

UNIVERSITY OF MADRAS
M.Sc. DEGREE PROGRAMME IN CHEMISTRY
 SYLLABUS WITH EFFECT FROM 2023-2024

Title of the Course	ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY						
Paper No.	Core I						
Category	Core	Year	I	Credits	4	Course Code	424C1A
		Semester	I				
Instructional hours per week	Lecture	Tutorial	Lab Practice		Total		
	4	1	-		5		
Prerequisites	Basic concepts of organic chemistry						
Objectives of the course	<p>To understand the mechanism of various organic reactions.</p> <p>To correlate the methods of determination of reaction mechanisms.</p> <p>To understand the various factors influencing the various types of organic reactions.</p> <p>To correlate and appreciate the differences involved in the various types of organic reaction mechanisms.</p> <p>To understand the stereochemistry of organic reactions.</p>						
Course Outline	<p>UNIT-I: Methods of Determination of Reaction Mechanism: Thermodynamic and kinetic requirements of reactions: Hammond postulate. Methods of determining mechanism: non-kinetic methods - product analysis, determination of intermediates-isolation, detection, and trapping. Cross-over experiments, isotopic labelling, isotope effects and stereo chemical evidences. Kinetic methods - relation of rate and mechanism-mechanistic implications of rate law. Effect of structure on reactivity: Hammett and Taft equations. Linear free energy relationship, partial rate factor, substituent and reaction constants.</p> <p>UNIT-II: Electrophilic and Nucleophilic Substitution: Aromaticity: Aromaticity in benzenoid, non-benzenoid, fused ring, heterocyclic compounds and annulenes. Aromatic electrophilic substitution: Orientation and reactivity of di- and polysubstituted phenol, nitrobenzene and halobenzene. Reactions involving nitrogen electrophiles: nitration, nitrosation and diazonium coupling; Sulphur electrophiles: sulphonation; Halogen electrophiles: chlorination and bromination; Carbon electrophiles: Friedel-Crafts alkylation and limitations, acylation and arylation reactions. Scholl reaction, Vilsmeier-Haack formylation, Gattermann reaction, Reimer-Tiemann and Bischler-Napieralski reactions. Aliphatic electrophilic substitution Mechanisms: S_E2 and S_Ei, S_Ei- Mechanism and evidences. Aromatic nucleophilic substitution: Mechanisms - S_NAr, S_N1 and Benzyne mechanisms - Evidences - Reactivity, Effect of structure, leaving group and attacking nucleophile. Reactions: Oxygen and Sulphur-nucleophiles, Bucherer and Rosenmund reactions, von Richter, Sommelet-Hauser and Smiles rearrangements. S_N1, ion pair, S_N2 mechanisms and evidences.</p>						

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	<p>Aliphatic nucleophilic substitutions at an allylic carbon, aliphatic trigonal carbon and vinyl carbon. S_N1, S_N2, S_Ni, and S_E1 mechanism and evidences, Swain- Scott, Grunwald-Winstein relationship - Ambident nucleophiles.</p> <p>UNIT-III: Elimination and Addition to Carbon Multiple Bonds: Mechanisms: $E2$, $E1$, and $E1cB$ mechanisms. Syn- and anti-eliminations. Orientation of the double bond: Hoffmann and Saytzeff rules. Reactivity: Effect of substrate, attacking bases, leaving group and medium. Stereochemistry of eliminations in acyclic and cyclic systems, pyrolytic elimination. Mechanisms: (a) Addition to carbon-carbon multiple bonds- Addition reactions involving electrophiles, nucleophiles, free radicals, carbenes and cyclic mechanisms- Orientation and reactivity, hydrogenation of double and triple bonds, Michael reaction, addition of oxygen and Nitrogen; (b) Addition to carbon- hetero atom multiple bonds: Mannich reaction, acids, esters, nitrites, addition of Grignard reagents, Wittig reaction, Prins reaction. Stereochemical aspects of addition reactions. Addition to Carbon-Hetero atom Multiplebonds: Addition of Grignard reagents, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Mechanism of condensation reactions involving enolates –Stobbe reactions. Hydrolysis of esters and amides, ammonolysis of esters.</p>
	<p>UNIT-IV: Stereochemistry: Optical isomerism due to asymmetric and dissymmetric molecules with C, N, S based chiral centers. Optical purity, prochirality, enantiotopic and diastereotopic atoms, groups, faces, axial and planar chirality, chirality due to helical shape, methods of determining the configuration. Racemic modifications: Racemization by thermal, anion, cation, reversible formation, epimerization, mutarotation. D, L system, Cram's and Prelog's rules: R, S-notations, proR, proS, side phase and re phase Cahn-Ingold- Prelog rules, absolute and relative configurations. Configurations of allenes, spiranes, biphenyls, cyclooctene, helicene, binaphthyls, ansa and cyclophanic compounds, exo-cyclic alkylidene-cycloalkanes. Topicity and prostereoisomerism, chiral shift reagents and chiral solvating reagents. Criteria for optical purity: Resolution of racemic modifications, asymmetric transformations, asymmetric synthesis, destruction. Stereoselective and stereospecific synthesis. Conformation and reactivity of acyclic systems, neighbouring group participation, chemical consequence of conformational equilibrium - Curtin-Hammett Principle. Stability of five and six-membered rings: mono-, di- and polysubstituted cyclohexanes, conformation and reactivity in cyclohexane systems. Fused and bridged rings: bicyclic, poly cyclic systems, decalins and Brett's rule. Optical rotation and optical rotatory dispersion, conformational asymmetry, ORD curves, octant rule, configuration and conformation, Cotton effect, axial haloketone rule and determination of configuration</p>

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	<p>UNIT-V: Oxidation and Reduction Reactions: Mechanisms: Direct electron transfer, hydride transfer, hydrogen transfer, displacement, addition-elimination, oxidative and reductive coupling reactions. Mechanism of oxidation reactions: Dehydrogenation by quinones, selenium dioxides, ferricyanide, mercuric acetate lead tetraacetate, permanganate, manganese dioxide, osmium tetroxide, oxidation of saturated hydrocarbons, alkyl groups, alcohols, halides and amines. Reactions involving cleavage of C-C bonds - cleavage of double bonds, oxidative decarboxylation, allylic oxidation, oxidation by chromium trioxide-pyridine, DMSO-Oxalyl chloride (Swern oxidation) and Corey-Kim oxidation, dimethyl sulphoxide- dicyclohexyl carbodiimide (DMSO-DCCD). Mechanism of reduction reactions: Wolff-Kishner, Clemmenson, Rosenmund, reduction with Trialkyl and triphenyltin hydrides, McFadyen-Steven's reduction, Homogeneous hydrogenation, Hydroboration with cyclic systems, MPV and Bouveault-Blanc reduction.</p>
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<p>Extended Professional Component (is a part of internal component only, Not to be included in the external examination question paper)</p>	<p>Questions related to the above topics, from various competitive examinations UPSC / TRB / NET/ UGC-CSIR / GATE /TNPSC others to be solved (To be discussed during the Tutorial hours)</p>
<p>Skills acquired from this course</p>	<p>Knowledge, Problem solving, Analytical ability, Professional Competency, Professional Communication and Transferable skills.</p>
<p>Recommended Text</p>	<ol style="list-style-type: none"> 1. J. March and M. Smith, Advanced Organic Chemistry, 5th edition, John-Wiley and Sons.2001. 2. E. S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston Inc., 1959. 3. P.S.Kalsi, Stereochemistry of carbon compounds, 8th edition, New Age International Publishers, 2015. 4. P. Y. Bruice, Organic Chemistry, 7th edn, Prentice Hall, 2013. 5. J.Clayden, N. Greeves, S. Warren, Organic Compounds, 2ndedition, Oxford University Press, 2014.

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Reference Books	<ol style="list-style-type: none"> 1. F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry Part-A and B, 5th edition, Kluwer Academic / Plenum Publishers, 2007. 2. D. G. Morris, Stereochemistry, RSC Tutorial Chemistry Text 1, 2001. 3. N.S. Isaacs, Physical Organic Chemistry, ELBS, Longman, UK, 1987. 4. E. L. Eliel, Stereochemistry of Carbon Compounds, Tata-McGraw Hill, 2000. 5. I. L. Finar, Organic chemistry, Vol-1 & 2, 6th edition, Pearson Education Asia, 2004. 6. D. Nasipuri, Stereochemistry of Organic Compounds, New Age International (P) Ltd, Reprint, 2005.
Website and e-learning source	<ol style="list-style-type: none"> 1. https://sites.google.com/site/chemistrybookscollection02/home/organic-chemistry/organic 2. https://www.organic-chemistry.org/
Course Learning Outcomes (for Mapping with POs and PSOs)	
<p>Students will be able</p> <p>CLO1: To recall the basic principles of organic chemistry.</p> <p>CLO2: To understand the formation and detection of reaction intermediates of organic reactions.</p> <p>CLO3: To predict the reaction mechanism of organic reactions and stereochemistry of organic compounds.</p> <p>CLO4: To apply the principles of kinetic and non-kinetic methods to determine the mechanism of reactions.</p> <p>CLO5: To design and synthesize new organic compounds by correlating the stereochemistry of organic compounds.</p>	

CO-PO Mapping (Course Articulation Matrix)

	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10
CO 1	S	S	S	S	M	S	S	S	S	M
CO 2	M	S	S	S	S	M	S	S	S	S
CO 3	S	S	M	S	S	S	S	M	S	S
CO 4	M	S	S	S	S	M	S	S	S	S
CO 5	M	S	M	S	S	M	S	M	S	S

Strong - 3

Medium-2

Low-1 Level of Correlation between

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PSO's and CO's

CO /PO	PSO1	PSO2	PSO3	PSO4	PSO5
CO1	3	3	3	3	3
CO2	3	3	3	3	3
CO3	3	3	3	3	3
CO4	3	3	3	3	3
CO5	3	3	3	3	3
Weightage	15	15	15	15	15
Weighted percentage of Course Contribution to Pos	3.0	3.0	3.0	3.0	3.0

3 – Strong, 2 – Medium, 1 – Low

Methods of Evaluation			
Internal Evaluation	Continuous Internal Assessment Test		25 Marks
	Assignments		
	Seminars		
	Attendance and Class Participation		
External Evaluation	End Semester Examination		75 Marks
	Total		100 Marks
Methods of Assessment			
Recall (K1)	Simple definitions, MCQ, Recall steps, Concept definitions.		
Understand/ Comprehend (K2)	MCQ, True/False, Short essays, Concept explanations, short summary or overview.		
Application (K3)	Suggest idea/concept with examples, suggest formulae, solve problems, Observe, Explain.		
Analyze (K4)	Problem-solving questions, finish a procedure in many steps, Differentiate between various ideas, Map knowledge.		
Evaluate (K5)	Longer essay/ Evaluation essay, Critique or justify with pros and cons.		
Create (K6)	Check knowledge in specific or offbeat situations, Discussion, Debating or Presentations.		

In order to avoid pull the score down of each PO, it is suggested that the usage L-Low (1) to the minimum.

The S, M, L is based on the course outcome. The mapping is based on the revised Bloom's Taxonomy Verbs used to describe your course outcome.

- Remember and Understanding – Lower level
- Apply and Analyze – Medium Level
- Evaluate and Create – Strong Level