

## SEMESTER - III

### Course III (ORGANIC CHEMISTRY & SPECTROSCOPY) 60hrs (4 h / w)

#### Course outcomes:

At the end of the course, the student will be able to;

1. Understand preparation, properties and reactions of haloalkanes, haloarenes and oxygen containing functional groups.
2. Use the synthetic chemistry learnt in this course to do functional group transformations.
3. To propose plausible mechanisms for any relevant reaction

#### ORGANIC CHEMISTRY

34h

##### UNIT – I

#### 1. Chemistry of Halogenated Hydrocarbons:

6h

Alkyl halides: Methods of preparation and properties, nucleophilic substitution reactions – SN1, SN2 and SNi mechanisms with stereochemical aspects and effect of solvent etc.;

nucleophilic substitution vs. elimination, Williamson's synthesis.

Aryl halides: Preparation (including preparation from diazonium salts) and properties, nucleophilic aromatic substitution; SNAr, Benzyne mechanism.

Relative reactivity of alkyl, allyl, benzyl, vinyl and aryl halides towards nucleophilic substitution reactions.

#### 2. Alcohols & Phenols

6h

Alcohols: preparation, properties and relative reactivity of 1°, 2°, 3° alcohols, Bouvaelt Blanc Reduction; Oxidation of diols by periodic acid and lead tetra acetate, Pinacol- Pinacolone rearrangement.

Phenols: Preparation and properties; Acidity and factors affecting it, Ring substitution reactions, Reimer-Tiemann and Kolbe's-Schmidt Reactions, Fries and Claisen rearrangements with mechanism.

##### UNIT-II

#### Carbonyl Compounds

10h

Structure, reactivity, preparation and properties;

Nucleophilic additions, Nucleophilic addition-elimination reactions with ammonium derivatives

Mechanisms of Aldol and Benzoin condensation, Claisen-Schmidt, Perkin,

Cannizzaro and Wittig reaction, Beckmann haloform reaction and Baeyer-Villiger oxidation,  $\alpha$ -

substitution reactions, oxidations and reductions (Clemmensen, Wolff-Kishner, with  $\text{LiAlH}_4$  &  $\text{NaBH}_4$ ).

Addition reactions of  $\alpha, \beta$ -unsaturated carbonyl compounds: Michael addition.

Active methylene compounds: Keto-enol tautomerism. Preparation and synthetic applications of diethyl malonate and ethyl acetoacetate.

### UNIT-III

#### Carboxylic Acids and their Derivatives

12

General methods of preparation, physical properties and reactions of monocarboxylic acids, effect of substituents on acidic strength. Typical reactions of dicarboxylic acids, hydroxy acids and unsaturated acids. Preparation and reactions of acid chlorides, anhydrides, esters and amides; Comparative study of nucleophilic substitution at acyl group - Mechanism of acidic and alkaline hydrolysis of esters, Claisen condensation, Reformatsky reactions and Curtius rearrangement

Reactions involving H, OH and COOH groups - salt formation, anhydride formation, acid chloride formation, amide formation and esterification (mechanism). Degradation of carboxylic acids by Hunsdiecker reaction, decarboxylation by Schmidt reaction, Arndt-Eistert synthesis, halogenation by Hell-Volhard-Zelinsky reaction.

### SPECTROSCOPY

26 h

#### UNIT-IV

##### Molecular Spectroscopy:

18h

Interaction of electromagnetic radiation with molecules and various types of spectra.

**Rotation spectroscopy:** Selection rules, intensities of spectral lines, determination of bond lengths of diatomic and linear triatomic molecules, isotopic substitution.

**Vibrational spectroscopy:** Classical equation of vibration, computation of force constant, Harmonic and anharmonic oscillator, Morse potential curve, vibrational degrees of freedom for polyatomic molecules, modes of vibration. Selection rules for vibrational transitions, Fundamental frequencies, overtones and hot bands.

**Electronic spectroscopy:** Energy levels of molecular orbitals ( $\sigma$ ,  $\pi$ ,  $n$ ). Selection rules for electronic spectra. Types of electronic transitions in molecules, effect of conjugation. Concept of chromophore, **auxochrome**. bathochromic and hypsochromic, **hyperchromic and hypochromic shifts**. Beer-Lambert's law and its limitations.

**Nuclear Magnetic Resonance (NMR) spectroscopy:** Principles of nuclear magnetic resonance, equivalent and non-equivalent protons, position of signals. Chemical shift, NMR splitting of signals - spin-spin coupling, coupling constants. Applications of NMR with suitable examples - ethyl bromide, ethanol, acetaldehyde, 1,1,2-tribromo ethane, ethyl acetate, toluene and acetophenone.

## UNIT-V

8h

### Application of Spectroscopy to Simple Organic Molecules

#### Application of visible, ultraviolet and Infrared spectroscopy in organic molecules.

Application of electronic spectroscopy and Woodward rules for calculating  $\lambda_{\max}$  of conjugated dienes and  $\alpha,\beta$  – unsaturated compounds.

Infrared radiation and types of molecular vibrations, functional group and fingerprint region. IR spectra of alkanes, alkenes and simple alcohols (inter and intramolecular hydrogen bonding), aldehydes, ketones, carboxylic acids and their derivatives (effect of substitution on  $>C=O$  stretching absorptions).

**Co-curricular activities and Assessment Methods** Continuous Evaluation: Monitoring student's learning Class Tests, Worksheets and Quizzes,

Presentations, Projects and Assignments and Group Discussions: Enhance critical thinking skills and personality

Semester-end Examination: critical indicator of student's learning and teaching methods adopted by teachers throughout the semester.

### List of Reference Books

1. A Textbook of Organic Chemistry by Bahl and Arunbahl
2. A Text Book of Organic chemistry by I L Finar Voll
3. Organic chemistry by Bruice
4. Organic chemistry by Clayden
5. Spectroscopy by William Kemp
6. Spectroscopy by Pavia
7. Organic Spectroscopy by J. R. Dyer
8. Elementary organic spectroscopy by Y.R. Sharma
9. Spectroscopy by P.S. Kalsi
10. Spectrometric Identification of Organic Compounds by Robert M Silverstein, Francis X Webster
11. Mann, F.G. & Saunders, B.C. Practical Organic Chemistry, Pearson Education (2009)
12. Furniss, B.S., Hannaford, A.J., Smith, P.W.G. & Tatchell, A.R. Practical Organic Chemistry, 5th Ed. Pearson (2012)
13. Ahluwalia, V.K. & Aggarwal, R. Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis, University Press (2000).

**Practical Course-III Organic preparations and IR Spectral Analysis**

(At the end of Semester- III)

**Course outcomes:**

On the completion of the course, the student will be able to do the following:

1. how to use glassware, equipment and chemicals and follow experimental procedures in the laboratory
2. how to calculate limiting reagent, theoretical yield, and percent yield
3. how to engage in safe laboratory practices by handling laboratory glassware, equipment, and chemical reagents appropriately
4. how to dispose of chemicals in a safe and responsible manner
5. how to perform common laboratory techniques including reflux, distillation, recrystallization, vacuum filtration.
6. how to create and carry out work up and separation procedures
7. how to critically evaluate data collected to determine the identity, purity, and percent yield of products and to summarize findings in writing in a clear and concise manner.

**Organic preparations:****40M**

i. Acetylation of one of the following compounds:

amines (aniline, o-, m-, p-toluidines and o-, m-, p-anisidine) and phenols ( $\beta$ -naphthol, vanillin, salicylic acid) by any one method:

- a. Using conventional method.
- b. Using green approach

ii. Benzoylation of one of the following amines

(aniline, o-, m-, p-toluidines and o-, m-, p-anisidine)

iii. Nitration of any one of the following:

- a. Acetanilide/nitrobenzene by conventional method
- b. Salicylic acid by green approach (using ceric ammonium nitrate).

**IR Spectral Analysis****10M**

IR Spectral Analysis of the following functional groups with examples

- a) Hydroxyl groups
- b) Carbonyl groups
- c) Aminogroups
- d) Aromatic groups

**MODEL PAPER**  
**SECOND YEAR B.Sc., DEGREE EXAMINATION**  
**SEMESTER-III**  
**CHEMISTRY COURSE-III: ORGANIC CHEMISTRY**  
**&SPECTROSCOPY**

Time: 3 hours

Maximum Marks: 75

**PART-A**

5 X 5 = 25Marks

Answer any **FIVE** of the following questions. Each carries **FIVE** marks

1. Discuss two methods for preparation of arylhalides.
2. Explain the mechanism for Pinacol-Pinacolone rearrangement.
3. Discuss the mechanism for Bayer-villiger oxidation reaction.
4. Explain the effect of substituents on acidic strength of mono-carboxylic acids.
5. Write the mechanism for Claisen Condensation reaction.
6. Write the selection rules in rotational spectroscopy.
7. Explain Spin – Spin coupling and Coupling Constant.
8. Explain types of electronic transitions in UV spectroscopy.

**PART-B**

5 X 10 = 50Marks

Answer **ALL** the questions. Each carries **TEN** marks

- 9 (a). Give the mechanism & stereochemistry of  $SN^1$  &  $SN^2$  reactions of alkyl halides with suitable example.  
(or)
- (b). Explain the following reactions with mechanism.  
(i) Reimer-Tiemann reaction (ii) Fries rearrangement.
- 10 (a). Discuss the mechanism for following reactions.  
(i) Perkin reaction. (ii) Cannizzaro reaction  
(or)
- (b). Write the preparation and any three synthetic applications of diethyl malonate.
- 11.(a). Explain acid and base hydrolysis reaction of esters with mechanism.  
(or)
- (b). Explain the mechanisms of Curtius rearrangement & Arndt –Eistert reaction.
- 12.(a). (i) Write a note on vibrational degrees of freedom for polyatomic molecules.  
(i) Explain different modes of vibrations & selection rules in IR spectroscopy.  
(or)
- (b).(i) Define Bathochromic shift. Explain the effect of conjugation in U.V. spectroscopy.  
(ii) Discuss the principle of NMR spectroscopy.
- 13.(a). Write Woodward-Fieser rules for calculating  $\lambda_{max}$  for conjugated dienes and  $\alpha,\beta$  – unsaturated carbonyl compounds, and apply them for one example each.  
(or)
- (b).(i) What is Fingerprint region. Explain its **significance** with an example.  
(ii) Write IR spectral data for any one alcohol, aldehyde and ketone