

PAPER-V: ORGANIC REACTION MECHANISMS AND REARRANGEMENTS

Semester	Subject Code	Category	Instruction Hours						Credits
			Lecture		Theory		Practical		
			Per Week	Per Semester	Per Week	Per Semester	Per Week	Per Semester	
II	21CPCH2B	Core	3	45	3	45	0	0	3

COURSE OBJECTIVES:

- ❖ Understanding addition, elimination, rearrangement and naming reactions along with their mechanism and synthetic utility.
- ❖ Understanding various types of oxidation and reduction reactions along with their mechanism and synthetic utility.

COURSE OUTCOMES:

- On the successful completion of course, students will be able to

CO Number	CO statement	Knowledge level
CO1	Get a clear picture about the addition reactions happening through nucleophilic, electrophilic groups and to learn about the addition reactions between double bonded carbon compounds	K2 & K3
CO2	Gain knowledge on the nucleophilic and electrophilic additions to carbonyl compounds and naming reactions	K2 & K3
CO3	Obtain an outline about elimination reactions and the rules used to study elimination reactions with some specific examples	K3
CO4	Acquire knowledge about the reagents which causes various rearrangement reactions	K2 & K3
CO5	Learn about the basic mechanism of oxidation in various organic compounds such as alcohols, aldehydes, ketones, olefins etc and two types of reduction reactions like complete reduction and selective reduction using different reducing agents	K2 & K4

* CO-Course Outcomes

Knowledge level K1-Remember; K2-Understand; K3-Apply; K4-Analyze

MAPPING WITH PROGRAM OUTCOMES

COS	PO1	PO2	PO3	PO4	PO5	PO6
CO1	M	M	M	M	S	S
CO2	M	M	S	S	S	M
CO3	M	M	M	M	S	M
CO4	M	S	S	S	S	M
CO5	M	S	S	S	M	S

UNIT-I: ADDITION TO CARBON-CARBON DOUBLE BOND**9 hours**

Electrophilic addition to carbon – carbon double and triple bonds – Nucleophilic addition to carbon–carbon multiple bonds – Generation and addition of carbenes-mechanism of 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. Homogenous, heterogeneous and Transfer hydrogenation – Hydroboration – Hydration of carbon-carbon double and triple bonds.

UNIT-II: ADDITION TO CARBON-OXYGEN DOUBLE BOND**9 hours**

Nucleophilic addition to $\text{C}=\text{O}$ bond – A study of mechanism of Mannich, benzoin, Darzen's glycidic ester, Stobbe and Knoevenagel condensation reactions – Wittig, Wittig-Horner olefination reactions; Sulfur and Sulfonium ylides and their reactions – Julia olefination.

UNIT-III: ELIMINATION**9 hours**

Elimination reactions: E_1 , E_2 , $\text{E}_{1\text{cb}}$ and E_{i} -elimination – Conformation of mechanism; solvent, substrate, leaving group effects – Typical elimination reactions – dehydration, dehydrohalogenation and dehalogenation – Saytzeff's and Hoffmann 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.

UNIT-IV: MOLECULAR REARRANGMENTS AND REACTIONS**9 hours**

A study of mechanism of the following rearrangements: Beckmann, Curtius, Hofmann, Schmidt, Lossen, Pinacol, Wagner – Meerwin, Demjanov, Dienone – Phenol, Favorski, Benzidine, Claisen, Cope, Sommelet – Hauser, Pummerer, Baeyer – Villiger, Wolff, Stevens and Von – Richter rearrangements.

A study of the following name reactions: Dieckmann cyclization, Hofmann – Löffler Freytag reaction, Mitsunobu reaction, Shapiro reaction.

UNIT-V: OXIDATION AND REDUCTION REACTIONS**9 hours**

Oxidation of methylene to carbonyl, oxidation of aryl methenes – allylic oxidation of olefins – Oxidation with Cr (including PCC, PDC, Jones) and Mn (including MnO_2 and BaMnO_4) reagents; Oxidation with LTA, DDQ, $\text{Hg}(\text{OAc})_2$ and SeO_2 ; Oxidation using DMSO either with DCC or Ac_2O or Oxaloyl chloride; Oxidation using IBX and Dess-Martin Periodinane (DMP) reagent.

Clemmenson and Wolf-Kishner reduction – Huang Millon modification – Birch reduction and MPV reduction. Reduction with sodium borohydride, lithium aluminium hydride, tritertiarybutoxyaluminium hydride, sodium Cyanoborohydride, $\text{Zn}(\text{BH}_4)_2$, DIBAL-H, Red-Al, Et_3SiH and Bu_3SnH . Selectrides – Selectivity in reduction 4-t-butylcyclohexanone using selected hydride reductions.

Distribution of hours: Theory-90%; Problems-10%

TEXT BOOKS

S.No	Authors	Title	Publishers	Year of publication
1	Jerry March	Advanced Organic Chemistry	John Wiley & Sons, 5 th Ed	2001
2	F. Carey and R. J. Sundberg	Advanced Organic Chemistry-Part A and B	Springer Science 5 th Ed	2007
3	M. B. Smith and Jerry March	Advanced Organic Chemistry	John Wiley & Sons, 5 th Ed	2001
4	J. Clayden, N. Greeves and S. Warren	Organic Chemistry,	Oxford University Press, 2 nd Ed	2012.
5	M. B. Smith	Organic Synthesis,	Academic Press 3 rd Ed	2011
6	R. O. C. Norman and J. M. Coxon,	Principles of Organic Synthesis	Chapman & Hall, 3 rd Ed	1993
7	Stuart Warren	Organic Synthesis	Disconnection Approach, Wiley India (P) Ltd	2007

8	V.K.Ahluwalia	Oxidation in Organic Synthesis	CRC Press, 1 st Ed	2012
9	V.K.Ahluwalia	,Reduction in Organic Synthesis	CRC Press, 1 st Ed	2012

TEACHING METHODOLOGY:

- PowerPoint presentation
- Models
- Group discussion
- Seminar and Assignments
- Animated videos
- Board and chalk

SYLLABUS DESIGNERS:

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