# DR. C. S. RAO P.G. CENTRE SRI Y N COLLEGE (AUTONOMOUS) Narsapur, W.G.Dt., A.P.

NAAC Accredited 'A' Grade College; Affiliated to Adikavi Nannaya University

# BOARD OF STUDIES OF DEPARTMENT OF ORGANIC CHEMISTRY (M.Sc.)



# M.Sc. ORGANIC CHEMISTRY COURSE STRUCTURE & SYLLABUS (W.e.f. 2020-21 Admitted Batch)



# DEPARTMENT OF ORGANIC CHEMISTRY Dr.C. S. RAO.P.G.CENTRE: SRI Y.N.COLLEGE (AUTONOMOUS) BOARD OF STUDIES OF DEPARTMENT OF ORGANIC CHEMISTRY (M.Sc.) SYLLABUS

(With effect from the admitted batch of 2020-2021 academic year)

#### **Programme Outcomes:**

The study of M.Sc. Organic Chemistry will enable the students:

- To enrich the student's theoretical knowledge in basic, core and specialized papers of
  Organic chemistry and to develop competency in research in the field of Chemistry.
- ii. To train the students with hands on experience and enhance their critical thinking, constructive planning and analytical skills.
- iii. To train the students to acquire advanced laboratory skills required for placements in the industries.

#### **Programme Specific Outcomes:**

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The study of M.Sc. Organic Chemistry will enable the students:

- i. To understand and apply the principles of Organic Chemistry.
- ii. To attain the ability to plan synthetic scheme and synthesis for elementary compounds.
- iii. To identify the organic compound structure by using spectroscopic techniques.
- iv. To master the sophisticated analytical techniques.



# REGULATIONS

- 1. The duration of the course is for two academic years with total four semesters. The nature of the course is full-time.
- 2. Candidates for the degree of Master of Science in Organic Chemistry shall be required to have passed the B.Sc. /B.Sc. (Vocational) with Chemistry /Applied Chemistry as one of the Subjects.
- 3. Eligibility for admission into the M.Sc. Programme is a graduation degree with 50% of marks or equivalent CGPA in case of OC category and 45% of marks in case of BC and SC categories
- 4. Intake for M.Sc. Organic Chemistry is 30 (Convener- 24 + Management-06).
- 5. Mode of admission is through (APPGCET) Entrance examination and Counselling.
- 6. Candidates have to undergo practical training for four weeks during the second year in any Industry/ Chemical R&D / Organization at their own expense and have to submit a project report.
- 7. Each paper carries 100 marks out of which 25 marks are internal and 75 marks are external. The pass mark in each paper is 40.
- 8. Two internal theory examinations are conducted in every paper for 20 Marks. The average marks are awarded finally. In addition, two marks are awarded for two assignments in each paper and three marks are awarded for seminar presentation.
- 9. The course will be evaluated and the students will be graded on ten point scale with seven letter grades i.e., 0, A+, A, B+, B, C, P, and F. A candidate shall be declared to have passed in any paper if he /she secures not less than `P' grade in theory and not less than 'C' grade in the practical's/projects/Industrial Training, provided the result otherwise is withheld .There is no minimum pass mark for internal assessment both in theory and practical's.
- 10. The practical examinations will be conducted and, valued by both internal and external examiners at the end of each semester. The Viva- Voce examination will be conducted on the project work done by both internal and external examiners (from other Autonomous Colleges) at the end of the IV semester.
- 11. Each practical paper carries 75 marks for external evaluation process in which both the internal and external examiners conduct the examination. Out of these 75 marks, 10marks are allocated for the Record work and 10 marks are allotted for the Viva-Voce examination.
- 12. The Minimum attendance of 75% in theory and 90% in the practical prescribed for the course is necessary for a student to get qualified for the Semester-End Examination. The Principal/Director is authorized to condone the shortage of attendance in theory papers in deserving cases on recommendation of the Head of the Department, by collecting the prescribed fee. However, the student should have to put in a minimum attendance of 65% in aggregate of the total number of instructional days in theory classes.



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# **13.** Blue Print for Internal Examinations

Max.Marks: 25	Duration: 1:30 hrs.		
Theory Exam			
Essay Questions 1 out of 2	1 x 14 = 14 Marks	20 Marks	
Short notes 2 out of 3	$2 \times 3 = 6$ Marks		
Assignments	2	5 Marks	
Total		25 Marks	

### 14. Blue Print for External Semester – End Examinations

Max. Marks: 75

**Duration: 3 hrs.** 

S.No.	Type of question	No. of questions to be given	To be answered No. of questions	Marks allotted to each question	Total marks
1	Section – A Essay type question (Internal choice)	4 + 4 (either or choice)	4	15	60
2	Section – B Short answer question (External choice)	8	5	3	15
				Total Marks	75



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Chapter Name	Essay type questions (15 marks)	Short answer questions (3 marks)	Marks allotted to each unit
Unit – I	2	2	36
Unit – II	2	2	36
Unit – III	2	2	36
Unit – IV	2	2	36

### **15.** Blue Print for Semester End Examination Question Paper:

Laboratory Course Semester End Examination:

Practical Examination	55 marks
Viva	10 marks
Record	10 marks
Total	75 Marks

#### **19.** Gradation system:

The Grading Table suggested by the University Grants Commission, New Delhi under Choice Based Credit System is followed.

Grade points are allotted based on percentage of marks as shown in the table

S. No.	Range of Marks %	Grade	<b>Grade Points</b>	
1	90 - 100	0	10	Out standing
2	80-89.99	$A^+$	9	Excellent
3	70-79.99	А	8	Very Good
4	60-69.99	$\mathbf{B}^+$	7	Good
5	55-59.99	В	6	Above Average
6	50-54.99	C	5	Average
7	40-49.99	Р	4	Pass
8	0-39.99	F	0	Fail
9			0	Ab (Absent)



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#### Terms used and their explanation:

Credit Point: It is the product of grade point and number of credits for a course.

**Credit:** A unit by which the course work is measured. It determines the number of hours of instructions required per week. One credit is equivalent to one hour of teaching (lecture or tutorial) or two hours of practical work / field work per week.

Grade Point: It is a numerical weight allotted to each letter grade on a 10 point scale.

**Letter Grade:** It is an index of the performance of students in a said course. Grades are denoted by letters O, A<sup>+</sup>, A, B<sup>+</sup>, B, C, P and F.

#### Calculation of SGPA (Semester Grade Point Average):

For example if a student gets the grades in one semester A<sup>+</sup>, B, B<sup>+</sup>, C, O, A<sup>+</sup> in six subjects having credits 2(S1), 4(S2), 4(S3), 4(S4), 4(S5), 2(S6), respectively.

The SGPA is calculated as: SGPA(S<sub>i</sub>) =  $\frac{\sum (C_i \times G_i)}{\sum C_i}$ 

Where C<sub>i</sub> is number of credits of i<sup>th</sup> course and G<sub>i</sub> is the grade point scored by the student.

$$SGPA = \frac{\{2 \times 9 + 4 \times 6 + 4 \times 7 + 4 \times 5 + 4 \times 10 + 2 \times 9\}}{\{2 + 4 + 4 + 4 + 2\}} = \frac{148}{20} = 7.40$$

If a student gets the grades in another semester A, C, A, C, A<sup>+</sup>, B<sup>+</sup>, A, in seven subjects having credits 4(S1), 2(S2), 4(S3), 2(S4), 4(S5), 4(S6), 2(S7) respectively. The SGPA is calculated as follows:

$$SGPA = \frac{\{4 \times 8 + 2 \times 5 + 4 \times 8 + 2 \times 5 + 4 \times 9 + 4 \times 7 + 2 \times 8\}}{\{4 + 2 + 4 + 2 + 4 + 4 + 2\}} = \frac{164}{22} = 7.45$$

#### Calculation of CGPA (Cumulative Grade Point Average):

For example if a student gets SGPA's 7.40 and 7.45 respectively for two Semesters in a year, then.

The CGPA is calculated as follows: CGPA =  $\frac{\sum (C_i \times S_i)}{\sum C_i}$ 

Where Si is the SGPA of i<sup>th</sup> semester and C<sub>i</sub> is total number of credits in that semester.

$$CGPA = \frac{\{20 \times 7.40 + 22 \times 7.45\}}{\{20 + 22\}} = \frac{312}{42} = 7.09$$



#### **Examination Rules & Regulations:**

- CGPA will be calculated from II Semester onwards upto the final semester. CGPA multiplied by '10' gives aggregate percentage of marks obtained by a candidate.
- A candidate shall be declared to have passed in a subject / paper if the candidate secures a minimum of 'P' grade in theory examination and a minimum of 'C' grade in Practical Examination / Project / field Work / Viva Voce / Industrial Training. This includes sessional marks wherever applicable.
- Further, a candidate has to secure a minimum of 40% in theory examination (excluding sessional marks) and a minimum of 50% (excluding sessional marks) in the Practical Examination / Project / field Work / Viva Voce / Industrial Training.
- Further, a candidate will be permitted to choose any paper (s) to appear for improvement in case the candidate fails to secure the minimum prescribed SGPA / CGPA to enable the candidate to pass at the end of any semester examination.
- Minimum Qualification for Physically Challenged: 10% reduction of marks in each semester in each subject will be allowed for Physically Challenged candidates against the prescribed minimum to secure a pass.
- Revaluation:

The candidate has to apply for revaluation on or before 10 days from the date of publication of the results.





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#### M.Sc. ORGANIC CHEMISTRY

#### SCHEME OF INSTRUCTION AND EXAMINATION

Paper/ Paper	Title of the	Instruction Hours Per Week			Credits	Evaluation			Total
code	Paper	т	т	р		CIA	S	SEE	Marks
		L	I	r		Marks	Marks	Duration	
Paper – I 200CHT11	General Chemistry – I	4	-	-	4	25	75	3 hours	100
Paper – II 200CHT12	Inorganic Chemistry – I	4	-	-	4	25	75	3 hours	100
Paper – III 20OCHT13	Organic Chemistry-I	4	-	-	4	25	75	3 hours	100
Paper – IV 20OCHT14	Physical Chemistry-I	4	-	-	4	25	75	3 hours	100
Practical –I 200CHP15	Inorganic Chemistry-I	-	-	6	3	25	75	3 hours	100
Practical –II 200CHP16	Organic Chemistry – I	-	-	6	3	25	75	3 hours	100
Practical – III 200CHP17	Physical Chemistry-I	-	-	6	3	25	75	3 hours	100

#### <u>Semester – I</u>

CIA- Continuous Internal Assessment, SEE – Semester End examination

#### Semester - II

Paper/ Paper	Title of the	Instruction Hours Per Week			Credits	Evaluation			Total
code	Paper	т	т	D		CIA	S	SEE	Marks
		L	1	Г		Marks	Marks	Duration	
Paper – I 20OCHT21	General Chemistry– II	4	-	-	4	25	75	3 hours	100
Paper – II 200CHT22	Inorganic Chemistry–II	4	-	-	4	25	75	3 hours	100
Paper – III 20OCHT23	Organic Chemistry-II	4	-	-	4	25	75	3 hours	100
Paper – IV 20OCHT24	Physical Chemistry-II	4	-	-	4	25	75	3 hours	100
Practical –I 200CHP25	Inorganic Chemistry-II	-	-	6	3	25	75	3 hours	100
Practical –II 200CHP26	Organic Chemistry–II	-	-	6	3	25	75	3 hours	100
Practical – III 200CHP27	Physical Chemistry-II	-	-	6	3	25	75	3 hours	100



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Paper/	Title of the Paper	Instruction Hours Per Week		Credits	Evaluation			Total	
Paper code		т	т	D		CIAS		SEE	Marks
		L	1	Г		Marks	Marks	Duration	
Paper – I 20OCHT31	Organic Reaction Mechanism-I and Organic Photochemistry	4	-	-	4	25	75	3 hours	100
Paper – II 20OCHT32	Organic Spectroscopy- I	4	-	-	4	25	75	3 hours	100
Paper – III 20OCHT33	Modern Organic Synthesis-I	4	-	-	4	25	75	3 hours	100
Paper – IV 20OCHT34	Chemistry of Natural Products	4	-	-	4	25	75	3 hours	100
Practical –I 200CHP35	Multistep Synthesis of Organic Compounds	-	-	6	3	25	75	3 hours	100
Practical –II 200CHP36	Estimations and Chromatography	-	-	6	3	25	75	3 hours	100
То	tal	16		12	22	150	450	18 hours	600

Semester - III

Semester - IV

Paper/ Title of the Paper		Instruction Hours Per Week		Credits	Evaluation			Total	
Paper code		т	т	п		CIA		SEE	Marks
		L	1	P		Marks	Marks	Duration	
Paper – I 200CHT41	Organic Reaction Mechanism-II and Pericyclic Reactions	4	-	-	4	25	75	3 hours	100
Paper – II 200CHT42	Organic Spectroscopy-II	4	-	-	4	25	75	3 hours	100
Paper – III 200CHT43	Modern Organic Synthesis-II	4	-	-	4	25	75	3 hours	100
Paper – IV 200CHT44	Bio-Organic Chemistry	4	-	-	4	25	75	3 hours	100
Practical –I 200CHP45	Chromatographic Separations and Isolations & Identification of Natural Products	-	-	6	3	25	75	3 hours	100
Practical –II 200CHP46	Spectral Identification of Organic Compounds	-	-	6	3	25	75	3 hours	100
Project 200CHP47	* Project Work & Viva Voce	-	-	-	6	25	75	-	100

\*4 Week Training in Industry / Chemical R & D / Organization Total Credits: 100, total Marks: 2700



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#### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – I (W.e.f. 2020-2021 Admitted Batch) Paper – I: General Chemistry – I

# UNIT-I

**Basic Quantum Chemistry-I:** Wave equation-interpretation of wave function-properties of wave function-normalization and orthogonalisation, Operators- linear and non-linear-commutators of operators. Postulates of quantum mechanics; setting up of operators to observables; Hermitian operator- Eigen values and Eigen functions of Hermitian operator; Expansion theorems. Eigen functions of commuting operators-significance. Simultaneous measurement of properties and the uncertainty principle.

# UNIT-II

**Basic Quantum Chemistry-II:** Wave mechanics of simple systems with constant potential energy, particle in one-dimensional box- factors influencing color transition- dipole integral, Symmetry arguments in deriving the selection rules, the concept of tunneling- particle in three -dimensional box. Calculations using wave functions of the particle in a box-Orthogonality, measurability of energy, position and momentum, average values and probabilities. Rigid rotor, Wave mechanics of systems with variable potential energy-simple harmonic oscillator-solution of wave equation- selection rules.

# UNIT-III

**Fundamentals of Molecular Spectroscopy-I:** Microwave and IR- Spectroscopy- Rotational spectra of diatomic molecules-Rigid rotor-Selection rules- Calculations of bond length-Isotopic effect, Second order stark effect and its applications. Infrared spectra of diatomic molecules- harmonic and anharmonic oscillators- Selection rules- Overtones- Combination bands- Calculation of force constant, anharmonicity constant and zero point energy. Fermi resonance, simultaneous vibrational-rotational spectra of diatomic molecules.

# UNIT- IV

**Fundamentals of Molecular Spectroscopy-II:** Raman and Electronic Spectra- Classical and quantum mechanical explanations- Rotational Raman and Vibrational Raman spectra. Electronic spectra of diatomic molecules- Vibrational Coarse structure- intensities of spectral lines- Franck-Condon principle- applications, Rotational Fine structure- band head and band shading. Charge transfer spectra.

# **References/** Text books

- 1. Fundamentals of Molecular spectroscopy: by C.N. Banwell
- 2. Molecular spectroscopy: by B.K.Sharma
- 3. Molecular spectroscopy: by Aruldas
- 4. Introductory quantum mechanics: by A.K. Chandra
- 5. Quantum chemistry: by R.K. Prasad



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#### DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – I (W.e.f. 2020-2021 Admitted Batch)

Paper – I: General Chemistry – I (200CHT11)

Time: 3 hrs

4.

Max. Marks: 75

# SECTION – A $(4 \times 15 = 60 \text{ Marks})$

# Answer ALL questions

1. a) Give a detail account of uncertainty principle and properties of simultaneous measurement.

(Or)

- b) Discuss the setting up of operators for different observables.
- 2. a) Derive the Schrodinger's wave equation for a particle in one dimensional box with constant potential energy.

(Or)

(b) Derive the solution for Schrodinger wave equation for simple harmonic oscillator. Add a note on selection rules

3. a) i) How do you explain rotational and vibrational spectra of diatomic molecules based on Infrared spectroscopy.

(ii) What is zero point energy? Explain.

- (Or)
- (b) (i) Discuss harmonic and an harmonic oscillations with schematic diagram.
- (ii) Write notes on characteristic features of microwave and Infrared Spectroscopy
- a) i) How do you explain Raman Spectrum on the basis of classical and quantum mechanical theories?

(ii) Write the selection rules and explain the nature of pure rotational and pure vibrational Raman Spectra.

(Or)

b) (i) Describe the origin of PQR Spectrum in rotational fine structure of the electronic spectrum of a diatomic molecule.

(ii) What is Frank-Condon principle? Write its application?



# SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. What are Hermitian operators? Prove that kinetic energy operator is Hermitian
- 6. Write a note on Heisenberg uncertainty principle
- 7. Describe the phenomenon of tunneling.
- 8. Write a note on selection rules for color transitions in 1-D box
- 9. Give an account on rigid rotor model.
- 10. Explain isotopic effect.
- 11. Write a note on Charge transfer-spectra
- 12. Write a note on vibrational coarse structure.





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### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – I (w.e.f. 2020-2021 Admitted Batch)

# Paper – II: INORGANIC CHEMISTRY - I

### UNIT-I

**Structure & Bonding:** Applications of VSEPR, Valence Bond and Molecular orbital theories in explaining the structures of simple molecules- role of p and d orbitals in  $\pi$ -bonding. Application of MO theory to Tetrahedral  $[CoCl_4]^{2^-}$ , Square planar  $([PtCl_4]^{2^-})$  and octahedral

complexes  $([CoF_6]^{3-}, [Co(NH_3)_6]^{3+})$ . Classification of ligands based on  $\pi$ -bonding using MO

theory. Walsh diagram for H<sub>2</sub>O molecule.

### UNIT-II

**Inorganic cage and ring compounds** - preparation, structure and reactions of boranes, carboranes, metallocarboranes. Electron counting in boranes - Wades rules (Polyhedral skeletal electron pair theory).

Heterocyclic inorganic ring systems: Boron - Nitrogen (H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>), Phosphorus-Nitrogen (N<sub>3</sub>P<sub>3</sub>C1<sub>6</sub>) and Sulphur-Nitrogen (S<sub>4</sub>N<sub>4</sub>,(SN)<sub>x</sub>)cyclic compounds.

Cage Compounds: Phosphorous oxides and Phosphorous sulphides.

Isopoly and heteropoly anions.

### UNIT-III

**Coordination compounds:** Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries. Calculation of crystal field stabilization energies. Factors affecting crystal field splitting energies - Spectrochemical series – Jahn - Teller effect, nephelauxetic effect - ligand field theory.

Term symbols - Russell - Sanders coupling - derivation of term symbols for various configurations. Spectroscopic ground states.

#### UNIT- IV

**Electronic spectra of transition metal complexes:** Types of electronic transitions - d-d transitions - Selection rules, break down of selection rules - Orgel and Tanabe-Sugano diagrams for  $d^1 - d^9$  octahedral and tetrahedral transition metal complexes of 3d series - Calculation of Dq, B and  $\beta$  parameters. Charge transfer spectra.

Magnetic properties of transition and inner transition metal complexes - spin and orbital moments - quenching of orbital momentum by crystal fields in complexes.

#### **Reference books & Text books:**

- 1. Advanced Inorganic Chemistry by F.A. Cotton and G. Wilkinson, IV Edition, John Wiley and Sons, New York, 1980.
- 2. Inorganic Chemistry by J.E. Huheey, III Edition, Harper International Edition, 1983.
- 3. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated to East West Press Pvt. Ltd., New Delhi.
- 4. Inorganic Chemistry by Shriver and Atkins Oxford University Press 1999



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#### DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – I (W.e.f. 2020-2021 Admitted Batch)

Paper – II: Inorganic Chemistry – I (20OCHT12)

Time: 3 hrs.

Max. Marks: 75

#### **SECTION** – A (4 x 15 = 60 Marks)

#### **Answer ALL questions**

 a) What are the rules of LCAO method? Draw MO energy level diagrams for NO; NO<sup>-</sup> and NO<sup>+</sup> and predict the decreasing order of Bond energies.

(Or)

b) Draw the Mo energy level diagram for  $[Co(NH_3)_6]^{3+}$  and  $[Co(F_6)]^{3-}$  and discuss their magnetic properties.

2. a) Describe the preparation, structure and reactions of Boron – Nitrogen and Sulphur – Nitrogen cyclic compounds.

(Or)

(b) Explain the preparation of carboranes and discuss Wade's rules to explain the structures higher boranes.

3. a) State and explain John – Teller effect. How this theorem could explain the distortions in octahedral complexes?

(Or)

(b) Explain the crystal field splitting patterns in Tetrahedral and square planar geometries with suitable example.

4. a) How do Tanabe – Sugano diagrams differ from Orgel diagrams? Draw Tanabe – Sugano diagram for  $\left[ Cr(H_2O)_6 \right]^{3+}$ .

(Or)

b) Discuss differential types of paramagnetic behavior of transition metal complexes.



# SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. Explain valence bond theory.
- 6. Draw the Walsh diagram for  $H_2O$  molecule.
- 7. Write a short note on Metallocarboranes.
- 8. Write a short note on isopoly acids.

- 9. Write a short note on Spectro chemical series of ligands.
- 10. Write a short note on Nephelauxetic effect.
- 11. Explain Ligand to metal charge transfer transitions with examples.
- 12. Write a short note on Electronic transitions.



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### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – I (W.e.f. 2020-2021 Admitted Batch)

#### Paper – III: ORGANIC CHEMISTRY - I

#### UNIT-I

#### Nature of bonding in organic molecules and Aromaticity

(A) **Electronic Effects and Reactive intermediates**:-Inductive effect, Mesomeric effect (Resonance), Hyper conjugation, Steric effect, Tautomerism, Generation, structure, stability and reactivity of carbocation's, carbanions, free radicals, carbenes, nitrenes and arynes

(B) **Criteria of Aromaticity:**- Huckle's rule and MO Theory, Aromaticity in Charged and Fused-Ring Systems, Hetero-aromatic Systems, Annulenes: Cyclobutadiene, Benzene, 1,3,5,7-Cyclooctatetraene, [10] Annulenes- [12], [14], [16] and [18] annulus's, azulenes, fulvenes, fullerenes, ferrocene, anti- aromaticity and homo-aromaticity.

#### UNIT-II

#### Stereo Chemistry & Molecular representation of organic molecules

- (A) Molecular Symmetry and Chirality: Symmetry elements, definition and classification of stereoisomers, enantiomer, diastereomer, homomer, epimer, anomer, configuration and conformation, configurational nomenclature: D, L and R, S nomenclature, Molecules with a single chiral center: Molecules with two or more chiral centers.
- (B) Geometrical Isomerism and conformation of Cyclic Systems: Cis trans, E, Z and Syn & anti nomenclature, methods of determining configuration of Geometrical isomers using physical, spectral and chemical methods, stability, Cis trans inter conversion. Conformations of cyclobutane, cyclopentane, cyclohexane, mono and disubstituted cyclohexane's.
- (C) Prochirality and Pro-stereoisomerism: Homotopic ligands and faces; enantiotopic ligands and faces; diastereotopic ligands and faces; nomenclature of enantiotopic ligands and faces (Pro R, Pro S, Re, Si carbonyl compounds and Alkenes).
- (D) Stereoisomerism in molecules without chiral center Axial chirality Allenes, Alkylidene Cycloalkanes, spiranes, nomenclature, atropisomerism: Biphenyl derivatives, nomenclature, planar chirality: Ansa compounds, paracyclophanes, trans-cyclooctene and helicity.

#### UNIT – III

#### **Heterocyclic Compounds**

Importance of heterocyclic compounds as drugs. Nomenclature of heterocyclic systems based on ring size (1. Hantzsch-Widman nomenclature. 2. Common nomenclature 3. Replacement nomenclature), number and nature of hetero atoms. Chemistry of heterocyclic compounds, synthesis and reactivity of the following systems: Aziridines, Thiranes, Azetines, Thietanes, Quinoline, Isoquinoline, Indole, Pyrazole, Imidazole, Oxazole, Isoxazole, Pyridazine, Pyrimidine and Pyrazine.



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15 Hrs.

20 Hrs.

#### $\mathbf{UNIT} - \mathbf{IV}$

#### Chemistry of some typical natural products (Alkaloids and Terpenoids)

A study of the following compounds involving their isolation, structure elucidation, synthesis and biogenesis of Alkaloids; Atropine, Nicotine, and Quinine.

Terpenoids:  $\alpha$  - Terpenol,  $\alpha$  - Pinene and Camphor.

#### **Books Suggested:**

- Advanced Organic Chemistry-Reactions. Mechanism and structure, Jerry March, 6th Ed. (John Wiley & Sons).
- 2. Organic Chemistry, Paula Yurkanis Bruice, 4th Ed. (Printice Hall)
- 3. Organic chemistry-Clayden J. (Oxford)
- 4. Organic Chemsitry, Wade, L.G. Jr. 5th Ed. (Pearson)
- 5. Advanced Organic Chemistry: Reactions and mechanisms, Miller Bernard & Other, 2nd Ed. (Pearson)
- 6. Mechanism and Theory in Organic Chemistry, Thomas H. Lowry, Kathleen S. Richardson. Harper & Row, (Publishers, Inc.).
- 7 A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, 6th Ed., (Longman).
- 8. Reaction Mechanism in Organic Chemistry, P.S. Kalsi, 2nd Ed. (New Age International).
- 9. Organic Chemistry, R. T. Morrison and R. N. Boyd (Prentice-Hall)
- 10. Stereochernistry to Organic Compounds, E.L. Eliel (John Wiley).
- 11. Stereochemistry, P.S. Kalsi. 5th Ed. (New Agc International).
- 12. Organic Chemistry Structure and Reactivity, Ege Seyhan, 3<sup>rd</sup> Ed. (AITBS)
- 13. Heterocyclic Chemistry, J.A.Joule, K. Kills and G. F. Smith, Chapman and Hall
- 14. Heterocyclic Chemistry, T.L.Gilchrist. Longman Scientific Technical
- 15. Heterocyclic Chemistry, Raj.K. Bansal.
- 16. An Introduction to the Heterocyclic Compounds, R. M. Acheson, John Wiley.
- 17. Chemistry of Natural Products, K.W.Bentley
- 18. Stereochemistry of carbon compounds by E.Eliel, John Wiley & Sons, Inc.
- 19. Stereochemistry to Organic Compounds, D. Nasipuri, 2nd Ed. (New Age International).
- 20. Chemistry of Natural products by R.S. Kalsi Kalyani Publishers. 1983.





Time: 3 hrs.

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> DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – I (W.e.f. 2020-2021 Admitted Batch)

Paper – III: ORGANIC CHEMISTRY – I (20OCHT13) M

Max. Marks: 75

# SECTION - A (4 x 15 = 60 Marks)

# Answer ALL questions

		Allswei ALL y	uestions							
1.	a) Write about the fo	ollowing.								
	i) Inductive effect	ii) Mesomeric effect	iii) Hyper conjugation							
		(Or)								
	b) Write about the following.									
	i) Huckles rule									
	ii) Aromaticity in benzenoid and non benzenoid systems									
	iii) Homo aromaticit	y								
2.	a) Write about the m	ethods of determining	configuration of geometrical isomers using							
	physical, spectral an	d chemical methods.								
		(Or)								
	b) Write about the fo	ollowing.								
	i) Chirality	ii) Pro-chirality	iii) Pro-stereoisomerism							
3.	a) Write any three m	ethods of preparation f	for the following compounds.							
	i) Pyrimidine	ii) Imidazole	iii) Quinoline							
		(Or)								
	b) Which is the prop	er site for electrophilic	substitution among the following? Explain.							
	i) Indole	ii) Oxazole	iii) Pyrazole							
4.	a) Explain the struct	ure elucidation & synth	nesis of atropine.							
		(Or)								
	b) Explain the struct	ure elucidation and syr	thesis of camphor.							



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#### Answer any FIVE questions

- 5. Give 1 example of anullenes, fullerenes and fulvenes.
- 6. Write the structures of primary, secondary and tertiary carbonium ions and give their order of stability.
- 7. Give one example for allenes, biphenyls and spiranes.
- 8. Differentiate diastereomers and enantiomers.
- 9. Write one method for the preparation of iso-quinoline.
- 10. Why isoxazole is less basic than oxazole.
- 11. Write the structures of quinine and  $\alpha$  terpeneol.
- 12. Write the structures of Nicotine and  $\alpha$  pinene.





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#### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – I (W.e.f. 2020-2021 Admitted Batch) Paper – IV: PHYSICAL CHEMISTRY - I

#### UNIT-I

**Thermodynamics-I:** Concepts of partial molar properties - partial molar volume and its significance; Determination of partial molar volume: Graphical method, intercept method and apparent molar volume method. Partial molar free energy, chemical potential, Variation of chemical potential with T and P. Gibbs-Duhem equation-derivation and significance. Phase equilibrium- Derivation of phase rule from the concept of chemical potential. Ideal solutions - Thermodynamic properties of ideal solutions mixing quantities; Vapor pressure-Raoult's law: Thermodynamic properties of ideally dilute solutions. Vapor pressure- Henry's law.

Non-ideal systems -Concept of fugacity, fugacity coefficient. Determination of fugacity; Non ideal solutions. Activities and activity coefficients; Standard-state conventions for non-ideal solutions; Determination of activity coefficients from vapour pressure measurements. Activity coefficients of non-volatile solutes using Gibbs-Duhem equation. Chemical equilibrium-effect of temperature on equilibrium constant- Van'tHoff equation

#### UNIT-II

**Micelles and Macro molecules:** Surface active agents, classification of surface active agents, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization- phase separation and mass action models, Solubilization, micro emulsion, reverse micelles.

Polymer- definition. Types of polymers. Electrically conducting, fire resistant, liquid crystal polymers, kinetics of free radical polymerization. Molecular mass- Number and mass average molecular weight, molecular weight determination-End group analysis, Osmometry, viscometry, ultracentrifugation and light scattering methods.

#### UNIT-III

**Chemical Kinetics:** Theories of reaction rates- Collision theory- Limitations, Transition state theory. Effect of ionic strength - Debye Huckel theory-Primary and secondary salt effects; Effect of dielectric constant, effect of substituent, Hammett equation-limitations. Taft equation; Prediction of rate constants- Consecutive reactions, parallel reactions, opposing reactions (Uni molecular steps only, no derivation). Specific and general acid-base catalysis; Skrabal diagram; Fast reactions- different methods of studying fast reactions- flow methods, relaxation methods- temperature jump and pressure jump methods.

#### UNIT-IV

**Photochemistry:** Electronic transitions in molecules. Franck-Condon principle. Electronically excited molecules- singlet and triplet states, spin-orbit interaction. Quantum yield and its determination; Actinometry - ferrioxalate and uranyl oxalate actinometers-problems. Derivation of fluorescence and phosphorescence quantum yields. Quenching effect- Stern Volmer equation. Photochemical



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equilibrium and delayed fluorescence – E type and P type. Photochemical primary processes, types of photochemical reactions – photodissocoation, addition and isomerization reactions with examples.

#### Books

- 1. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford Universiyt Press.
- 2. Physical Chemistry by G.W. Castellon, narosha Publishing House
- 3. Physical Chemistry by W J Moore, Prentice Hall
- 4. Thermodynamics for Chemists, Samueal Glasstone
- 5. Chemical Kinetics by K J Laidler, McGraw Hill Pub.
- 6. Photochemistry, R P Kundall and A Gilbert, Thomson Nelson
- 7. Poymer Chemistry by Billmayer
- 8. Introduction to Polymer Science, V R Gowriker, N V Viswanadhan and J Sreedhar, Wiley Easter.
- 9. Micells, Theoretical and applied aspects, V Morol, Plenum Publishers.





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#### DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – I (W.e.f. 2020-2021 Admitted Batch) Paper – IV: Physical Chemistry – I (200CHT14)

Time: 3 hrs. SECTION – A Max. Marks: 75 (4 x 15 = 60 Marks)

### **Answer ALL questions**

1. a) i) Explain partial molar properties and describe a method for the determination of partial molar property.

ii) Explain chemical potential and derive Gibbs – Duhem equation.

(or)

b) i) Derive an expression for the mixing of free energy and entropy change in ideal solutions.

ii) An ideal solution is made from 5.00 mole of benzene and 3.25 mole of toluene. Calculate at 298 K and 1 bar pressure.

2. a) i) write a short note on surfactants.

ii) Explain the process of micellization and discuss the factors effecting CMC of surfactants.

(or)

b) i) Explain briefly number average & weight average molecular weight of a polymer.ii) Explain the methods Osmometry and Viscometer for the determination of molecular weight of a polymer.

3. a) i) Explain the drawbacks of collision theory and how it overcome by transition state theory.

ii) Discuss the effect of dielectric constant of solvent on the rates of reactions.

(or)

b) i) Write a note on Skrabal plots.

ii) Discuss the principle involved in Relaxation techniques to study the kinetics of fast reactions.

4. a) i) Define quantum yield and explain the reasons for low and high quantum yield for the reactions and how it is determined?

ii) Explain Quenching effect and derive Stern – Volmer equation.

(or)

- b) i) Discuss fluorescence and E and P type delayed fluorescence.
- ii) Explain photo isomerization and photochemical oxidation reactions with examples.



# SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. Explain how partial molar volume is determined by density measurements?
- 6. What is vapor pressure? Derive Raoul's law.
- 7. Outline any two methods of determination of CMC.
- 8. Explain briefly end group analysis.
- 9. Write short notes on potential energy diagram for a chemical reaction.
- 10. Discuss the kinetics of consecutive reactions.
- 11. State and explain Frank Condon principle.
- 12. Discuss briefly photochemical equilibrium.





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#### LABORATORY WORK (6 hrs /Week)

#### Practical – 1

I.

#### Inorganic Chemistry Practical's - I

- Inorganic Synthesis: Preparation of i) Tetraamminecopper (II) sulphate ii) Potassium tris (oxalate) ferrate (III) trihydrate iii) Tris (thiourea) copper (I) sulphate
- II. Semi micro qualitative analysis of six radical mixtures (One interfering anion and one less familiar cation for each mixture) Anions:  $CO_3^{2-}$ ,  $S^{2-}$ ,  $SO_3^{2-}$ ,  $CI^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CH_3COO^-$ ,

Cations: Ammonium  $(NH_4^+)$ 

1<sup>st</sup> group: Hg, Ag, Pb, Tl, W 2<sup>nd</sup> group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo 3<sup>rd</sup> group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be 4<sup>th</sup> group: Zn, Mn, Co, Ni 5<sup>th</sup> group: Ca, Ba, Sr 6<sup>th</sup> group: Mg, K, Li

#### **Reference Books:**

Vogel's textbook of semi micro qualitative analysis, 5th Edition by G. Svehla.

#### Practical – 2

#### **Organic Chemistry Practical – I**

Preparation, recrystallization and determination of melting point & yield of the following compounds:

i) Aspirin,	ii) Nerolin,	iii) Chalcone
iv) p-nitro acetanilide,	v) 2, 4, 6-tribromoaniline	vi) m-dinitrobenzene
vii) Phthalimide	viii) Diels-Alder adduct	

#### Practical – 3

#### Physical Chemistry practical – I

- 1. Determination of critical solution temperature of phenol water system.
- 2. Effect of added electrolyte on the CST of phenol water system.
- 3. Conductometric titration of strong acid versus strong base.
- 4. Dissociation constant of weak acid (CH<sub>3</sub>COOH) by conductometric method.
- 5. Conductometric titration of weak acid vs strong base.
- 6. Determination of cell constant.
- 7. Adsorption of acetic acid on animal charcoal or silica gel.
- 8. Acid catalyzed hydrolysis of methyl acetate.
- 9. Determination of partial molar volume of solute  $-H_2O$  system by apparent molar volume method.

#### **Books Suggested**

- 1. Vogel's Text Book of Quantitative Chemical Analysis, J Mendham, R C Denney, J D Barnes and M J Thomas, 4<sup>th</sup> & 6<sup>th</sup> Ed. (Pearson Education Asia).
- 2. Vogel's Text Book of Organic Chemistry, B S Furniss, A J Hannaford, P W G Smith, A R Tatchell, 5 Ed (Longman Scientific & Technical)



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#### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – II (W.e.f. 2020-2021 Admitted Batch)

### Paper – I: GENERAL CHEMISTRY - II

#### UNIT - I

**Basic Quantum Chemistry-III**- Hydrogen atom- solution of R(r),  $\phi(\phi)$  and  $\theta(\theta)$  equations. Probability density in orbitals- shapes of orbitals- Perturbation theory- Time independent perturbation theory(only first order perturbation is to be dealt with)- application to ground state energy of Helium atom- Variation principle- applications- calculation of zero-point energy of harmonic oscillator- many electron atom- Hartee-Fock self-consistent field method(qualitative treatment only).

#### UNIT-II

Molecular symmetry and Group Theory in chemistry: Basic concepts of symmetry and Group theory-Symmetry elements, symmetry operations and point groups- Schoenflies symbols- Classification of molecules into point groups-Axioms of Group theory- Group multiplication tables for  $C_{2v}$  and  $C_{3v}$ , point groups- Similarity transformations- and classes-Representations- reducible and irreducible representations, Mullikan symbols, Orthogonality theorem and its implications, Character table and its anatomy.

#### UNIT-III

Treatment of analytical data: Accuracy and precision- Classification of errors- Determinate and Indeterminate errors-Minimization of errors- Absolute and Relative errors, propagation of errors-Distribution of Indeterminate errors- Gaussian distribution- Measures of central tendency-Measures of precision- Standard deviation- Standard error of mean- students t-test- Confidence interval of mean-Testing for significance- Comparison of two means- F-test- Criteria of rejection of an observation-Significant figures and computation rules.

#### UNIT- IV

Introduction to computer programming- FORTRAN 77: Basic structures and functioning of computer with P.C. as an illustrative example- Main memory- Secondary storage memory- input/output devices-computer languages- operating systems- principles of algorithms-and flow charts-constants and variables- Arithmetic expressions- Arithmetic statements-Replacement statement- IF statement- logical IF and BLOCK IF statements- GOTO statements-subscripted variable and DIMENSION statement. DO statement- Rules for DO statement- Functions and subroutines- Development of FORTRAN statements for simple formulae in chemistry such as Vander Waals equation- pH of a solution- First order rate equation- Cell constant-Electrode potential. Flowcharts and computer programs for

- a) Program for the calculation of Cell Constant, Specific Conductance and Equivalence.
- b) Rate Constant of First order reaction or Beer's law by linear least square method.
- c) Hydrogen ion concentration of a strong acid solution/Quadratic equation.



- d) Solution for Vander Waals equation or Hydrogen ion concentration of a monoprotic weak acid
- e) Standard deviation and Variance of univariant data.

#### **References/ Text Books:**

- 1. Introductory Quantum Chemistry; by A K Chandra
- 2. Group Theory for Chemistry: by A K Battacharya,
- Chemical Applications of Group Theory by F A Cotton, 3<sup>rd</sup> Edition, Wiley Inter science New York
- 4. Introductory Group theory for Chemists: by George Davidson
- 4. Vogel's text book of quantitative analysis: by Vogel
- 5. Fundamentals of Analytical Chemistry: by Skog and West
- 6. Principles of Computer Programming (FORTRAN 77 IBM PC): by V Rajaraman
- 7. Basics of Computers for Chemists: by P C Jurs.





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Time: 3 hrs.

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> DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – II (W.e.f. 2020-2021 Admitted Batch)

Paper – I: GENERAL CHEMISTRY – II (200CHT21)

Max. Marks: 75

# SECTION - A (4 x 15 = 60 Marks)

#### Answer ALL questions

1. a) Explain the time independent perturbation theory deals with only for first order.

(Or)

b) Derive the Schrodinger wave equation for the hydrogenation and explain separation of variables.

- 2. a) i) what is character table? Explain its significance with an example.
  - ii) Write the Schoenflies notation of point groups.

(Or)

b) i) what is point group? Find out the point group of the molecules.

a) H<sub>2</sub>O b) BCl<sub>3</sub>

ii) Describe the great orthogonally theorem and its implications.

- 3. a) i) Discuss in detail the classification of errors. Explain how they are minimized.
  - ii) Explain importance of standard deviation treatment of analytical data.

(Or)

- b) i) Write notes on significant figures and computation rule.
- ii) Explain the following

a) Absolute and relative errors b) standard error of mean

4. a) Discuss the significance of flow charts in computer programming and explain computer programming of the calculation of hydrogen ion concentration of a strong acid solution.

(Or)

b) Explain the development of FORTRAN statements for simple formulae in Chemistry such as Vander wall's equation.



# SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. Write the wave function of 1S orbital and explain its shape?
- 6. Write the Schrodinger wave equation of He + ion and separate the variables.
- 7. Define symmetry and symmetry operations and explain with an example.
- 8. Deduce the point groups for  $C_6H_6$ .
- 9. Write a short note on student's t-test.
- 10. What is the standard deviation for the replicate measurements given below? 3.056, 3.080, 3.094, 3.107, 3.112, 3.174, 3.198
- 11. Give the various input and output devices in computers.
- 12. Write the flow chart for calculating the roots of a quadratic equation.





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### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – II (W.e.f. 2020-2021 Admitted Batch) Paper – II: INORGANIC CHEMISTRY - II

#### UNIT-I

**Metal Cluster Compounds** – definition – evidences for existence of M - M bonds – conditions favourable for formation of M-M bonds – preparation, structure and bonding of the following metal cluster compounds.

 $Re_{2}Cl_{8}^{2-}, Mo_{2}Cl_{8}^{4-}, Re_{2}(RCOO)_{4}X_{2}, Mo_{2}(RCOO)_{4}(H_{2}O)_{2}, Cr_{2}(RCOO)_{4}(H_{2}O)_{2}, Cu_{2}(RCOO)_{4}(H_{2}O)_{2}, Cu_$ 

Povatomic clusters – Zintle ions, chevrel phases.

#### Unit – II

**Organometallic compounds** – 16 and 18 electron rules. Isoelectronic relationship – synthesis, structure, bonding and reactions of carbon monoxide, dinitrogen and nitric oxide complexes. Isolobal relationship – H, Cl, CH<sub>3</sub>,  $Mn(CO)_5$ ; S, CH<sub>2</sub>, Fe(CO)<sub>4</sub>;P,CH, Co(CO)<sub>3</sub>. Synthesis, structure, bonding and reactions of metallocenes with special reference to ferrocene. Catalysis by organometallic compounds – homogeneous, heterogeneous catalysis – alkene hydrogenation – Wilkinson's catalyst, hydro formylation.

#### UNIT – III

#### Metal Ligand equilibria in solution

Stepwise and overall formation constants and their interaction – trends in stepwise constants – factors affecting the stability of metal complexes – Pearson's theory of hard and soft acids and bases (HSAB), chelate effect and its thermodynamic origin, determination of stability constants of complexes – spectrophotometric method and pH – metric method. Reactivity of metal complexes – inert and labile complexes. Explanation of lability on the basis of VBT & CFT.

**Bio** – **Inorganic Chemistry:** Metalloporphyrins with special reference to Hemoglobin & Myoglobin. Biological role of alkali and alkaline earth metal ions with special reference to  $Ca^{2+}$ . Biological and a biological Nitrogen fixation.

#### **UNIT-IV**

**Inorganic reaction mechanisms:** Substitution reactions of metal complexes – D, Id, Ia and A mechanisms – Ligand replacement reactions of octahedral complexes – acid hydrolysis – factors affecting acid hydrolysis – Anation and base hydrolysis of Cobalt (III) complexes. Ligand displacement reactions of square planar complexes of platinum (II). Factors affecting square planar substitution – Trans effect (theories).

Electron transfer reactions of complexes – concept of complementary and non-complementary reactions with examples. Inner and outer sphere mechanisms.



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#### **Text Books:**

- 1. Advanced Inorganic Chemistry by F.A. Cotton and R.G. Wilkinson, IV Edition, John, John Wiley and Sons, New York, 1980.
- 2. Inorganic Chemistry by J E Huheey, III edition, Harper International Edition, 1983.
- 3. Organometallic Chemistry: A unified approach by A. Singh and R C Mehrotra, Wiley Eastern Ltd.
- 4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999)
- 5. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West Press Pvt. Ltd.
- 6. Mechanisms of Inorganic reactions in solution by D. Benson, MG Graw Hill, London, 1968
- 7. Inorganic Chemistry by K.F. Purcell and J.C.Kotz, W.B. Saunders Company, New York, 1977
- 8. Elements of Bioinorganic Chemistry by G N Mukherjee and Aroinda Das, U N Dhur & Sons Pvt. Ltd. Calcutta.





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> DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – II (W.e.f. 2020-2021 Admitted Batch)

Paper – II: Inorganic Chemistry – II (20OCHT22)

Time: 3 hrs.

Max. Marks: 75

# SECTION – A (4 x 15 = 60 Marks) Answer ALL questions

1. a) Discuss the preparation, structure, bonding and magnetic behavior of  $Re_2 Cl_8^{2-}$ .

(Or)

b) Define metal cluster compounds. And write the evidences and favorable conditions for formation of M-M bonds.

2. a) Explain the types of metal carbonyl and discuss their preparation and structure.

(Or)

b) What are metallocenes? Explain the synthesis, structure and bonding of ferrocene.

3. a) Define stepwise and overall formation Constants of Metal – ligand complexes with examples. Explain the factors influencing the stability of metal complexes.

(Or)

b) What are oxygen transport enzymes? Discuss the mechanism of oxygen transport by hemoglobin.

4. a) What is acid hydrolysis? Discuss its mechanism and explain the evidences in support of the mechanism.

(Or)

b) Discuss the mechanism of electron transfer reactions of complexes with suitable examples.



#### Answer any FIVE questions

#### (5 x 3 = 15 Marks)

- 5. What are zintle ions?
- 6. Explain the structure of  $Re_3Cl_9$ .
- 7. Write a short note on alkene hydrogenation.
- 8. What are isolable fragments? Give examples.
- 9. Explain the lability of complexes based on Crystal Field Theory.
- 10. Explain the role of  $Ca^{2+}$  in muscle contraction.
- 11. Write a short note on Trans effect.
- 12. Write a short note on complementary and non complimentary reactions.





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### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester - II (W.e.f. 2020-2021 Admitted Batch)

### Paper – III: ORGANIC CHEMISTRY – II (200CHT23)

#### **UNIT-I**

**Reaction Mechanism:** 

(A) Aliphatic Nucleophilic Substitution and Nucleophilic Aromatic substitution: Stereochemistry of SN<sub>2</sub> and SN<sub>1</sub> mechanisms, Neighboring Group Participation (Anchimeric assistance), NGP by O, S, N: Aromatic Nucleophilic substitution: Ar  $SN_2$  (Addition — Elimination), Ar  $SN_1$  and benzyne mechanisms (Elimination - Addition): evidence for the structure of benzyne. Von Richter Sommelet-Hauser rearrangements.

(B) Elimination Reactions: Type of elimination reactions, mechanisms. Stereochemistry and Orientation, Hofmann and Saytzeff rules, Syn elimination versus anti-elimination, competition between elimination and substitution, dehydration, dehydrogenation, dehalogenation, decarboxylative eliminations and pyrolytic eliminations.

#### UNIT-II

#### **Addition Reactions:**

(A) Addition to Carbon - Carbon Multiple Bonds: Mechanistic and stereo chemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, region and chemo selectivity, orientation and reactivity, Hydrogenation of double and triple bonds, hydrogenation of aromatic rings, Hydroboration.

(B) Addition to Carbon-Hetero Multiple Bonds: Steric course of addition reactions to C=O and C=N, Aldol, Cannizzaro, Perkin, Knoevenagel, Claisen- Schmidt, Claisen, Dieckman, Benzoin and Stobbe condensations, Reformatsky reaction, Tollens's reaction, Prins reaction: Wittig, Grignard, Mannich and Michael reaction.

#### **UNIT-III**

#### **Molecular Rearrangements:**

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Types of molecular rearrangements, migratory aptitude; Rearrangements to electron deficient carbon: Pinacol-pinacolone, Wagner-Meerwein, Tiffeneau - Demjanov, Dienone - Phenol, Arndt-Eistert synthesis:

Rearrangements to electron deficient nitrogen: Beckmann, Hofmann, Curtius, Schmidt and Lossen rearrangements,

Rearrangements to electron deficient oxygen: Baever-villiger, Hydro peroxide rearrangement and Dakin rearrangements, Neber rearrangement, Benzil-Benzilic acid and Favorskii rearrangements. **UNIT-IV** 

#### **Spectroscopy (Theoretical aspects only):**

- U V. Visible absorption laws, Electronic excitations and absorption shifts i)
- I.R.: Fundamental modes of vibrations in IR Spectroscopy. Finger Print Region and its importance. ii) iii) NMR: Chemical shift and its importance, coupling constant and its importance, Factors affecting
- chemical shift and coupling constant, Dueteration-deuterium exchange and Deuterium Labeling. iv) Mass: Some useful terms used in Mass spectrometry: Molecular ion, Fragmentation, Cleavage, Rearrangement, Loss of small molecules. Isotope, Abundance, Metastable ions, Even - electron rule, Nitrogen rule, Mc Lafferty Rearrangement.

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#### 15 Hrs.

15Hrs

15 Hrs.

15 Hrs.

#### **Books Suggested:**

- Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I Fleming Tata
  McGraw Hill, New Delhi, 1990.
- 2. Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
- 3. Applications of absorption spectroscopy of Organic Compounds J.R.Dyer, Prentice Hall of India, New Delhi, 1984.
- 4. Spectrometric identification of Organic Compounds-Fourth Edition, R.M. Silverstein: G.C.Vassiellr and T.C. Merill, Jaime Willey, Singapore, 1981.
- 5. Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd (Harcourt college publishers).
- 6. Organic reaction Mechanisms by V.K Ahluwalia Rakesh Kumar Parashar.





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#### DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – II (W.e.f. 2020-2021 Admitted Batch)

Paper –III: ORGANIC CHEMISTRY-II (20OCHT23) Max. Marks: 75

Time: 3 hrs.

3.

# SECTION - A (4 x 15 = 60 Marks)

#### **Answer ALL questions**

1. a) Describe  $ArSN_1 \& ArSN_2$  reaction with mechanism and examples.

(Or)

b) Describe elimination reactions with particular reference to saytzef and Hoffmann's rules.

2. a) Write a note on Stereo chemical aspects of addition reactions involving electrophiles.

(Or)

b) Write about the following.

- i) Cannizzaro reaction ii) Reformatsky reaction iii) Witting reaction
- a) Write about the following.
  - i) Pinacol Pinacolone rearrangement
  - ii) Tiffeneau demjanov rearrangement
  - iii) Curtius rearrangement

(Or)

- b) Write a short note on the following.
- i) Beckmann rearrangement
- ii) Dakin rearrangement
- iii) Favourskii rearrangement
- 4. a) i) Explain fundamental modes of vibrations in IR spectroscopy.
  - ii) Explain types of electronic transitions.

(Or)

- b) i) Define Molecular Ion, Meta stable ions, Nitrogen rule in mass spectrometry.
- ii) Explain chemical shift and its importance.



# SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. Write about Hofmann rule.
- 6. Write the Von Richter Sommelet Hauser rearrangement
- 7. Write a short note on Pyro lytic eliminations.
- 8. Hydrogenation of double and triple bonds.
- 9. Write about Schmidt rearrangement.
- 10. Write about Baeyer Veliger rearrangement
- 11. Write a note on Grignard reaction.
- 12. Write a note on Finger Print region in IR spectroscopy.





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#### DEPARTMENT OF CHEMISTRY M.Sc. I Year Semester – II (W.e.f. 2020-2021 Admitted Batch)

#### Paper – IV PHYSICAL CHEMISTRY - II

#### UNIT-I

**Physical methods of molecular structural elucidation:** NMR: Principle and theory, Nature of spinning particle and its interaction with magnetic field. Chemical shill and its origin. Spin-Spin interaction, Application of NMR to structural elucidation- Structure of ethanol, dimethyl formamide, styrene and acetophenone.

**Electron Spin Resonance:** Principle and experimental technique- g-factor, line shapes and line widthshyperfine interactions- applications of ESR studies.

#### UNIT -II:

**Thermodynamics-II- Brief review on entropy:** entropy changes accompanying specific process - expansion, phase transition, heating, measurement of entropy. Nernst heat theorem; Third law of thermodynamics- Determination of the absolute entropy- Apparent exceptions to Third law of thermodynamics.

Statistical Thermodynamics: Objectives of statistical thermodynamics. Concept of distributions, Types of ensembles. Thermodynamic probability, Most probable distribution Law - Partition Function, (Definition and significance): Molar and molecular partitions-translational, rotational, vibrational and electronic partition functions- Relation between thermodynamic functions (E, H, S, G and  $C_v$ ) and the partition functions.

#### UNIT-III:

**Electrochemistry I:** Electrochemical cell- Galvanic and electrolytic cell. Concentration cell with and without transference, Effect of complexation on redox potential- ferricyanide/ ferrocyanide couple, Iron (III) phenonthroline / Iron (II) phenonthroline couple. Determination of standard potential, solubility product equilibrium constant and activity coefficients from EMF data.

Bjerrum theory of ion association (elementary treatment) Concept of activity and activity coefficients in electrolytic solutions. The mean ionic activity coefficient. Debye-Huckel theory of electrolytic solutions. Debye-Huckel limiting law (derivation not required), Calculation of mean ionic activity coefficient; Limitations of Debye-Huckel theory. Effect of dilution on equivalent conductance of electrolytes - Anomalous behavior of strong electrolytes. Debye Huckel-Onsagar equation — verification and limitations, Fuel Cells.

#### **UNIT-IV:**

**Electrochemistry II:** The electrode-electrolyte interface. The electric double layer. The Helmholtz-Perrin parallel-plate model, the Gouy-Chapman diffuse-charge model and the Stem model. Electrodics: Charge transfer reactions at the electrode-electrolyte interface. Exchange current density and overpotential. Derivation of Butler-Volmer equation. High field approximation, Tafel equation, Low field equilibrium, Nernst equation. Voltametry-Concentration polarization, experimental techniques.



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#### **Books:**

- 1. Text book of Physical Chemistry by Samuel Glasstone, McMillan Pub.
- 2. Physical Chemistry by W.J.Moore, Prentice Hall
- 3. Physical Chemistry by G.W. Castellon, Narosha Publishing House
- 4. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
- 5. Modern Electrochemistry, 2A & 2B. JOM Bockris & A.K.N.Reddy, Plenum publishers
- 6. Introduction to Electrochemistry, S.Glasstone.
- 7. Fundamentals of Molecular Spectroscopy, Banwell
- 8. Spectroscopy by Straw & Walker.
- 9. Statistical thermodynamics, M.C.Gupta
- 10. Statistical Thermodynamics, M.Dol





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Time: 3 hrs

DR. C. S. RAO P.G. CENTRE SRI Y N COLLEGE (AUTONOMOUS), Narsapur, W.G.Dt., A.P. NAAC Accredited 'A' Grade College; Affiliated to Adikavi Nannaya University

> DEPARTMENT OF ORGANIC CHEMISTRY M.Sc. I YEAR SEMESTER – II (w.e.f. 2020-2021 Admitted Batch)

Paper –IV: PHYSICAL CHEMISTRY – II (20OCHT24) Max. Marks: 75

#### SECTION - A (4 x 15 = 60 Marks)

#### **Answer ALL questions**

- 1. a) i) Explain the principle involved in NMR spectroscopy and write about chemical shift & factors affecting.
  - ii) Discuss the NMR spectrum of pure and acidified ethanol.

(Or)

- b) i) Discuss the hyperfine splitting in ESR with two examples.
- ii) Write a short note on line widths and line shapes in ESR.
- 2. a) i) what is entropy? How the absolute entropy of solids, liquids and gases are determined.

ii) Derive the rotational partition function.

(Or)

b) i) Discuss the various attempts leads to Nernst heat theorem and its significance.

ii) Based on thermodynamic probability, derive the Maxwell Boltzmann distribution law.

3. a) i) Discuss how standard potential and activity coefficient are determined from EMF data.

ii) Explain the anomalous behavior of strong electrolytes. Give the Debye Huckel – Onsager equation. Discuss how it is verified.

(or)

b) i) Discuss the effect of complication on redox potentials with examples.

ii) Write a short note on fuel cells.

- 4. a) i) Explain the stern model for double layer. How is it better compared to parallel plate and Gouy Chapmann model?
  - ii) Give the Tafel equation. Show that it is special case of Butler Volmer equation.

(or)

- b) i) Explain the principle involved in voltammetric techniques.
- ii) Define concentration polarization and discuss the factors affecting it.



## SECTION – B (5 x 3 = 15 Marks) Answer any FIVE questions

- 5. Write a short notes on g-factor in ESR spectra.
- 6. Discuss briefly the importance of chemical shift in NMR spectroscopy.
- 7. The enthalpy of vaporization of methanol is 35.27 kJ mol<sup>-1</sup> and its normal boiling point of 64.1<sup>o</sup>C. Calculate the entropy of vaporization of methanol at this temperature.
- 8. Write a short note on ensemble.
- 9. Explain fuel cells with an example.
- 10. Calculate the EMF of the concentration cell.

 $Cu/CuSO_4(a=0.1)//CuSO_4(a=0.004)/Cu$  at  $25^{\circ}C$ , if the transport number of copper ion is 0.396.

- 11. What are Tafel plots and outline its importance.
- 12. Calculate the ionic strength and the mean activity coefficient of 1.00 m mol kg<sup>-1</sup> CaCl<sub>2</sub> (aq) at 25<sup>o</sup>C.





#### Laboratory work (6 hrs /week)

#### Practical – 1

#### Inorganic chemistry practical-II

#### Quantitative analysis:

#### Volumetric:

- 1. Determination of Ferric ion by photochemical reduction.
- 2. Determination of Nickel by EDTA.
- 3. Determination of calcium and magnesium by EDTA.
- 4. Determination of Ferro cyanide by ceric sulphate.
- 5. Determination of Copper (II) in presence of iron (III).

#### Gravimetric:

- 6. Determination of zinc as zinc pyrophosphate.
- 7. Determination of nickel from a mixture of copper and nickel.

#### **Reference books:**

Vogel's textbook of quantitative chemical analysis, 5th edition by G H Jeffery et al.

#### Practical – 2

#### **Organic Chemistry Practical – II**

#### Systematic qualitative analysis of an organic mixture containing two compounds.

Identification of method of separation and the functional group (s) present in each of them and preparation of one solid derivative for the conformation of each of the functional group (s).

#### Practical – 3

#### Physical Chemistry practical – II

- 1. Distribution of iodine between CHCl<sub>3</sub> and water.
- 2. Distribution of  $I_2$  between CHCl<sub>3</sub> and KI solution calculation of equilibrium constant.
- 3. Determination of coordination number of cuprammonium cation.
- 4. Titration of mixture strong acid and weak acid versus strong base by conductometry.
- 5. Titration of strong acid Vs strong base pH metry.
- 6. Titration of mixture of  $(NaHCO_3 + Na_2CO_3)$  Vs HCl pH metry.
- 7. Titration strong acid Vs strong base using Quinhydrone electrode.
- 8. Titration of  $Fe^{+2}$  Vs  $K_2Cr_2O_7$  potentiometry.
- 9. Determination of single electrode potential of  $Cu^{2+}/Cu$  an estimate the given unknown concentration.





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## DEPARTMENT OF CHEMISTRY

## M.Sc. II YEAR SEMESTER - III

(W.e.f. 2020-2021 Admitted Batch)

Paper – I: ORGANIC REACTION MECHANISMS-I & PHOTO CHEMISTRY

## UNIT – I

**Organometallic Compounds:** Introduction- Organocadmium compounds (preparationproperties- applications), Organomercury compounds (preparation- properties- applications), Organolead compounds (preparation- properties- applications), Organ chromium compounds (Preparation- properties- applications), Organoiron compounds (preparation- propertiesapplications), Organorhodium compounds (preparation- properties- applications), Organotellurium compounds (preparation- properties- applications),

Organotellurium compounds (preparation- properties- applications)

## UNIT – II

## Principles of asymmetric synthesis:

Introduction-Stereo selective reactions: Substrate stereo selectivity, product stereo selectivity, Enantioselectivity and diastereoselectivity. Conditions for stereo selectivity: Methods for Inducing enation and diastereoselectivity. Analytical methods: % Enantiomeric excess, Enantiomeric ratio, optical purity, % diastereomeric excess and diastereomeric ratio. Techniques for determination of enantiomeric excess, specific rotation, Chiral NMR; Chiral Derivatizing agents, chiral solvent, chiral shift reagents and Chiral HPLC.

## UNIT – III

## Photo Chemistry-I

Photochemical energy, Frank Condon Principle, Types of Electronic Excitation and Molecular orbital view of excitation, Jablonski Diagram, singlet and triplet states, photosensitization, quenching, quantum efficiency and quantum yield.

Photo Chemistry of Carbonyl Compounds: Norrish Type I reaction (alpha cleavage reaction), Norrish Type – II reaction, Paterno- Buchi reaction, Photo reduction & photo enolisation; photochemical Oxidations [Backstrom mechanism], Photo oxidation of alkenes with singlet oxygen.

## UNIT-IV

## Photochemistry-II

Di – Pi methane Rearrangement, Oxa di – Pi methane rearrangement; Aza di – Pi methane rearrangement; Photochemistry of Benzene and substituted benzene, 1, 2, 1,3, & 1, 4-additions; Photo Fries rearrangement of Phenolic acetates and Anilides; Photochemistry of unsaturated systems, Cis-Trans Isomerization of alkenes (Direct and sensitized) (Photoisomerisation of Stilbene), Photochemistry of Butadiene; Dimerization's of alkenes, Intramolecular dimerisation.Photochemical rearrangement of Cyclohexadienenones; Photochemistry of alpha, beta Unsaturated ketones (dimerization's and addition across the double bond); Photochemical rearrangement reactions of Cyclohexenone, Photo rearrangements of Beta, gamma unsaturated systems (Mechanism of 1,2 & 1,3 – acyl shifts); Photochemistry of Nitrite esters (Barton reaction),Hoffman Loeffler- Freytag reaction

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and Photolysis of organic hypothalites.

15 Hrs.

15 hrs.

15 Hrs.

15 Hrs.

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#### **Text Books and Reference Books:**

- Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, McGraw Hill and Kogakush.
- 2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
- 3) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Rich grandson.
- 4) The modern structural theory in Organic Chemistry by L.N.Ferguson, Pretice Hall
- 5) Physical Organic Chemistry by jack Hine, Mc. Graw Hill
- 6) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 7) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 8) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 9) Organic Synthesis, M. B. Smith, Mc Graw Hill, International Edition.
- 10) Organic Chemistry, Calydon, Greeves and Stewarts Warren.
- Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz,W. H. Freeman & company, New York.
- 12) Organic Photochemistry by Turro Photochemistry by C W J Wells

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#### Time: 3 hours

#### SECTION-A

Maximum marks: 75M (4x15=60marks)

#### Answer all questions

- 1. a) i) Write a note on organo mercury compounds and its synthetic applications.
  - ii) Write a note on preparation and properties of organo lead compounds.

#### (OR)

- b) i) Write a note on organo rhodium compounds and its synthetic applications.
  - ii) Write a note on preparation and properties of organotellurium compounds.
- 2. a) i) Write a short note on substrate stereoselectivity and product stereoselectivity.ii) Write a note on chiral shift reagents in asymmetric synthesis.

#### (OR)

- b) i) Explain the terms % diastereomeric excess and stereo selectivity.
  - ii) Discuss Crams rule with appropriate example.
- a) i) Discuss in detail about Norrish type I and Norrish type -II reaction
  ii) Write photo oxidation of alkenes with singlet oxygen.

#### (OR)

#### b) Explain:

- i) Paternobuchi reaction.
- ii) Photo reduction.
- 4. a) Explain the following reactions with mechanism
  - i) Aza di-  $\pi$  methane rearrangement
  - ii) Barton reaction.

#### (OR)

- b) Explain the following reactions with mechanisms
  - i) Photo Fries rearrangement.
  - ii) Photo chemistry of pyridinium ylides.



#### **SECTION-B**

#### Answer any FIVE Questions.

(5×3=15)

- 5. Write a note on preparation of organocadmium compounds.
- 6. Write a note on organoiron compounds.
- 7. Describe methods for introducing enantioselectivity.
- 8. Discuss Re and Si faces of acetophenone.
- 9. Explain Frank Condon principle.
- 10. Write short notes on types of electronic excitations.
- 11. Explain Photo aromatic substitution reactions.
- 12. Write about Photochemistry of Cis-Tran's isomerization of alkenes.







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SRI Y.N.COLLEGE (AUTONOMOUS), NARSAPUR W. G. Dt., A.P. NACC Accredited 'A' Grade College: Affiliated to Adikavi Nannaya University. **DEPARTMENT OF CHEMISTRY** M.Sc. II YEAR SEMESTER - III (W.e.f. 2020-2021 Admitted Batch) Paper – II: ORGANIC SPECTROSCOPY-I

#### 15 hrs.

#### UNIT-I

#### **UV-Visible spectroscopy:**

- Introduction-Instrumentation-Mechanics of measurement- UV absorption of Alkenes-A) Polyenes unsaturated cyclic systems.
- UV absorption of carbonyl compounds: α, β-unsaturated carbonyl systems-UV B) Absorption of aromatic systems-solvent effects-geometrical isomerism-acid and base effects-typical examples-calculation of  $\lambda$  max values using Woodward Fieser rules, applications.

#### **UNIT-II**

#### **Infrared spectroscopy:**

- A) Introduction-Instrumentation (Dispersive instrument & Fourier Transform instrument) Mechanics of measurement- Factors effecting Vibrational frequency-hydrogen bonding-Sampling Techniques and Applications of IR Spectroscopy.
- B) Typical group frequencies for -CH,-OH, N-H, C-C, C-O and aromatic systems-Application in structural determination–Examples-simple problems.

#### **UNIT-III**

#### Nuclear Magnetic Resonance Spectroscopy (1HNMR):

- A) Introduction: Basic principle of- NMR Nuclear spin- nuclear resonance-saturation-Relaxation-Instrumentation.
- B) Shielding and deshielding of magnetic nuclei-chemical shift and its measurements, factors Influencing chemical shift - spin-spin interactions- factors influencing coupling constant J and factors effecting J value.
- 13C NMR Spectroscopy: Similarities and Differences between PMR and CMR, general C) Considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, hetero aromatic



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#### 15 hrs.

15 hrs.

and Carbonyl carbon), coupling constants, typical examples of CMR spectroscopysimple Systems.

#### UNIT-IV

#### Mass spectrometry:

Introduction: Ion production-E1, C1, ES, MALDI and FAB- determination of Molecular Weight and formulae-Behavior of organic compounds in mass spectrometer- factors affecting Fragmentation.

Mass spectral fragmentation of Common functional groups, Examples of mass spectral Fragmentation of organic compounds with respect of their structure determination.

#### **Suggested Books:**

- Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I.Fleming Tata McGraw Hill, New Delhi, 1990.
- 2. Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
- Applications of absorption spectroscopy of Organic Compounds J.R.Dyer, Prentice Hall of India, New Delhi, 1984.
- Spectrometric identification of Organic Compounds-Fourth Edition, R.M. Silverstein: G.C.Vassiellr and T.C. Merill, Johne Willey, Singapore, 1981.
- 5. Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd (Harcourt College publishers).
- 6. Absorption spectroscopy of organic molecules-V.M.Parkih.
- Nuclear Magnetic Resonance-Basic principles-Atta-Ur-Rehman, Springer-Verlag, 1986.

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15 hrs.

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Time: 3 hrs

I.

#### Max marks: 75

#### **SECTION-A**

(4X15=60Marks)

1. a) Write a note on Instrumentation of UV-Visible Spectroscopy.

Answer ALL of the fallowing questions

(OR)

b) Using Woods ward-Fieser rules, calculate the values of absorption maxima for the following compounds.



2. a) Write a note on Factors effecting Vibrational Frequency in IR spectroscopy.

(OR)

- b). How would you distinguish the following sets of compounds using IR Spectra?
- i) Phenol & Cyclo hexanol.
- ii) Ethyl benzene and O-Xylene.
- iii) Cis and Trans alkenes
- 3. a) Write a note on fallowing terms with suitable examples.i) Nuclear spin. ii) Nuclear Resonance. iii) spin-spin interactions.

(OR)

- b) i. Write a note on factors influencing chemical shift.
  - ii. Write a note on coupling constant (J) and factors effecting J value.



a) i. Explain the mass fragmentation pattern in Aromatic compounds and Amines.ii. Explain the mass fragmentation pattern in carbonyl compounds and hydrocarbons.

(OR)

b) Explain any three techniques used for ion production in mass spectrometry.

#### SECTION-B

#### II. ANSWER ANY FIVE QUESTIONS.

(5×3=15M)

- 5. Write a note on UV absorption values for  $\alpha$ ,  $\beta$  unsaturated carbonyl compounds.
- 6. Explain why UV absorption bands appear broad.
- 7. How do you identify aromatic aldehydes and aromatic ketones by IR spectra?
- 8. Write the IR frequencies for Benz aldehyde.
- 9. What is non- first order spectra .give suitable examples.
- 10. Predict the chemical shift positions for the carbons of Benz aldehyde and cinnamadehyde.
- 11. Write a note on Mc lafferty rearrangement.
- 12. Write a note on mass spectral fragmentation of alchohol.





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## Dr. C.S.RAO.P.G.CENTRE. SRI Y.N.COLLEGE (AUTONOMOUS), NARSAPUR W. G. Dt., A.P. NACC Accredited 'A' Grade College: Affiliated to Adikavi Nannaya University. DEPARTMENT OF CHEMISTRY M.Sc. II YEAR SEMESTER - III (W.e.f. 2020-2021 Admitted Batch) Paper – III: MODERN ORGANIC SYNTHESIS -I

#### UNIT-I

#### Formation of C-C single bonds

# Alkylation's via enol ate, Thermodynamic and kinetic enol ate, asymmetric Aldol reaction: a) Chiral enol ate and achiral aldehyde b) Achiral enol ate and chiral aldehyde – explanation by Zimmerman Traxler model; stork enamine reaction and its synthetic applications; **Organosulphur chemistry:** Ump lung and its synthetic applications (Corey Seebach Reaction), sulphurylides: dimethyl sulphoniummethylide, dimethyloxosulphoniummethylide preparations and their synthetic applications.

**Organo Palladium Chemistry:** Heck Reaction, Stille coupling, Suzuki coupling, onogashira coupling, Negeshi coupling, Wacker Oxidation.

**Organo copper chemistry:** Gilman's reagent and synthetic applications; Synthetic applications of carbenes and carbenoids; BaylisHilman reaction.

#### UNIT-II

#### Formation of Carbon-Carbon double bonds

Stereochemistry of E1 and E2 reactions (Different examples of acyclic and cyclic molecules, Saytzeff rule, Hofmann rules and Bredt's rule); Pyrolytic Syn eliminations (focus should be given on stereochemistry of syn eliminations of amine oxides, xanthates and esters of acyclic and cyclic molecules); Sulphoxide-Sulphenate rearrangement (Mislow-Evansrearrangement); Wittig reaction, Wittig-Horner reaction and stereo chemistry of Wittig reaction; Shapiro reaction, Claisen rearrangement of allyl vinyl ethers, Julia Lythgoe olefination, Mc Murray coupling, Peterson Olefination, Tebbs reagent and its application, Metathesis: Grubbs 1st and 2nd generation catalysts, Olefin cross coupling (OCM), ring closing (RCM) and ring opening (ROM) metathesis, olefination by Nysted reagent.

UNIT-III



#### 15 Hrs

# 15 Hrs

#### Chemistry of Silicon and Boron containing reagents.

- 15 Hrs
- a) **Organo Silicon Chemistry;** synthetic applications of  $\alpha$ -silyl carbanion and  $\beta$ -silyl carboniumions. Synthetic applications of silyl enol ethers, Preparation and synthetic applications of alkynyl silanes, aryl silanes, allyl silanes and vinyl silanes, Nazarov cyclization, Synthetic conversion of  $\alpha$ ,  $\beta$ -epoxy silanes, Peterson Olefination, Brook rearrangement and Rubottom oxidation.
- b) Organo Boron Chemistry: Preparation of Organobornaes, hydroboration with BH3-THF, dicylohexyl borane, disiamyl borane, thexyl borane, 9- BBN mono isopinocamphlyl borane (IPCBH2) and diisopinocamphenyl borane (IPC2BH) functional group transformations of Organo boranes-Oxidation, protonolysis and isomerization. Formation of carbon-carbon-bonds vizorgano boranes carbonylation and cyanidation.

#### UNIT-IV

## Phase Transfer Catalysts, Sono chemistry and Ionic Liquids.15 Hrs

- a) Phase Transfer Catalysts: Introduction-Mechanism of PTC Reaction- Types of Phase Transfer Catalysts, Reactions, Advantages and Synthetic Applications.
- b) Sono chemistry: Introduction-Types of Sono chemical Reactions and Applications.
- c) Ionic Liquids: Introduction-Properties-Types of Ionic Liquids-Synthetic Applications.

#### **Textbooks and Books for Reference Books:**

- Some Modern Methods of Organic Synthesis W. Carruthers, Third & Fourth Edition, Cambridge University Press, Cambridge, 1988.
- Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 4) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 5) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 6) Organic Synthesis, M. B. Smith, McGraw Hill, International Edition.
- 7) Organic Chemistry, Clayden, Greeves and Stuwart Warren.
- 8) Guide Book to Organic Synthesis (3rd edition), R. Mackie, D. M. Smith and Aitken.
- 9) Organo Boranes and Silanes, Thomson, Oxford Chemistry primers.
- 10) Strategic applications of named reactions in organic synthesis, Laszlo Kurti and Barbara Czako.
- 11) Modern Synthetic Reactions, Herbet O. House, Second Edition, W.A.Benzamine Inc. Menio Park, California, 1972.



- 12) Organic Synthesis viz Boranes, Herbet C. Brown Gray, W.Kramer Alan B. Levy and M. Mark Midland John Wiely &. Sons, New York, 1975.
- Organic Synthesis: Special Techniques, V. K. Ahluwalia and Renu Agarwal. 13)
- Organic Synthesis, Jagadamba Singh and Dr. A. Yadav, Pragati Edition. 14)

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## Dr.C.S.RAO.P.G.CENTRE. SRI Y.N.COLLEGE (AUTONOMOUS), NARSAPUR W.G.Dt., A.P. NACC Accredited 'A' Grade College: Affiliated to Adikavi Nannaya University. **DEPARTMENT OF CHEMISTRY** M.Sc. II YEAR SEMESTER – III (W.e.f. 2020-2021 Admitted Batch) Paper- III: MODERN ORGANIC SYNTHESIS-I (20**OCHT33**) Max marks: 75

Time: 3 hrs

#### **SECTION-A**

#### I. Answer ALL of the following questions

1. a) Write a note on Asymmetric Aldol reaction by using Zimmerman Traxler model.

#### (OR)

- b) Discuss the following reactions
- i. Suzuki coupling.
- ii. Baylis-Hillman reaction.
- iii. Stork Enamine Reaction.
- 2. a) Explain the following reactions with mechanism and examples.
  - i. Mc Murry coupling.

ii. Wittig reaction.

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#### (OR)

- b) Describe the following reactions
- i. Grubbs catalyst and its applications.
- ii. Shapiro reactions with examples.
- 3. a) Explain preparation and synthetic applications of Alkynyl silanes, Allyl silanes and Vinyl silanes.



(4X15=60Marks)

b) i. Write a note on synthetic applications of 9-BBN, IPCBH<sub>2</sub> and IPC<sub>2</sub>BH.

- ii. Write a note on Oxidation, Protonalysis by using Organo boranes.
- 4. a) Write a note on Phase transfer catalysts and its synthetic applications.

(OR)

b) Write a note on Ionic Liquids and its synthetic applications.



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**SECTION-B** 

# II.ANSWER ANY FIVE QUESTIONS. $(5\times3=15)$

- 5. Write a short note on dimethylsulfonium methylide.
- 6. Describe Wacker oxidation with examples.
- 7. Write a short note on Bredts rule.
- 8. Explain Brook rearrangement with mechanism.
- 9. Explain Isomerization of organoboranes.
- 10. Write a note on Nazarov cyclization.
- 11. Write a short note on Types of Sono chemical reactions.
- 12. Write a short note on types of Ionic Liquids.





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#### UNIT-I:

#### Alkaloids

Introduction, isolation, general methods of structure elucidation and physiological action, classification based on nitrogen heterocyclic ring, structure, stereochemistry, synthesis and biosynthesis of morphine, strychnine, colchicine and reserpine.

#### UNIT-II:

#### Terpenoids

Occurrence, isolation, general methods of structure determination, isoprene rule. Structure determination, stereochemistry, biosynthesis and synthesis of Farnesol, Zingiberene, Forskolin, Taxol, Azadirachtin and  $\beta$ -amyrin.

#### UNIT-III:

#### Steroids

Occurrence, nomenclature, basic skeleton, Diel's hydrocarbon and its stereochemistry. Isolation, structure determination and synthesis of cholesterol (total synthesis not expected), androsterone, testosterone and progesterone.

#### UNIT-IV:

#### Flavonoids and Isoflavonoids

Occurrence, nomenclature and general methods of structure determination, Isolation, structure elucidation and synthesis of Kaempferol, Quercetin, Cyanidin, Genestein, Butein and Daidzein. Biosynthesis of flavonoids and Isoflavonoids.

## 15 Hrs

15 Hrs

15 Hrs

#### 15 Hrs



#### **Books Suggested:**

- Natural Products: Chemistry and Biological Significance, J. Mann, R.S.Davidson, J. B. Hobbs, D. V. Banthrope and J. B. Hatrbnome, Longman, Essex.
- 2. Organic Chemistry, Vol. 2, I. L. Finar, ELBS.
- 3. Chemistry of Organic Natural Products, O. P. Agrawal, Vols. 1 & 2, Goel Pubs.
- 4. Natural Products Chemistry K. B. G. torssell, John Wiley, 1983
- 5. New Trends in Natural Products Chemistry, Atta-ur-Rahman and M.I.Choudhary, Harwood Academic Publisher.
- 6. Chemistry of Natural products P. S. Kalsi, Kalyani Publishers
- 7. Biosynthesis of steroids, terpenes and acetogenins, J. H. Richards & J. R. Hendrieson
- 8. The biosynthesis of secondary metabolites, R. D. Herbert, Chapman & Hall
- 9. The Biosynthesis of Secondary Metabolite, R. D. Herbert, Second edn, Chapman and Hall 1984
- 10. Chemical aspects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996.

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#### Time: 3 hours

#### **SECTION-A**

Maximum marks: 75M (4x15=60marks)

#### Answer all questions

1.	a) W	rite stru	ctural e	lucidatio	on of	Reserpine.
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(OR)

b) Write the general methods for structural elucidation of alkaloids.

- 2. a) Give an account on isolation and structural elucidation of Zingeberene. (OR)
  - b) Write synthesis and stereochemistry of Azadirachtin.
- 3. a) Give a detail about structural elucidation of Cholesterol.

(OR)

- b) Write structural elucidation and synthesis of Androsterone.
- 4. a) Explain structure elucidation and synthesis of Genestein. (OR)
  - b) Explain structure elucidation and synthesis of Quercetin.

#### SECTION-B Answer any FIVE questions. (5×3=15M)

- 5. Explain physiological action of alkaloids with examples.
- 6. Write about the bio-synthesis of monoterpenoids.
- 7 .Write the synthesis of Progesterone from cholesterol.
- 8 .Explain Diels Hydrocarbon and its preparation.
- 9 .Write nomenclature of flavonoids and iso flavonoids with examples.
- 10 .Write about the synthesis of Daidazine.
- 11. How Hoffmann exhaustive methylation is one of the important tool in structure elucidation of alkaloids.
- 12. Explain classification of terpenoids with examples.



#### **III SEMESTER**

## Laboratory Course-1 100 Marks

#### **Multistep Synthesis of Organic Compounds:**

The experiments should illustrate the use of organic reagents and may involve purification of the products by chromatographic techniques.

- 1. Beckmann rearrangement: Benzanilide from Benzophenone Benzophenone  $\rightarrow$ Blenzophenone oxime  $\rightarrow$  Benzanilide
- 2. Benzilic acid rearrangement: Benzilic acid from benzoin Benzoin → Benzil → Benzilic acid
- P-Bromo Aniline from Aniline: Aniline → Acetanilide → P-Bromo Acetanilide → P-Bromo Aniline
- 4. Symmetrical Tribromo Benzene from aniline: Aniline  $\rightarrow$  Tribromoaniline $\rightarrow$ Tribromobenzene
- 5. 2,4,6-trimethylquinoline from p-toluidine p-toludine  $\rightarrow$  4-(p-tolylamino) pent-3-ene-2one  $\rightarrow$  2,4,6-trimethylquinoline
- 6. Flavone from o-hydroxy acetophenone o-hydroxy acetophenone  $\rightarrow$  o-benzoyl acetophenone  $\rightarrow$  o-hydroxydibenzoylmethane  $\rightarrow$  Flavone
- 7. 2-phenylindole from phenylhydrazine phenylhydrazine  $\rightarrow$  acetophenone phenylhydrazone $\rightarrow$  2-phenylindole

#### Laboratory Course-2

#### **Estimations and Chromatography 100 Marks**

- Estimation of (a) Glucose (b) Phenol (c) Aniline (d) Acetone (e) Aspirin (f) Ibuprofen
   (g) Paracetamol
- 2. Separation by column chromatography: Separation of a mixture of ortho and para nitroanilines using silicagel as adsorbent and chloroform as the eluent. The column chromatography should be monitored by TLC.

#### **Books Suggested**

- 1. Modern Organic Synthesis in the Laboratory A Collection of Standard Experimental Procedures, Jie Jack Li, Chris Limberakis, Derek A. Pflum
- 2. Practical organic chemistry by Mann & Saunders
- 3. Text book of practical organic chemistry by Vogel
- 4. Text book of practical organic chemistry including qualitative organic analysis by A.I. Vogel (Longman)





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## Paper – I: ORGANIC REACTION MECHANISMS-II & PERICYCLIC REACTIONS UNIT – I 15 Hrs.

#### A) Free Radical Reactions:

Neighboring group assistance in free radical reactions; Reactivity for aliphatic substrates; Reactivity in aromatic substrates; Reactivity at bridge head; Allylic halogenations using NBS (Wohl – Ziegler bromination); Hydroxylation at aromatic carbon by Fentons reagent; Oxidation of aldehydes to carboxylic acids; Formation of cyclic ethers usingLeadtetraacetate; Formation of hydroperoxides (autooxidation); Coupling of alkynes (Eglinton reaction and Glacer reaction);Arylation of Aromatic compounds by diazoinum salts(Gomberg – Bachman reaction); Mechanisms of Sandmeyer reaction, Hunsdiecker reaction, Reed reaction.

**B)** Rearrangements: Wagner – Meerwein Rearrangement, Demyanov Rearrangement, Wittig Rearrangement and Stevens Rearrangement

UNIT-II:

#### 15 Hrs

15 Hrs.

#### Methodologies in asymmetric synthesis

Strategies in Asymmetric Synthesis: 1. chiral substrate controlled, 2. chiral reagent controlled, 3. Chiral catalyst controlled and 4. Chiral Auxiliary controlled.

1. Chiral Substrate controlled asymmetric synthesis: Nucleophilic additions to chiral

Carbonyl compounds. 1, 2- asymmetric induction, Cram's rule and Felkin-Anh model.

2. Chiral reagent controlled asymmetric synthesis: Asymmetric reductions using

BINAL-H. Asymmetric hydroboration using IPC2 BH and IPCBH2.

3. Chiral catalyst controlled asymmetric synthesis: Sharpless and Jacobsen asymmetric Epoxidations. Sharpless asymmetric dihydroxylation. Asymmetric hydrogenations using chiral Wilkinson biphosphine and Noyori catalys. Enzyme mediated enantioselective synthesis.

4. Chiral auxiliary controlled asymmetric synthesis: chiral auxiliary –controlled aldol reactions, Aldol reactions catalyzed by proline.

## UNIT – III

#### **Pericyclic Reactions-I**

Molecular orbital symmetry, frontier orbitals of ethylene, 1, 3 Butadiene, 1, 3, 5- Hexatriene, allyl system, classification of pericyclic reactions FMO approach, Woodward- Hoffman correlation diagram method and perturbation of molecular (PMO) approach for the explanation



of pericyclic reactions under thermal and photochemical conditions. Electrocyclic Reactions: Conrotatory and disotatory motions (4n) and (4n+2), allyl systems Cycloadditions: Antarafacial and suprafacial additions, notation of cycloadditions, (4n) and

(4n+2) systems with a greater emphasis on (2+2) and (4+4) - cycloadditions, (2+2) - additions of ketenes and chelotropic reactions.

#### $\mathbf{UNIT} - \mathbf{IV}$

#### 15 Hrs

## **Pericyclic Reactions-II**

FMO approach and perturbation of molecular (PMO) approach for the explanation of sigma tropic rearrgements under thermal and photochemical conditions. suprafacial and antarafacial shifts of H Sigmatropic shift involving carbon moieties, retention and inversion of configurations, (3, 3) and (5, 5) sigmatropic rearrangements detailed treatment of Claisen and Cope rearrangements, aza-Cope rearrangement and Barton reaction.

#### **Text Books and Reference Books:**

- Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
- 2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, PrenticeHall.
- 3) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Rich gardson.
- 4) The modern structural theory in Organic Chemistry by L.N.Ferguson, Pretice Hall
- 5) Physical Organic Chemistry by jack Hine, Mc. Graw Hill
- 6) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 7) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 8) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 9) Organic Synthesis, M. B. Smith, Mc Graw Hill, International Edition.
- 10) Organic Chemistry, Clayden, Greeves and Stuwart Warren.
- Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz,W. H. Freeman & company, New York.
- 12) Organic Photochemistry by D Coyle
- 13) Molecular Photochemistry by Gilbert & Baggo
- 14) Pericyclic Reactions a problem solving approach, Lehr and Merchand..
- 15) Conservation of Orbital Symmetry by Woodward and Hoffmann.
- 16) Pericyclic reactions by S.N. Mukharji, Mcmilan.

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#### Time: 3 hours

#### **SECTION-A**

Maximum marks: 75M

#### (4x15=60marks)

#### I. Answer all of the fallowing questions

- 1. a) Explain the following with mechanisms
  - i) Wagner Meerwein Rearrangement
  - ii) Hunsdiecker reaction
  - iii) Stevens Rearrangement

#### (OR)

- b) Write short notes on
- i) Free radical substitution reaction
- ii) Gomberg Bachman reaction (Arylation of aromatic compounds by diazonium salts)
- 2. a) What is Asymmetric induction? Write types of asymmetric induction and explain crams rule.

#### (OR)

b) Explain:

- i) Sharpless asymmetric epoxidation.
- ii) Asymmetric hydrogenation using chiral Wilkinson biphosphine.
- 3. a) i) Write the Frontier Molecular Orbitals of 1,3,5- hexatriene and allyl cation. Indicate symmetry properties.
  - ii) Write a note on cheletropic reactions.

(OR)

- b) i) Discuss [2+2] cycloaddition of ketenes with olefins by FMO approach.
- ii) Explain the terms CON- rotatory and DIS-rotary motions.
- 4. a) i) Claisen rearrangement is thermally allowed and photochemically forbidden-Explain by FMO approach.

ii) Discuss the stereochemistry involved in [1, 3] sigmatropic rearrangement of carbon substituent thermally and photochemically.

#### (OR)

b) i) Explain [1,5] sigmatropic rearrangement thermally and photochemically.



ii) Write a note on flixinol tautomerism and Barton reaction.

#### **SECTION-B**

#### II. Answer any FIVE questions. (5

(5×3=15)

- 5. Explain allylic halogenations using NBS.
- 6. Describe Neighbouring group assistance in free redical reactions.
- 7. What is Asymmetric synthesis? Write different types of asymmetric synthesis.
- 8. Explain the use of chiral auxillaries in Diels alder reaction.
- 9. Explain the terms Antarafacial and Suprafacial with appropriate examples.
- 10. Write [4n+2] cycloaddition under thermal condition by PMO approach.
- 11. Discuss [5+5] sigmatropic rearrangements.
- 12. Explain [1,3] sigmatropic rearrangements by PMO approach.







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#### UNIT-I:

**Optical Rotatory Dispersion (ORD) and CD spectroscopy**: Optical Rotation, Circular birefringence, Circular dichroism and Cotton effect. Plane curves and Anomalous curves. Empirical and Semi empirical rules – The axial halo ketone rule, the Octant rule and Helicity rule. Application of the rules to the study of absolute configuration and confirmations of organic molecules.

#### UNIT-II

A) **Improving the PMR spectrum:** Chemical and Magnetic Equvalence. Chemical exchange, First and Non-First Order Spectra and analysis of AB, AMX and ABX systems.

B) **Simplification of complex spectra-**: Nuclear Magnetic double resonance, Lanthanide shift reagents, solvent effects, Fourier transforms technique, Nuclear Overhauser Effect (NOE), Deuterium Exchange, spectra at higherfields. Hindered Rotations and Rate processes. Resonance of other nuclei-19F and 31 P

C) **2D NMR spectroscopy:** Definitions and importance of COSY, DEPT, HOMCOR, HETCOR, INADEQUATE, INDOR INEPT, NOESY.

#### UNIT-III

Solution of structural problems by joint application of UV, IR, NMR (1H&13C) and mass spectrometry.

#### UNIT-IV

A) Separation Techniques: Solvent extraction chromatography-paper-thin layer partitioncolumn chromatography, Electrophoresis.

B) Instrumentation – Gas Chromatography, High performance Liquid Chromatography, X – Ray diffraction (XRD).



#### **Suggested Books:**

- Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I. Fleming Tata – McGraw Hill, New Delhi, 1990.
- 2) Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
- Spectrometric identification of Organic Compounds-Fourth Edition, R.M. Silverstein: G.C.Vassiellr and T.C. Merill, Johne Willey, Singapore, 1981.
- 4) Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd (Harcourt college publishers).
- 5) "Applications of Optical rotation and Circular Dichroism", G.C. Barret, in "Elucidation of Organic structures by Physical and Chemical Methods" Part I (Eds) K.W. Bentley and G.W.Rirty John Wiley, 1972, Chapter VIII (only those aspects mentioned in the syllabus).
- 6) Instrumental methods of chemical analysis by H.Kaur, Pragati Prakasan, meerut.
- 7) Separation Techniques by M.N.Sastri, Himalaya publishing House (HPH), Mumbai.

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Time: 3 hrs

**SECTION-A** 

Max marks: 75 (4X15=60Marks)

#### I. Answer ALL of the fallowing questions.

1. a) i) Define octant rule, apply octant rule in the determination of absolute configuration of cyclohexanones.

ii) Sketch the ORD curves and how are they useful in determining the configuration of chiral molecule. Illustrate your answer with an example..

#### (OR)

b) i) Define positive cotton and negative cotton effect curves? Explain the term circular, dichroism and write its use in stereochemical studies.

ii) Explain how the following two compounds could be distinguished by applying octant rule?



a) i) Explain about J value for AB2, ABX.ii) Explain Nuclear Overhauser Effect (NOE).

(OR)

b) i)What is the difference between HOMOCOSY and HETROCOSY NMR spectra? ii)Draw the HETCOR spectrum of ethylbenzoate and explain the correlations.



3. a) A compound containing only C H N O shows the molecular ion peak at m/z 175 followed by an isotopic peak at m/z 176. The intensity of the latter peak is about 12% of the former. The compound exhibits strong absorption near 400nm in u.v and near 1680 and 1600 cm<sup>-1</sup> in the IR spectrum. Its NMR spectrum consists of a doublet around  $\delta 9.5$ , a cluster of peaks  $\delta 7.5$ -7.3, a doublet around  $\delta 6.6$ , a quartet around  $\delta 6.4$  and a singlet at  $\delta 3.0$ . The relative intensities of these signals are 1:4:1:1:6respectively. Assign a structure to this compound showing in detail your reasoning.

#### (OR)

 b) One of the constituents of famous antipyretic, analgesic drug APC, has the molecular formula C10H13NO2 and displays the following spectral characteristics. IR cm-1 : 3250,1650,1275,1050.

1HNMR δ : 1.4(triplet, 3H), 2.05(singlet,3H),3.9(quartet,2H),6.7(doublet,2H,J=8Hz), 7.4 (doublet,2H,J=8Hz).

Assign the structure of this compound.

a) Write a short note on :i) Solvent extraction.

ii) Thin layer chromatography.

#### (OR)

- b) Explain briefly on:
- i. Electrophoresis

ii. X-Ray diffraction.

#### **SECTION-B**

#### I. ANSWER ANY FIVE QUESTIONS.

(5×3=15 Marks)

- 5. Define positive and negative cotton effect curves.
- 6. Explain the similarities and differences between ORD and CD curves.
- 7. Explain about lanthanide shift reagents.
- 8. What do you understand by nuclear overhauser effect (NOE)?
- 9. Predict IR, 1HNMR and mass spectral data for ethyl benzoate.
- 10. Write a short note on lanthanide shift reagents.
- 11. Explain applications of HPLC.
- 12. Write a note on Gas chromatography.



534 275. W.G.Dt



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#### **UNIT-I** Oxidation

Synthetic applications of the following reagents in the oxidation of functional groups like alkenes, alkynes, alcohols, aldehydes and ketones: 1) Pb(OAC)4 2) HIO4 3) SeO2 4) Collins reagent, Jones reagent, PCC (Coreys reagent), PDC, Babler oxidation) 4) MnO2 5) KMnO4 6) OsO4 7) Sworn oxidation, 8) Oxidations by using IBX, TEMPO 9) Bayer villager oxidation 10) Oxidation of alkenes using Woodward and Prevost reagents 11) Oxidation by using DDQ 12) Shapeless asymmetric epoxidation and sharpless asymmetric dihydroxylation 13) Thallium nitrate.

**UNIT-II** 

#### Reduction

(1) Catalytic reductions: Homogeneous (Wilkinson's Catalytic reduction) and heterogeneous catalytic reductions and their synthetic applications. (2) Reductions by using electrophilic nucleophilic metal hydrides: LiAlH4 (Various examples of reductions and cram's rule), related reagents of LAH, NaBH4, NaBH3CN, Trialkyl Borohydrides (Super Hydride and Selectride). (3) Reductions by using electrophilic metal hydrides: BH3, DIBAL-H (4) Reductions by dissolving metals: Clemenson reduction, Acyloin condensation, Bouveault-Blanc reduction, Birch reduction (Various examples should be discussed). (5) Reductions by using Diimide and Wolf-Kishner Reduction (6) Reductions by using tri n-butyl tin hydride.

#### **UNIT-III**

#### **Protecting groups and Synthetic applications**

Protecting Groups 1) Protection of alcohols as ethers [methyl ether (RO-Me), Tertiary butyl ether (ROCMe3), Benzyl ethers (RO-Bn), as Silyl ethers [Trimethylsilylether (R-OTMS), tri ethyl silvl ethers (RO-TES), t-butyldimethylsilvl ether (ROTBDMS in the presence of imidazole), t-butyl diphenylsilyl ether (RO-TBDPS)], as acetals [tetrahydopyranyl ethers (ROTHP), 2) Protection of 1,2-diols by acetal, ketal and carbonate formation. 3) Protection of amines by acetylation, benzoylation, benzoyloxy carbonyl, FMOC and triphenyl methyl groups. 4) Protection of carbonyl by acetal, ketal and thioacetal (Umpolung) groups. 5) Protection of carboxylic acids by esters and ortho ester formation.

#### **UNIT-IV**

#### **Retro Synthetic Analysis**

15 Hrs

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#### 15 Hrs

15Hrs

15 Hrs

1. Basic definitions of the following: a) Retro synthetic analysis b) Disconnection c) Target molecule d) Synthene) Synthetic equivalent f) Functional Group Inter Conversion (FGI) g) Functional Group Addition (FGA)

2. Guidelines for the order of events: One Group C-X disconnections (Carbonyl derivatives, ethers, sulphides and alcohols); Two group C-X disconnections (1,1-difunctionalised, 1,2-difunctionalised and 1,3-difunctionalised compounds), One group C-C disconnections (Alcohols and carbonyl compounds, 1,1- C-C, 1,2-C-C and 1,3-C-C). Linear and convergent synthesis.

#### **Textbooks and Books for Reference:**

- Some Modern Methods of Organic Synthesis W. Carothers, Third Edition, Cambridge University Press, Cambridge, 1988.
- Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourt edition, Kluwer academic publishers, New York.
- 4) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 5) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 6) Organic Synthesis, M. B. Smith, McGraw Hill, International Edition.
- 7) Organic Chemistry, Clayden, Greeves and Stuwart Warren.
- 8) Guide Book to Organic Synthesis (3rd edition), R. Mackie, D. M. Smith and Aitken.
- 9) Organo Boranes and Silanes, Thomson, Oxford Chemistry primers.
- Strategic applications of named reactions in organic synthesis, Laszlo Kurti and Barbara Czako.
- Organic Synthesis: The disconnection approach, S. Warrant John Wiley & sons, NewYork, 1984.
- Modern Synthetic Reactions, Herbet O. Horase, Second Edition, W.A. Benzamine Inc. Menio Park, California, 1972.

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Time: 3 hrs

#### **SECTION-A**

Max marks: 75 (4X15=60Marks)

#### I. Answer ALL of the fallowing questions

1. a) Write the synthetic application of the following reagents. i) DDQ ii) OsO4 iii) MnO2

#### (OR)

b) Write the synthetic applications of the following reagents. i) Collins reagent ii) Jones reagent iii) Etard reagent.

2. a).Write a note on Homogeneous catalytic reductions and their synthetic applications.

#### (OR)

- b). Write a note on Heterogeneous catalytic reduction and their synthetic applications.
- 3. a) Discuss any four methods for Protection of alcohols as ethers.

(OR)

- b) Write a note on Protection of carbonyl compounds and carboxylic acids.
- 4. a) Explain the following terms. i) FGI ii) Synthetic equivalent. iii) FGA.

#### (OR)

b) Write a note on Linear and convergent synthesis.

#### **SECTION-B**

#### II. ANSWER ANY FIVE QUESTIONS.

- 5. Explain how periodic acids used for oxidation.
- 6. Write a short note on Bouveault- Blanc reduction.



APPROVED

(5×3=15 Marks)

- 7. Write a short note on Babler Oxidation.
- 8. Write a short note on Wolf – Kishner reduction.
- 9. Write a short note on one group C-X disconnection for ethers.
- Write a note on t-butyldimethylsilyl ether. 10.
- 11. Write a short note on two group C-X disconnection for Diels alder reaction.
- 12. Write a short note on t-butyldiphenylsilyl ether.



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## **UNIT-I**

#### **Biopolymers and Enzymes**

Peptides: α-Amino acids, their general properties and synthesis, Synthesis of peptides by

Merrifield solid phase Synthesis. Chemistry of oxytocin and dolastain-10

Enzymes-Oxidoreductases, hydrolases, transferases, synthesis of ATP, Baker's Yeast. Enzyme models.

#### **UNIT-II**

#### Antimalarials & Antibiotics

i. Antimalarials: Chemotherapy, synthesis and activity of antimalarial drugs- quinoline groupquinine, acridine group- quinacrine and guanidine group-paludrine.

ii. Antibiotics: General characteristics, structure- activity relationships, synthesis and activity of antibiotics: Pencillin G, Cephalosporin-C and streptomycin.

#### **UNIT-III**

#### Vitamins

Definition, occurrence, structural formulae, physiological functions and synthesis of Vitamins. Vitamins: Structure determination and synthesis of Retinol (A), Thiamine (B1), Riboflavin (B2), Pyridoxine (B6) and Biotins (H), Nicotinic acid.

#### **UNIT-IV**

#### **Nucleic Acids:**

## APPROVED



## **15 Hours**

**15 Hours** 

**15 Hours** 

**15 Hours** 

Nucleic acids: Basic concepts of the structures of RNA and DNA and their hydrolysis products, nucleotides, nucleosides and heterocyclic bases, Genetic Code (Viruses, Bacteria, Vector based Viruses, RNA based Viruses, Code breaker Casper method) Finger Print test.

Application of recombinant DNA technology in production of pharmaceuticals, diagnosis of diseases, insect control, improved biological detergents, gene therapy-examples.

#### **Reference Books and Material:**

- 1. Chemical Aspects of Biosynthesis, John Man, Oxford University Press, Oxford, 1996.
- Chemistry of Natural Products: A Unified Approach, N. R. Krishnaswamy, University Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999.
- Introduction to Organic Chemistry, A Streitweiser, CH Heathcock and E.M./Kosover IV Edition, Mc.Millan, 1992. (For Merrifield synthesis of peptides and also for other aspects of Unit IV)
- 4. Bio-organic Chemistry, H.Dugas and C. Penney, springer, New York, 1981.
- Details of Primary literature: Nomenclature: Structure: Dolastatin-10: JACS, 1987, 109, 6883 (structure), ibdi, 1989, 111, 5463, JCS, Parkin I, 1996, 859 (synthesis).

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#### Time: 3 hours

1.

#### SECTION-A

(4x15=60marks)

Maximum marks: 75M

#### I. Answer all of the fallowing questions

- a) i) Write the chemical properties of  $\alpha$  amino acids.
  - ii) Explain the chemistry of Oxytocin and its physiological functions. (OR)

b) i) Discuss the reactions involving the enzymes oxidoreductases, hydrolases and transferases.

- ii) What are enzyme models and explain their importance by taking suitable example.
- 2. a) Outline the synthesis of 2,5 dichloro-7-mehoxyacridine, 4-dimethylamino-1methylbutylamine and quinacrine and discuss the structure – activity relationship of Quinacrine.

#### (OR)

- b) Describe the synthesis, SAR study and mode of action of pencillin G.
- 3. a) Write a note on the occurrence, structural formulae and biological functions of Retinol and Pyridoxine.

#### (OR)

b) Discuss the structure determination and synthesis of Nicotinic acid.

- 4. a) i) Describe the Watson-Crick model of DNA
- ii) What is genetic code and explain its importance in protein synthesis
  - (OR)
  - b) What is Recombinant DNA technology and write its application in the production
  - of Pharmaceuticals and in diagnosis of diseases.

#### SECTION-B

Answer any five questions

(5x3=15marks)


- 5. What is isoelectric point?
- 6. Write the advantages of Merrifield peptide synthesis.
- 7. Explain the chemotherapy of Pauldrine
- 8. Discuss about structure activity relationship of Streptomycin.
- 9. Write a brief note on the significance of Biotins.
- 10. Explain the Genetic code.
- 11. What is Finger print test?
- 12. Define Gene therapy.
- 13.

## **IV SEMESTER**

## Laboratory Course-1 100Marks

# Chromatographic Separation and Isolation & identification of Natural Products

- 1. Thin layer chromatography: Determination of purity of a given sample, monitoring the progress of chemical reactions, identification of unknown organic compounds by comparing the Rf values of known standards.
- 2. Isolation and identification of Natural Products
  - (a) Isolation of caffeine from tea leaves
  - (b) Isolation of euginol from cloves
  - (c) Isolation of casein and lactose from milk
  - (d) Isolation of limonene from lemon peel
  - (e) Isolation of piperines from black pepper
  - (f) Isolation of lycopene from tomatoes
  - (g) Isolation of  $\beta$ -carotene from carrots

## Laboratory Course-2 100 M

## Spectral Identification of Organic Compounds (UV, IR, 1H- NMR, 13C- NMR and MASS).

A minimum of 40 representative examples should be studied

### **Books Suggested:**

- 1. Ikan, R. Natural Products, A Laboratory Guide, 2nd ed.; Academic Press: New York, 1991.
- 2. Adapted from Introduction to Organic Laboratory Techniques: A Microscale Approach. Pavia, Lampman, Kriz and Engel. (1999) Saunders College Publishing.
- 3. Pharmaceutical drug analysis by Ashutoshkar
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