

CY703 Advanced Organic Chemistry

Credit: 3-0-0 - 3

Approval: Approved in 1st Senate

Elective or core: Core

Students intended for: Ph.D.

Prerequisite: M.Sc.

Semester: Even/Odd

Course Objective:

Better understanding of the key concepts in Organic chemistry and to prepare students for solving advanced research problems in organic chemistry

Course content:

Stereochemistry and Conformational Analysis (5 hours)

Enantiomeric relationships, diastereomeric relationships, stereochemistry of reactions, acyclic sp^3 - sp^2 systems, cyclohexane and substituted cyclohexanes, A values, cyclohexene, decalins, anomeric effect, strain.

Kinetics and thermodynamics of Organic Reactions (7 hours)

Free energy relationships, Transition state theory, Intramolecular versus Intermolecular reactions, Kinetic and thermodynamic control, Hammond postulate, principle of microscopic reversibility, isotope effects, isotopes in labeling experiments, characterization of reaction intermediates, catalysis by

bronsted acids and bases, catalysis by Lewis acids and bases.

Reactive Intermediates: Carbanion, carbocation, radical & carbene (12 hours)

Carbanions, stability of carbanions, generation of carbanions, SN1 and SN2 mechanisms, carbocations, nucleophilicity and solvent effects, leaving group effects, neighboring group participation, the norbornylcation and other nonclassical carbocations. E1 and E2 mechanisms, regiochemistry of elimination reactions, stereochemistry of E2 elimination reaction, acidity of hydrocarbons, electrophilic aromatic substitution reactions, Structure reactivity relationships, nucleophilic aromatic substitution, generation and characterization of free radicals, characteristics of free radicals, characteristics of reaction mechanisms involving radical intermediates, free radical substitution reactions and free radical addition reactions, generation of carbenes, addition to double bonds, insertion reactions.

Pericyclic reactions, Photochemistry and Aromaticity: (5 hours)

Rules governing electrocyclic reactions, sigmatropic rearrangements, cycloaddition reactions, the concept of aromaticity, the annulenes, aromaticity in charged rings, homo aromaticity, fused ring systems, heterocyclic rings, Norrish type I and II reactions and Paterno Buchi reaction, Di-pi-methane rearrangement.

Strategic applications of named reactions in organic synthesis (6 hours)

Alder (ene) reaction, aldol reaction, olefin metathesis, aza Cope rearrangement, Bayer villiger oxidation, Baylis Hillman reaction, Birch reduction, Buchwald-Hartwig reaction, Claisen rearrangement, Cope rearrangement, Dess Martin oxidation, Diels Alder cycloaddition, enyne metathesis, Friedel-Crafts acylation and alkylation, Grignard reaction, Heck reaction, Johnson Claisen rearrangement, Mannich reaction, Mc Murry coupling, Mitsunobu reaction, Nazrov cyclisation, Sharpless asymmetric epoxidation, Shi asymmetric epoxidation, Pausand Khand reaction, Wittig reaction.

Synthetic Analysis and Design: (5 hours)

Retrosynthetic analysis, strategic bond analysis, total synthesis of natural products. Assignment on a synthetic target and defend through seminar.

Text Books:

1. F. A. Carey and R. I. Sundberg, *Advanced Organic Chemistry, Part A*, 5th edition, Springer, 2007.
2. F. A. Carey and R. I. Sundberg, *Advanced Organic Chemistry, Part B*, 5th edition, Springer, 2007.
3. Michael B. Smith and Jerry March, *March's Advanced Organic Chemistry*, 5th edition, Wiley Interscience, 2001.
4. Jonathan Clayden, Nick Greeves, Stuart Warren and Peter Wothers, *Organic Chemistry*, Oxford University Press, 2001.
5. Ian Fleming, *Molecular Orbitals and Organic Chemical Reactions: Reference Edition*, John Wiley & Sons, 2010.
6. E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, John Wiley and Sons, 1994.
7. W. Carruthers and Iain Coldham, *Modern Methods of Organic Synthesis*, 4th edition, Cambridge University Press, 2004.
8. Peter Sykes, *Guidebook to Mechanism in Organic Chemistry*, 6th edition, Pearson Prentice hall, 1986.
9. Laszlo Kurti and Barbara Czako, *Strategic Applications of Named Reactions in Organic Synthesis*, academic press, 2005.

References:

1. A photo-thermal metathesis approach to perhydro-as-indacenes: rapid construction of the carbocyclic segment of ikarugamycin, Goverdhan Mehta, A. Narayana Murthy and D. Siva Kumar Reddy, *Tetrahedron Letters*, 1987, 28, 467-1468.
2. Total Synthesis of (+) Cyanthiwigin U, Matthew W. B. Pfeiffer and Andrew J. Phillips, *J. Am. Chem. Soc.*, 2005, 127 (15), pp 5334–5335.
3. Total Synthesis of (–) Psycotrimine, Timothy Newhouse and Phil S. Baran, *J. Am. Chem. Soc.*, 2008, 130 (33), 0886–10887