

KU7DSCCHE403: ORGANIC CHEMISTRY -IV

Semester	Course Type	Course Level	Course Code	Credits	Total Hours
VII	DSC	400	KU7DSCCHE403	4	75

Learning Approach (Hours/ Week)		Marks Distribution			Duration of ESE (Hours)
Lecture/ Tutorial	Practical/ Internship	CE	ESE	Total	
3	2	35	65	100	1.5

Course Description: The course is intended to develop a deep understanding in students about the reaction intermediates, mechanisms of various organic reactions, aromaticity and principles of photochemical reactions.

Course Prerequisite: Basic knowledge about reaction intermediates, electron displacement in molecules, types of reagents, electrophiles, nucleophiles, bond fission and basic idea regarding the photochemical reactions and mechanism of organic reactions.

Course Outcomes:

CO No.	Expected Outcome	Learning Domains
1	Associate the reaction conditions and reagents in the generation of intermediates and formulate a mechanism for the suggested reactions.	U
2	Analyze the structure-property relations in substitution and elimination reactions.	An
3	Understand various aromatic systems and their reactions and classify molecules based on the aromatic behaviour.	A

4	Distinguish between different photochemical reactions and understand the mechanism of natural photochemical reactions.	U
5	Acquire lab skills in the synthesis of organic compounds, determination of physical constants and purification techniques and in chromatographic techniques	A

**Remember (R), Understand (U), Apply (A), Analyse (An), Evaluate (E), Create (C)*

Mapping of Course Outcomes to PSOs

	PSO 1	PSO 2	PSO 3	PSO 4	PSO 5	PSO 6	PSO 7
CO 1	3	1	2	2	1	2	2
CO 2	3	1	2	1	2	2	2
CO 3	3	2	2	1	1	2	2
CO 4	3	1	2	2	1	2	2
CO 5	3	1	2	1	1	2	2

Course Contents for Classroom Transaction:

M O D U L E	U N I T	DESCRIPTION	HOURS
1	REACTION INTERMEDIATES AND REARRANGEMENTS		12
	1	Reaction intermediates and Rearrangements Structure, formation, and properties of carbenes, nitrenes, and arynes – singlet and triplet carbenes, nitrenes and arynes-Carbon free radicals: structure, formation, and stability	
	2	Structure, stability, and formation of Ylides, Enamines, 1,3-dithiane, Benzyne, and Enolates-Molecular rearrangement mechanism.	

		Carbon to carbon migration: Wagner Meerwein, Pinacol, Wolff, Benzilic acid, Demjanove, Dienone-phenol, Hoffmann-Martius	
	3	Carbon to nitrogen migration: Hofmann, Curtius, Schmidt, Lossen, Beckmann- Migration to electron-rich carbon: Wittig, Wittig-Hormer, Favorski, Stevens, Neber Orton, Bamberger. Migration to electron-deficient oxygen: Baeyer, villager, Darkin reaction	
	4	Aromatic rearrangements: Claisen, Benzidine, Fries, Von-Richter Sommet-Hauser	

		SUBSTITUTION AND ELIMINATION REACTIONS	12
	1	Aliphatic nucleophilic substitution reactions – saturated and unsaturated systems – Mechanism of nucleophilic substitution – S_N2 , S_N1 , S_Ni , Single Electron Transfer (SET)- Neighbouring group participation.	
	2	Non-classical carbocations, Substitution at allylic and vinylic carbon atoms-Effect of substrate structure, attacking nucleophile, leaving group, and reaction medium on reactivity and regioselectivity - Aliphatic Electrophilic Substitutions: S_E1 S_E2 and S_{Ei} mechanisms with suitable examples	
2	3	Elimination Reaction: Mechanistic and stereochemical aspects of $E1$, $E2$, and $E1cB$ eliminations-The effect of substrate structure, base, leaving group and reaction medium on elimination reactions. Elimination reaction in 4-t-Butylcyclohexyl tosylate (cis and trans), 2-Phenyl cyclohexanol (cis and trans), Menthyl and neomenthyl chlorides, and benzene hexachlorides.	
	4	Saytzev vs. Hofmann elimination, Bredt's rule- α - elimination, pyrolytic syn elimination (E_i) – Chugaev reaction, and Cope elimination. Dehydration of alcohols, Dehalogenation of vicinal dihalides, and Peterson olefination	

AROMATICITY AND AROMATIC REACTIONS		10
3	1	MO description of aromaticity and antiaromaticity. Homoaromaticity. Aromaticity of annulenes and heteroannulenes, fused ring systems, fulvenes, fulvalenes, azulenes, pentalenenes, and heptalenenes. Mesoionic compounds, metallocenes, cyclic carbocations, and carbanions. Effect of delocalized electrons on pKa
	2	Aromatic Electrophilic Substitution: Arenium ion mechanism, substituent effect on reactivity in mono and disubstituted benzene rings, <i>ortho/para</i> ratio, <i>Ipsso</i> Substitution-Relationship between reactivity and selectivity
	3	Aromatic Nucleophilic substitution: Addition-elimination (S _N Ar) mechanism, elimination-addition (benzyne) mechanism, <i>cine</i> substitution, S _N 1 and S _{RN} 1 mechanism
	4	The effect of substrate structure, nucleophile, and leaving group on aromatic nucleophilic substitution-Nucleophilic Substitution of Pyridine-Chichibabin Reaction

PHOTOCHEMISTRY		11
4	1	Photochemical excitation of molecules, spin multiplicity, Jablonski diagram, photosensitization, and quenching- Photochemistry of carbonyl compounds: Norrish type- I cleavage of acyclic, cyclic, and β , γ - unsaturated carbonyl compounds-Norrish type- II cleavage, photo reduction, photoenolization
	2	Photocyclo- addition of ketones with unsaturated compounds: Paterno-Büchi reaction, photodimerization of α , β - unsaturated ketones
	3	Photo rearrangements: Photo –Fries, di- π - methane, oxa di- π - methane, aza di- π - methane, lumi ketone rearrangements. Barton and Hoffmann- Loeffler- Freytag reactions

	4	Photo isomerization and dimerization of alkenes, photo isomerization of benzene and substituted benzenes, and photo-oxidation. Photochemistry of vision and photosynthesis	
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	TEACHER SPECIFIC MODULE		30
	*Total 10 experiments to be done A minimum of (five mixtures should be analysed and recorded, three preparations and any two experiment from chromatography to be carried out) Microscale analytical technique is preferred for carrying out the reactions		
5	1) Analysis of organic binary mixtures (minimum 5 binary mixtures): Separation of the binary mixture using physical and chemical methods. Checking its purity by Boiling points and Melting points. Preparation of the derivative of the compounds. The following types are expected: i) Solid-Solid ii) Non-volatile liquid & Non-volatile liquid iii) Water-soluble/insoluble solid and non-volatile liquid with compounds from the same or different chemical classes in all three categories. 2) Double-stage Preparation of organic compounds (minimum 3 compounds should be analyzed and recorded): a) Preparation of p-nitroaniline from acetanilide: Acetanilide----p-nitro acetanilide----p-nitroaniline b) Preparation of Methyl orange from aniline: Aniline---sulphanilic acid---methyl orange c) Preparation of p-aminoazobenzene from aniline: Aniline---diazoaminobenzene---p-aminoazobenzene d) Preparation of m-nitroaniline from nitrobenzene:		

Nitrobenzene---m-dinitrobenzene---m-nitroaniline e) Preparation of Benzilic acid benzoin: Benzoin----benzil----benzilic acid f) Preparation of Benzanilide from benzophenone: benzophenone---benzophenone oxime—benzanilide g) Preparation of 2-phenyl indole from phenyl hydrazine: Phenyl hydrazine----acetophenone phenyl hydrazone----2-phenyl indole h) Preparation of caprolactam from cyclohexanone: Cyclohexanone----cyclohexanone oxime---Caprolactum i) Preparation of m-nitrobenzoic acid from ethyl benzoate: Ethyl benzoate----ethyl m-nitrobenzene----m-Nitrobenzoic acid Purify the synthesized compound by means of recrystallization. (ii)Spot TLC, report the R_f value, and check the completion of the reaction and purity of the compound. 4)Chromatographic Analysis 1. Setting up a thin layer plate, Iodine chamber for chromatographic separation 2. Setting up paper (both horizontal and vertical) chromatography 3. Column packing and elution in Column chromatography 4. Separation of simple organic compounds (o-nitrophenol and p-nitrophenol) using different chromatographic techniques 5. Separation of plant pigments using TLC, Paper and Column Chromatography	
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Essential Readings:

1. R. Bruckner, Advanced Organic Chemistry: Reaction Mechanism, Academic Press, 2002.

2. F.A. Carey, R.A. Sundberg, Advanced Organic Chemistry, Part B: Reactions and Synthesis, 5/e., Springer, 2007.
3. J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford University Press, 2004.
4. R.O.C. Norman & J.M. Coxon, Principles of Organic Synthesis, 3/e, Nelson Thornes
5. J. March, M.B. Smith, March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 6/e, Wiley, 2007.
6. Ahluwalia Mukherjee and Singh, Organic reaction mechanisms
7. Maya Shankar Singh, Advanced organic chemistry: reactions and mechanisms, Pearson
8. Peter Sykes, A guidebook to mechanism in organic chemistry, 6th ed Pearson
9. I L Finar, Organic Chemistry Volume 2, Pearson Education.
10. P.S. Kalsi, Organic reactions & their mechanisms, 3/e revised, New Age International Publishers.
11. Modern methods of organic synthesis, Carruthers,
12. P.S. Kalsi, Organic reactions & their mechanisms, 3/e revised, New Age International Publishers.
13. J. Sing and J. Sing, *Photochemistry and Pericyclic Reactions*, 3/e, New Age International, 2012.
14. A I Vogel, A textbook of practical organic chemistry, Longman
15. A I Vogel, Elementary practical organic chemistry, Longman
16. F G Mann and B C Saunders, practical organic chemistry, Longman Shriver and Others, Systematic identification of organic compounds
17. Dey, Sitharaman and Govindachari, A laboratory manual of organic chemistry
18. PR Singh, DC Gupta & KS Bajpai, Experimental organic chemistry vol I & II
19. Vishnoi, Practical organic chemistry
20. Fieser, Experiments in Organic chemistry
21. S Sadasivam and A Manickam, Biochemical methods, New Age International Publishers
22. J B Harbone, Phytochemical methods, Chapman and Hall, London
23. Joseph Sharma, Gunter Zweig, TLC and LC Analysis of international importance, Vol. VI and VII, Academic Press

Assessment Rubrics:

Evaluation Type		Marks
End Semester Evaluation (ESE)		65 (50T+15P)
Continuous Evaluation (CCA)		35 (25T+10P)
Theory		25
a)	Test Paper*	10
b)	Assignment	5
c)	Viva-Voce	5
d)	Seminar	5
Practical		10
a)	Skill	4
b)	Record	4
c)	Punctuality	2
Total		100

* Average mark of the best two written tests may be considered for internal mark.