Explain the role of the following organometallic reagent in carbon-carbon bond forming reaction.

- (a) Reaction of  $\sigma$ -organochromium
- (b) Tebbe Reagents 4
- (c) (η²-alkene)palladium(II) complex.

#### Section C

**5.** How will you carry out the following reactions and suggest a suitable mechanism:





- **8.** Explain the following with suitable example(s) and mechanism:
  - (i) Rosenmund's Reduction. 4
  - (ii) Reductive amination. 4
  - (iii) Why reduction of alkynes by electron transfer method gives trans-product?

- 8. Explain the following with suitable example(s) and mechanism:
  - i) Rosenmund's Reduction.
  - (ii) Reductive amination. 4
  - (iii) Why reduction of alkynes by electron transfer method gives trans-product?

#### **Section D**

- 7. Discuss the mechanism of the the following reactions:  $4\times3$ 
  - (a) Barton reactions
  - (b) Photofries rearrangement
  - (c) Di- $\pi$ -methane rearrangement.
- 8. (a) Discuss the possible products after photo-irradiation of  $\alpha$ -santonin. Give mechanistic details.
  - (b) Discuss the formation of products giving suitable mechanism after photo-irradiation of benzene. **6+6**

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# LMDQ/D-23

6539

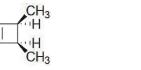
# ORGANIC CHEMISTRY SPECIAL-II CHEM-305

Time : Three Hours] [Maximum Marks : 60

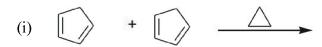
**Note**: Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks.

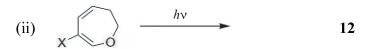
#### Section A

- 1. (a) Predict the product of cycloaddition of ethylene and cis-2-butene, addition being supramolecular on both the reactants. State under which condition (thermal or photochemical) the reaction will be symmetry allowed.
  - (b) The following compound can open by two conrotatory modes. Predict the products in each case and state which one will be formed predominantly.



- 2. (a) Giving proper reasoning, predict the reaction condition for disrotatory interconversion of 1,3,5-hexatriene ⇒ cyclohexadiene.
  - (b) Predict the products and give mechanism for their formation for the following reactions:





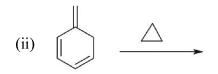
**3.** (a) Write down the mechanism for the following rearrangement:

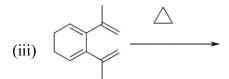


- (b) With the help of a suitable example discuss Sommlet-Houser and cope rearrangement. 12
- 4. Giving justification, predict the products in the following reactions under given reaction conditions:  $4\times3$

(i) 
$$CO_2$$
  $CO_2$ 

2





#### **Section C**

- 5. (a) Draw and discuss Jablonski diagram.
  - (b) Giving mechanism, predict the products of the photolysis of  $(CH_3)_3CO(CH_3)_3$ .
  - (c) Giving mechanism, predict the product(s) in the following reaction:

$$\xrightarrow{hv} \quad 4\times3$$

**6.** (a) Giving mechanism, predict the product(s) of the photolysis of following ketone:

- (b) Predict the product(s) when a solution of benzophenone in isopropyl alcohol is irradiated at 345 nm.
- (c) Discuss the photodimerisation of 1,3-butadiene.

 $4\times3$ 

#### Section D

- 7. Sketch an important method for the synthesis of guanine and caffeine.
- **8.** (a) Give the general methods for the structural determination of quercetin.
  - (b) Write down the product(s) of the following reaction.Also sketch the mechanistic pathway: 8,4

Roll No. ..... Total Pages: 04

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# PHARMACEUTICAL CHEMISTRY

SPECIAL-I CHEM-304

(CBCS-LOCF)

Time : Three Hours] [Maximum Marks : 60

**Note**: Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks.

#### Section A

- 1. (a) Discuss synthetic equivalents and FGI with examples.
  - (b) Analyze the molecule using disconnection approach:

(c) Discuss one group C-X disconnection of acid derivatives. 4,4,4

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P.T.O.

- 2. (a) What do you understand by masked  $H_2S$  equivalent? Explain.
  - (b) Define and discuss reversal of polarity.
  - (c) Disconnect the molecule to propose a suitable synthetic method: 4,4,4

**3.** (a) Disconnect the compound using synthon approach:

- (b) Explain the application of synthon approach in the synthesis of nafimidone. 5,7
- **4.** (a) Apply synthon approach in the synthesis of propanolol.
  - (b) Describe the role of (i) THP and (ii) Cbz as protective groups. 5,7

#### **Section C**

5. (a) Write the systematic name of:

- (b) How will you synthesize pyrazole starting from acetylacetone?
- (c) Complete the reaction. Also discuss the mechanism: 3,5,4

$$\begin{array}{c|c} & \text{NH} & \underline{\text{conc. } H_2SO_4} \\ & \text{Ph} & \\ \end{array}$$

- **6.** (a) Discuss the reactivity of 1, 2- and 1, 3-azoles towards nucleophilic reactions.
  - (b) Write the product(s)/mechanism: 4,8

(i) 
$$N \longrightarrow Br_2$$
 CHCl<sub>3</sub>

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3

P.T.O.

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#### Section III

- Discuss antipyretic agents in detail.
- Write the synthesis of the following:
  - Celecoxib
  - Diclofenac, and biosynthesis of eicosanoid.

#### **Section IV**

- Give recent advances of hormonal contraceptives in detail.
- Discuss calcium channel blockers and synthesis of clonidine and diltiazem.

**Total Pages: 02** Roll No. .....

## LMDQ/D-23

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# PHARMACEUTICAL CHEMISTRY SPECIAL-II **CHEM-305**

Time: Three Hours] [Maximum Marks: 60

**Note**: Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks.

#### **Section I**

- Explain the general mode of action, medicinal uses and synthesis of Thiotepa and 6-mercaptopurine drugs.
- Discuss antimalarial agents and mode of action of nucleoside reverse transcriptase inhibitors for AZT and ddC.

#### **Section II**

- Give synthesis, SAR, mechanism of action of sulphonamides.
- Illustrate structure, mode of action, synthesis of azithromycin and ampicillin.

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