

Name of the Programme: M.Sc. Part-II (Organic Chemistry)

Course Code: CHO-625 **Title of the course:** Organometallic Chemistry and

Rearrangement Reactions

Number of Credits: 4

Effective from AY: 2023-24

Prerequisites for the course:	Students should have studied chemistry courses at M.Sc. Part-I level.	
Course Objective:	1. To understand concepts and various strategies involved in organometallic chemistry. 2. To apply organometallic chemistry in the formation of carbon-carbon, carbon-hetero atom bonds. 3. To understand and apply molecular rearrangements for synthetic applications.	
Content	1. Introduction to organometallic chemistry a. Introduction to Organometallic Chemistry, Definitions, Types of Metal-carbon bonds with main-group metals and transition metals b. <i>Sigma</i> and <i>pi</i> bonds: linear pi system and cyclic pi system c. Organic ligands, Nomenclature, hapticity, Electron counting and 18-electron rule d. Orbital interactions and bonding e. Kinetic stability	No of hours 08
	2. Organometallic compounds of main group elements a. Preparation, properties and applications of Lithium, Magnesium, Cadmium, Zinc, Cerium, Mercury and Chromium Compounds. b. Heteroatom directed lithiation reactions	12
	3. Role of transition metals in organic synthesis a. Preparation and properties of Copper, Palladium, Nickel, Rhodium, Ruthenium and Gold reagents/complexes. b. Mechanisms and applications of Mizoroki-Heck, Suzuki, Stille, Hiyama, Negishi, Sonogashira, Wacker, Kumada, Buchwald-Hartwig, carbonylation, homogenous hydrogenation, carbonylation, allylic substitution)	20
	4. Molecular rearrangements and their synthetic applications a. Unifying principles and mechanisms of rearrangements taking place at an electron deficient and electron rich substrates. b. Rearrangements taking place at carbon: Arndt-Eistert, Wagner-Meerwein, benzil-benzilic acid, Pinacol-pinacolone, semipinacol, Tiffeneau Demjanov, dienone-phenol, Wittig, Favorskii, Stevens, Wolff, Baker-Venkatraman, Barton	20

	<p>decarboxylation, Pummerer rearrangement.</p> <p>c. Rearrangements at nitrogen: Hofmann, Curtius, Lossen, Schmidt, Beckmann, Neber, Stieglitz rearrangement.</p> <p>d. Rearrangements at oxygen: Payne (including aza- and thia-Payne) rearrangement, hydroperoxide rearrangement, Criegee rearrangement, Baeyer–Villiger oxidation</p> <p>e. Aromatic rearrangements: Benzidine, Fries, Von Richter, Sommelet-Hauser, Smile's, Jacobsen. Rearrangement on aniline derivatives- Bamberger rearrangement, Fischer-Hepp, Orton, Hofmann-Martius, Reilly-Hickinbottom, rearrangements of <i>N</i>-arylazoanilines, Phenylnitramines, Phenylsulfamines.</p> <p>f. Rearrangements involving fragmentations: Eschenmoser fragmentation.</p>	
Pedagogy	<p>Mainly lectures and tutorials. Seminars / term papers /assignments / presentations / self-study or a combination of some of these can also be used. ICT mode should be preferred. Sessions should be interactive in nature to enable peer group learning.</p>	
References / Readings	<ol style="list-style-type: none"> 1. A. Edward, Comprehensive Organometallic Chemistry, 2nd Ed., 14 vols. Pergman, 1995. 2. F. R. Hartley, Chemistry of Metal-Carbon Bond, 6 vols. Wiley, 1982-83. 3. M. Schlosser, Organometallics in Synthesis - A Manual, John & Wiley, 1994. 4. R. H. CraJohn, The Organometallic Chemistry of the Transition Metals, Wiley, 1994. 5. G. R. Stephenson, Transition Metal Organometallics for Organic Synthesis, Cambridge University Press, 1991. 6. L. S. Liebeskind, Advances in Metal Organic Chemistry, Vols. 1 and 2 (Ed.), JAI Press, 1989. 7. J. P. Colliman, L. S. Hegedus, J. R. Norton & R. G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, 1987. 8. A. Yamamoto, Organotransition Metal Chemistry - Fundamental Concepts and Applications, Wiley, 1986. 9. A. J. Pearson, Metallo-Organic Chemistry, John Wiley, 1985. 10. W. Caruthers & I. Colddham, Modern Methods of Organic Synthesis, 4th Ed., Cambridge University Press, 2016. 11. J. Clayden, N. Greeves and S. Warren, Organic Chemistry, Oxford, 2016. 12. F. A. Carey & R. J. Sundberg, Advanced Organic Chemistry: Part A and B, 5th Ed., Springer India Private Limited, 2007. 13. R. O. C. Norman & J. M. Coxon, Principles of Organic Syntheses, 3rd Ed. CRC Press Inc, 2009. 14. M. B. Smith & Jerry March, Advanced Organic Chemistry- 50 Reaction, Mechanism and Structure, 6th Ed., Wiley, 2006. 	

Course Outcome:	<ol style="list-style-type: none"> 1. Students will be in a position to understand how a carbon-carbon and carbon-hetero atom bonds can be constructed using organometallic chemistry. 2. Students will be able to understand and apply the concepts of organometallic chemistry in syntheses of organic molecules. 3. Students will be in a position to write synthetic routes for organic molecules using various molecular rearrangements.