

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

Title of the Course	ORGANIC REACTION MECHANISM AND PHOTOCHEMISTRY						
Paper No.	Core VII						
Category	Core	Year	II	Credits	4	Course Code	524C3A
		Semester	III				
Instructional hours per week	Lecture	Tutorial	Lab Practice		Total		
	4	1	-		5		
Prerequisites	Basic knowledge of organic chemistry						
Objectives of the course	<p>To understand the molecular complexity of carbon skeletons and the presence of functional groups and their relative positions.</p> <p>To study various synthetically important reagents for any successful organic synthesis.</p> <p>To apply disconnection approach and identifying suitable synthons to effect successful organic synthesis.</p> <p>To learn the concepts of pericyclic reaction mechanisms. To gain the knowledge of photochemical organic reactions.</p>						
Course Outline	<p>UNIT-I: Synthetic Organic Chemistry Preliminary Planning – knowns and unknowns of the synthetic system studied, analysis of the complex and interrelated carbon framework into simple rational precursors, retrosynthetic analysis, alternate synthetic routes, key intermediates that would be formed, available starting materials and resulting yield of alternative methods. Linear Vs convergent synthesis. synthesis based on umpolung concepts of Seebach, regiospecific control elements. Use of protective groups, activating groups and bridging elements. Examples on retrosynthetic approach, calculation of yield, advantages of convergent synthesis, synthesis of stereochemistry-controlled products. Retrosynthetic analysis; Alternate synthetic routes. Synthesis of organic mono and bifunctional compounds via disconnection approach. Key intermediates, available starting materials and resulting yields of alternative methods. Convergent and divergent synthesis, Synthesis based on umpolung concepts of Seebach. Protection of hydroxyl, carboxyl, carbonyl, thiol and amino groups. Illustration of protection and deprotection in synthesis. Control elements: Regiospecific control elements. Use of protective groups, activating groups, and bridging elements. Stereospecific control elements. Functional group alterations and transposition.</p> <p>UNIT-II: Pericyclic Reactions: Woodward Hoffmann rules; The Mobius and Huckel concept, FMO, PMO method and correlation diagrams. Cycloaddition and retrocycloaddition reactions; [2+2], [2+4], [4+4, Cationic, anionic, and 1,3-dipolar cycloadditions. Chelotropic reactions. ; Electrocyclization and ring opening reactions of conjugated</p>						

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	<p>dienes and trienes. Sigmatropic rearrangements: (1,3), (1,5), (3,3) and (5,5)-carbon migrations, degenerate rearrangements. Ionic sigmatropic rearrangements. Group transfer reactions. Regioselectivity, stereoselectivity and periselectivity in pericyclic reactions.</p> <p>UNIT-III: Reagents and Modern Synthetic Reactions: Lithium diisopropylamine (LDA), Azobisisobutyronitrile (AIBN), Sodium cyanoborohydride (NaBH₃CN), <i>meta</i>-Chloroperbenzoic acid (m-CPBA), Dimethyl aminopyridine (DMAP), n-Bu₃SnD, Triethylamine (TEA), Diazobicyclo[5.4.0]undec-7-ene (DBU), Diisopropylazodicarboxylate (DIAD), Diethylazodicarboxylate (DEAD), <i>N</i>-bromosuccinimide (NBS), Trifluoroacetic acid (TFA), Tetramethyl piperiridin-1-oxyl (TEMPO), Phenyltrimethylammonium tribromide (PTAB). Diazomethane and Zn-Cu, Diethyl maleate (DEM), Copper diacetylacetonate (Cu(acac)₂), TiCl₃, NaIO₄, Pyridinium chlorochromate (PCC), Pyridinium dichromate (PDC), Meisenheimer complex. Suzuki coupling, Heck reaction, Negishi reaction, Baylis-Hillman reaction.</p>
	<p>UNIT-IV: Molecular Rearrangements</p> <p>2.1 Rearrangements to electron deficient carbon: Pinacol-pinacolone and semi-pinacolone rearrangements - applications and stereochemistry, Wagner-Meerwein, Demjanov, Dienone-phenol, Baker-Venkataraman, Benzilic acid and Wolff rearrangements. Rearrangements to electron deficient nitrogen: Hofmann, Curtius, Schmidt, Lossen, Beckmann and abnormal Beckmann rearrangements. Rearrangements to electron deficient oxygen: Baeyer-Villiger oxidation and Dakin rearrangements. Rearrangements to electron rich atom: Favorskii, Quasi-Favorskii, Stevens, [1,2]-Wittig and [2,3]-Wittig rearrangements.</p> <p>2.2 Rearrangement from heteroatom to carbon - The Orton, Hofmann Martius and Fischer-Hepp rearrangements. Bamberger, Fries and Photo Fries rearrangement.</p> <p>2.3 Intramolecular rearrangements – Claisen, abnormal Claisen, aza Claisen, Claisen-Ireland, Cope, oxy-Cope and anionic oxy-Cope, Benzidine rearrangements.</p> <p>UNIT-V: Organic Photochemistry-I: Photochemical excitation: Experimental techniques; electronic transitions; Jablonskii diagrams; intersystem crossings; energy transfer processes; Stern Volmer equation. Reactions of electronically excited ketones; $\pi \rightarrow \pi^*$ triplets; Norrish type-I and type-II cleavage reactions; photo reductions; Paterno-Buchi reactions;</p>

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	<p>Organic Photochemistry-II: Photochemistry of α,β- unsaturated ketones; cis-trans isomerisation. Photon energy transfer reactions, Photo cycloadditions, Photochemistry of aromatic compounds; photochemical rearrangements; photo-stationary state; di- π-methane rearrangement; Reaction of conjugated cyclohexadienone to 3,4-diphenyl phenols; Barton's reactions.</p>
<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. F. A. Carey and Sundberg, Advanced Organic Chemistry, 5th ed, Tata McGraw-Hill, New York, 2003. 2. J. March and M. Smith, Advanced Organic Chemistry, 5th ed., John-Wiley and sons, 2007. 3. R. E. Ireland, Organic synthesis, Prentice Hall India, Goel publishing house, 1990. 4. Clayden, Greeves, Warren, Organic Chemistry, Oxford University Press, Second Edition, 2016. 5. M. B. Smith, Organic Synthesis 3rd edn, McGraw Hill International Edition, 2011.
<p>Reference Books</p>	<ol style="list-style-type: none"> 1. Gill and Wills, Pericyclic Reactions, Chapman Hall, London, 1974. 2. J.A. Joule, G.F. Smith, Heterocyclic Chemistry, Garden City Press, Great Britain, 2004. 3. W. Caruthers, Some Modern Methods of Organic Synthesis 4thedn, Cambridge University Press, Cambridge, 2007. 4. H. O. House. Modern Synthetic reactions, W.A. Benjamin Inc, 1972. 5. Jagdamba Singh and Jaya Singh, Photochemistry and Pericyclic Reactions, New Age International Publishers, New Delhi, 2012.
<p>Website and e-learning source</p>	<ol style="list-style-type: none"> 1. https://rushim.ru/books/praktikum/Monson.pdf

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Course Learning Outcomes (for Mapping with POs and PSOs)

Students will be able:

CO1: To recall the basic principles of organic chemistry and to understand the various reactions of organic compounds with reaction mechanisms.

CO2: To understand the versatility of various special reagents and to correlate their reactivity with various reaction conditions.

CO3: To implement the synthetic strategies in the preparation of various organic compounds.

CO4: To predict the suitability of reaction conditions in the preparation of tailor-made organic compounds.

CO5: To design and synthesize novel organic compounds with the methodologies learnt during the course.

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

3 – Strong, 2 – Medium, 1 - Low

Level of Correlation between 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