

| DEPARTMENT OF CHEMISTRY | | | | CLASS: I M.Sc. Chemistry | | | | |
|-------------------------|-------------|-------------|----------------------|--------------------------|--------------------|-----|-----|-------|
| Sem | Course Type | Course Code | Course Title | Credits | Contact Hours/week | CIA | Ext | Total |
| II | Major Core | 21P2CMC4 | Organic Chemistry-II | 4 | 5 | 25 | 75 | 100 |

| Nature of Course | | | |
|---------------------|---|--|---------------------------|
| Knowledge and skill | ✓ | | Employability oriented |
| Skill oriented | | | Entrepreneurship oriented |

Objectives: *The objective of this course is to make the student*

- *To illustrate mechanism involving in addition reactions across Carbon-Carbon multiple bonds and its synthetic utility.*
- *To study mechanisms in addition of Carbon-Heteroatom multiple bonds and Elimination reactions*
- *To identify the stereochemical aspects of organic molecules*
- *To apply various types of oxidation and reduction reagents along with their mechanism and synthetic utility.*
- *To analyse reaction mechanisms involved in rearrangements and name reactions*

| Unit | Description | Hours | K-Level | CLO |
|------|---|-------|----------|-------|
| I | ADDITION TO CARBON-CARBON MULTIPLE BONDS Mechanism of Carbon-Carbon Addition reactions: Electrophilic, Nucleophilic and Free radical addition to C-C double bond and triple bond-cyclic mechanism- orientation and reactivity. Addition to cyclopropane ring-Addition to conjugated system-Addition of carbenes-Michael addition and Robinson annulation. Hydroxylation of olefinic double bonds (OsO ₄ , KMnO ₄); Woodward and Prevost oxidation. Epoxidation using peracids including Sharpless epoxidation, Ozonolysis. Hydrogenation (homogenous and heterogeneous)- Transfer hydrogenation-Hydroboration-Hydration of carbon-carbon double and triple bonds. | 15 | Up to K4 | CLO-1 |
| II | ADDITION TO CARBON-HETERO ATOM MULTIPLE BONDS AND ELIMINATION REACTIONS Addition to Carbon-Hetero atom multiple bonds Nucleophilic addition to –C=O bond. A study of Darzen'sglycidic ester, Stobbe and Knoevenagel condensation reactions; Wittig, Wittig-Horner olefination reactions;, Julia olefination & Peterson alkene synthesis. Elimination reactions: E ₁ , E ₂ , E ₁ cb and E _i -elimination. Conformation of mechanism; solvent, substrate, leaving group effects-Saytzeff'sVs Hoffman elimination; Stereochemistry of E ₂ eliminations, Elimination in cyclohexane ring system; Mechanism of pyrolytic eliminations. Examples: Chugaev reactions and Cope elimination, Hoffmann degradation and pyrolysis of esters. | 15 | Up to K2 | CLO-2 |

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|-----|--|----|----------|-------|
| III | <p>STEREOCHEMISTRY Optical isomerism-Optical activity, Chirality, Symmetry elements, Asymmetric and Dissymmetric chiral molecules. specification by Cahn-Ingold-Prelog notations-Calculation of number of optical isomers. Description of various types of optically active compounds including allenes, cumulenes, spiranes, biphenyls, <i>trans</i>-cyclooctene.-<i>R&S</i> nomenclature of simple compounds, racemic modification & classification of racemic modifications, quasi racemates. Compounds containing two asymmetric centers: Nomenclature-D & L, R & S, R* & S*, <i>Erythro</i> and <i>threo</i> isomers Interpretation of homotopic, enantiotopic and diastereotopic atoms, groups and faces. Pro-chiral carbon. Concept of <i>Re</i>- and <i>Si</i>- faces. Stereospecific and Stereoselective reactions. Asymmetric Synthesis-Cram's rule, Prelog's rule and Felkin Anh Model-Stereochemistry of compounds containing nitrogen Geometrical isomerism-E and Z notation –Determination of configuration of geometrical isomers by simple techniques like hydroxylation, hydroboration and methods based on physical properties</p> | 15 | Up to K3 | CLO-3 |
| IV | <p>OXIDATION AND REDUCTION REACTIONS Oxidation: Introduction, Different oxidative processes Oxidation with Cr (including PCC, PDC, Jones) and Mn (including MnO₂ and BaMnO₄) reagents; Oxidation with LTA, DDQ and SeO₂; Oxidation using DMSO either with DCC or Ac₂O or Oxaloyl chloride; Oxidation using HIO₄ and Dess-Martin Periodinane (DMP) reagent-ruthenium tetraoxide-Thallium (III) Nitrate Reduction: Introduction. Different reductive processes:Reduction with NaBH₄, NaCNBH₃, Zn(BH₄)₂ LiAlH₄, Li(^tBuO)₃AlH, DIBAL-H, Red-Al, Et₃SiH and Bu₃SnH; Reduction using selectrides; Birch reduction.Lawesson reagent – TiCl₄ / Zn-Cu (Mac Murrays reagent) – TiCl₄ /Mg-Hg-Wilkinson's catalyst, Lindlar catalyst-BH₃/THF, 9-BBN, Baker's yeast</p> | 15 | Up to K3 | CLO-4 |
| V | <p>MOLECULAR REARRANGEMENTS & NAME REACTIONS General mechanism – nature of migration, migratory aptitude, memory effects -A study of mechanism of the following rearrangements:<i>Carbon-carbon migration: Carbon-nitrogen migration :Carbon-oxygen migration</i>Beckmann, Curtius, Hofmann, Schmidt, Lossen, Wolff, Pinacol, Wagner Meerwin, Demjanov, Dienone-Phenol, Favorski, Benzidine, Claisen, Cope, Sommler Hauser, Pummerer and Von-Richter rearrangements. A study of the following name reactions: Dieckmann cyclization, Hofmann-Löffler Freytag reaction, Mitsunobu reaction, Shapiro reaction, Eschenmoser-Tanabe and Ramburg-Backlund reactions.</p> | 15 | Up to K4 | CLO-5 |

Books for study:

1. F. Carey and R. J. Sundberg, Advanced Organic Chemistry-Part A and B, Springer Science & Business Media, 5 th Ed, 2007.
2. M. B. Smith and Jerry March, Advanced Organic Chemistry, John Wiley & Sons, 5th Ed, 2001
3. Nasipuri, D. "Stereochemistry of organic compounds" Second Edition, New Age International Pvt. Ltd., 2005.

Books for reference:

1. E.S. Gould Henry, Mechanism and structure in organic chemistry, Holtco INC 1963.
2. Graham Solomons, Organic chemistry, John Wiley and Sons INC 5th Edn 1992.
3. R.K. Mackie and D.M. Smith, Guide Book to organic synthesis, ELBS, 1982.
4. H.O. House, Modern synthetic reactions, Cambridge university press 3rd Edn, 1972.
5. W. Caruthers, Some modern methods of organic synthesis, Cambridge University.
6. Eliel, E.L., Wilen, S. H. "Stereochemistry of Carbon Compounds", First Edition, Wiley, 2008.

Web resources

1. <https://onlinelibrary.wiley.com/doi/10.1002/9780470084960.ch15>
2. [https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Book%3A_Radical_Reactions_of_Carbohydrates_\(Binkley\)/II%3A_Radical_Reactions_of_Carbohydrates/18%3A_Compounds_with_Carbon%E2%80%93Carbon_Multiple_Bonds_I%3A_Addition_Reactions](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Book%3A_Radical_Reactions_of_Carbohydrates_(Binkley)/II%3A_Radical_Reactions_of_Carbohydrates/18%3A_Compounds_with_Carbon%E2%80%93Carbon_Multiple_Bonds_I%3A_Addition_Reactions)
3. <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118093559.ch2>
4. <https://schoolbag.info/chemistry/organic/108.html>

Rationale for Nature of the course

This course will enable the students to understand the basic concepts about how the organic reactions are carried out and also to make the students to learn the mechanisms of different organic reactions including various stereo chemical and mechanistic aspects.

Activities having direct bearing on Skill development/ Employability/Entrepreneurship

This basic study of organic reactions, rearrangements stereochemistry concepts make the students to evaluate the organic reactions, based on the influence of the substituents on substrate molecules and nature of solvent and the parametric conditions. Students will also design new organic reactions in order to achieve the required product.

Pedagogy

- Chalk-Talk class room activities
- Group Discussion
- Quiz through ICT- Mode
- Animated video for chemical reactions

Lesson Plan

| Unit | Descriptions | Hours | Mode |
|------|--|-------|---|
| I | ADDITION TO CARBON-CARBON MULTIPLE BONDS | | |
| | Mechanism of Carbon-Carbon Addition reactions: Electrophilic, Nucleophilic and Free radical addition to C-C double bond and Triple bond-cyclic mechanism- orientation and reactivity. Addition to cyclopropane ring | 5 | PPT, Chalk and talk, Group discussion |
| | Addition of carbenes-Michael addition and Robinson annulation. Hydroxylation of olefinic double bonds (OsO ₄ , KMnO ₄); Woodward and Prevost oxidation. Epoxidation using peracids including Sharpless epoxidation, Ozonolysis. | 5 | |
| | Hydrogenation (homogenous and heterogeneous)- Transfer hydrogenation-Hydroboration-Hydration of carbon-carbon double and triple bonds. | 5 | |
| II | ADDITION TO CARBON-HETERO ATOM MULTIPLE BONDS AND ELIMINATION REACTIONS | | |
| | Addition to carbon-hetero atom multiple bonds -Nucleophilic addition to -C=O bond. A study of Darzen's glycidic ester, Stobbe and Knoevenagel condensation reactions; Wittig, Wittig-Horner olefination reactions | 3 | PPT, Chalk and talk, Group discussion |
| | Julia olefination & Peterson alkene synthesis. Asymmetric reduction of carbonyl functions (Corey's procedure) | 2 | |
| | Elimination reactions: E ₁ , E ₂ , E _{1c} b and E _i -elimination. Conformation of mechanism; solvent, substrate, leaving group effects-Saytzeff's Vs Hoffman elimination | 5 | |
| | Stereochemistry of E ₂ eliminations, Elimination in cyclohexane ring system; Mechanism of pyrolytic eliminations. Examples: Chugaev reactions and Cope elimination, Hoffmann degradation and pyrolysis of esters. | 5 | |
| III | STEREOCHEMISTRY | | |
| | Optical isomerism -Optical activity, Chirality, Symmetry elements, Asymmetric and Dissymmetric chiral molecules. Specification by Cahn-Ingold-Prelog notations-Calculation of number of optical isomers. Description of various types of optically active compounds including allenes, cumulenes, spiranes, biphenyls, <i>trans</i> -cyclooctene. | 4 | PPT, Chalk and talk, Group discussion |
| | <i>R</i> & <i>S</i> nomenclature of simple compounds, racemic modification & classification of racemic modifications, quasi racemates. Compounds containing two asymmetric centers: Nomenclature- <i>D</i> & <i>L</i> , <i>R</i> & <i>S</i> , <i>R</i> * & <i>S</i> *, <i>Erythro</i> and <i>threo</i> isomers and their inter conversion | 4 | |
| | Interpretation of homotopic, enantiotopic and diastereotopic atoms, groups and faces. Pro-chiral carbon. Concept of <i>Re</i> - and <i>Si</i> - faces. Stereospecific and Stereoselective reactions. Asymmetric Synthesis- Cram's rule, Prelog's rule and Felkin-Anh model- Stereochemistry of compounds containing nitrogen | 5 | |

| | | | |
|---|--|-----------|---|
| | Geometrical isomerism -E and Z notation –Determination of configuration of geometrical isomers by simple techniques like hydroxylation, hydroboration and methods based on physical properties | 2 | |
| IV | OXIDATION AND REDUCTION REACTIONS | | |
| | <i>Oxidation:</i> Introduction, Different oxidative processes Oxidation with Cr (including PCC, PDC, Jones) and Mn (including MnO ₂ and BaMnO ₄) reagents; | 4 | PPT, Chalk and talk, Group discussion |
| | Oxidation with LTA, DDQ and SeO ₂ ; Oxidation using DMSO either with DCC or Ac ₂ O or Oxaloyl chloride; Oxidation using HIO ₄ and Dess-Martin Periodinane (DMP) reagent-Ruthenium tetroxide-Thallium (III) Nitrate | 3 | |
| | <i>Reduction:</i> Introduction. Different reductive processes :Reduction with NaBH ₄ , NaCNBH ₃ , Zn(BH ₄) ₂ LiAlH ₄ , Li(^t BuO) ₃ AlH, DIBAL-H, Red-Al, Et ₃ SiH and Bu ₃ SnH; Reduction using selectrides; Birch reduction. | 4 | |
| SnCl ₂ , Lawesson reagent – TiCl ₄ / Zn-Cu (Mac Murrays reagent) – TiCl ₄ /Mg-Hg-Wilkinson’s catalyst, Lindlar catalyst-BH ₃ /THF, 9-BBN, Baker’s yeast | 4 | | |
| V | MOLECULAR REARRANGEMENTS & NAME REACTIONS | | |
| | General mechanism – nature of migration, migratory aptitude, memory effects -A study of mechanism of the following rearrangements: <i>Carbon-carbon migration: Carbon-nitrogen migration :Carbon-oxygen migration</i> Beckmann, Curtius, Hofmann, Schmidt, Lossen, Wolff, Pinacol | 5 | PPT, Chalk and talk, Group discussion |
| | Wagner Meerwin, Demjanov, Dienone-Phenol, Favorski, Benzidine, Claisen, Cope, Sommet Hauser, Pummerer and Von-Richter rearrangements. | 5 | |
| A study of the following name reactions: Dieckmann cyclization, Hofmann-Löffler Freytag reaction, Mitsunobu reaction, Shapiro reaction, Eschenmoser-Tanabe and Ramburg-Backlund reactions. | 5 | | |
| Total Hours | | 75 | |

BB-Blockboard/ChalkandTalk PPT-Powerpointpresentation

Course Learning outcome: After successful completion of this course, the student will be able

| CLOs | CLO statement | Knowledge level |
|-------------|---|-----------------|
| CLO1 | Correlate mechanisms of addition reactions and examine the synthetic routes for organic transformations in carbon-carbon multiple bonds | Up to K4 |
| CLO2 | Organise and analyse mechanisms involved in addition across carbon-heteroatom bonds and elimination reactions | Up to K2 |
| CLO3 | Inspect the molecule on the basis of chirality and other stereochemical aspects. | Up to K3 |
| CLO4 | Interpret usages of the various oxidizing and reducing reagents to synthesize organic compounds. | Up to K3 |
| CLO5 | Conclude the potential applications of various rearrangements and name reactions in the synthesis of organic compounds and giving mechanism pertaining to them. | Up to K4 |

Mapping of CLOs with PLOs

| | PLO 1 | PLO 2 | PLO 3 | PLO 4 | PLO 5 |
|-------------|--------------|--------------|--------------|--------------|--------------|
| CLO1 | 3 | 2 | 3 | 2 | 1 |
| CLO2 | 3 | 2 | 3 | 2 | 1 |
| CLO3 | 3 | 2 | 3 | 2 | 1 |
| CLO4 | 3 | 2 | 3 | 2 | 1 |
| CLO5 | 3 | 2 | 3 | 2 | 1 |

3-Advance application;

2-Intermediate level;

1-Basic level

| Components of Formative Assessment | Marks | K level |
|---|--------------|--------------------|
| Internal Test | 10 | As per below table |
| Assignment | 5 | K4 |
| Quiz | 5 | K4 |
| Seminar | 5 | K4 |
| Total | 25 | |

Learning Outcome Based Education (LOBE) & Assessment

Formative Examinations I & II – Blue Print

Articulation Mapping-K Levels with Courses Learning Outcomes (CLOs)

| S. No. | CLOs | K- Level | SectionA | | Section B (Either/or Choice) | Section C (Open Choice) |
|---------------------------------|-------------|-----------------|-----------------------------|--------------------|---|--|
| | | | Short Answers | | | |
| | | | No. of Questions | K Level | | |
| 1 | CLO x | Up to K3 | 2 | K2,K3 | 2 (K3&K3) | 2(K2/K3) |
| 2 | CLO y | Up to K4 | 3 | K2, K2, K3 | 2 (K4&K4) | 1(K3/K4) |
| No. of Questions to be asked | | | 5 | | 4 | 3 |
| No. of Questions to be answered | | | 5 | | 2 | 2 |
| Marks for each question | | | 2 | | 5 | 10 |
| Total Marks for each section | | | 10 | | 10 | 20 |

K1- Remembering and recalling facts with specific answers

K2- Basic understanding of facts and stating main ideas with general answers

K3- Application oriented- Solving Problems

K4- Examining, analyzing, presentation and make inferences with evidences

Learning Outcome Based Education (LOBE) & Assessment
Summative Examination – Blue Print
Articulation Mapping-K Levels with Courses Learning Outcomes (CLOs)

| S. No. | CLOs | K- Level | Section A | | Section B | | Section C (Either/or Choice) | Section D (Open Choice) |
|---------------------------------|-------|-----------|---------------------|----------|---------------------|----------|------------------------------------|-------------------------------|
| | | | MCQs | | Short Answers | | | |
| | | | No. of Questions | K- Level | No. of Questions | K- Level | | |
| 1 | CLO 1 | Up to K 4 | 2 | K3 & K4 | 1 | K3 | 2 (K4&K4) | 1(K4) |
| 2 | CLO 2 | Up to K 2 | 2 | K1 & K1 | 1 | K1 | 2 (K1&K1) | 1(K2) |
| 3 | CLO 3 | Up to K 3 | 2 | K2 & K3 | 1 | K2 | 2 (K3&K3) | 1(K3) |
| 4 | CLO 4 | Up to K 3 | 2 | K2 & K3 | 1 | K1 | 2 (K2&K2) | 1(K3) |
| 5 | CLO 5 | Up to K 4 | 2 | K3 & K4 | 1 | K2 | 2 (K4&K4) | 1(K4) |
| No. of Questions to be asked | | | 10 | | 5 | | 10 | 5 |
| No. of Questions to be answered | | | 10 | | 5 | | 5 | 3 |
| Marks for each question | | | 1 | | 2 | | 5 | 10 |
| Total Marks for each section | | | 10 | | 10 | | 25 | 30 |

K1-Rememberingandrecallingfactswithspecificanswers

K2-Basicunderstandingoffactsandstatingmainideaswithgeneralanswers

K3-Applicationoriented-SolvingProblems

K4-Examining,analyzing,presentationandmakeinferenceswith evidences

Distribution of Section-wise Marks with K Levels

| K Levels | Section A & B (No Choice) | Section C (Either / or) | Section D (Open Choice) | Total Marks | % of Marks without choice | Consolidated % |
|--------------------|---------------------------|-------------------------|-------------------------|-------------|---------------------------|----------------|
| K1 | 6 | 10 | - | 16 | 13.3 | 35 |
| K2 | 6 | 10 | 10 | 26 | 21.7 | |
| K3 | 6 | 10 | 20 | 36 | 21.7 | 30 |
| K4 | 2 | 20 | 20 | 42 | 43.3 | 35 |
| Total marks | 20 | 50 | 50 | 120 | 100 | 100 |

Name of the course Designers

1. Dr. J. Shanmugapriya
2. Dr. P.S.Harikrishnan