Anekant Education Society's

Tuljaram Chaturchand College, Baramati 413102 (Dist.Pune)

(Autonomous)

Revised Syllabus for

M.Sc. (Organic Chemistry) Part II (Semester III)

Choice based Credit System Syllabus To be implemented from Academic year 2022-2023

M. Sc. - II Organic Chemistry Semester–III

PSCH0231: Designing of organic synthesis and Heterocyclic Chemistry

(48L+12 T) (4 Credit)

Learning objectives :

1. Retrosynthetic analysis and synthesis.
2. Functional group interconversion and protective group methodology. Modern methods for carbon-carbon, and carbon-heteroatom bond formations**.**
3. To understand major classes of heterocyclic compounds

Learning Outcomes :

On completion of the course, the student should be able to:

1. Describe methods for synthesis and transformation of the most common functional groups
2. Identify, analyse and evaluate synthetic routes to target molecules using retrosynthesis
3. Apply organometallic reagents and reactions in organic synthesis
4.

1. Designing of organic synthesis (24 L)

Protection and de-protection of hydroxyl, amino, carboxyl, ketone and aldehyde functions as illustrated in the synthesis of polypeptide and polynucleotide, enamines, An introduction to Synthons and synthetic equivalents, disconnecttion approach, functional group interconversions. Importance of the Order of events in organic synthesis, Chemoselectivity, Regioselectivity. Umpolung in organic synthesis, FGI, divergent vs. convergent syntheses. Synthesis of some typical organic molecules-Abscisic acid, Longifolene

Ref. 1-9

2.Heterocyclic Chemistry (24 L)

a) Five and six membered heterocycles with one and two heteroatoms:
Synthesis, reactivity, aromatic character and importance of following heterocyclic compounds:
Furan, Pyrrole,Thiophene, Pyrazole, Imidazole, Pyridine

b) Synthesis, reactivity, aromatic character and importance of following heterocyclic compounds: Condensed five and six membered heterocycles:
Benzofuran, Indole, Quinoline

c) Condensed five membered heterocycles:
Benzoxazole, Benzthiazole, Benzimidazole

d) Synthesis of ranitidine, papavarine, amlodipine, bromouridine, tryptophan, thiamine, chloroquine
Ref.10-17

References:

1. Designing of organic synthesis–S.Warren(Wiley)
2. Some modern methods oforganic synthesis –W.Carruthers (Cambridge)
3. Organic chemistry–J. Clayden ,N .Greeves, S.Warren andP. Wothers (OxfordPress)
4. Organic synthesis – Michael B. Smith
5. Advanced organic chemistry,PartB – F.A Carey and R.J. Sundberg, 5 th edition (2007)
6. Guide book to organic synthesis- R K Meckie ,D M Smith and R A Atken
7. Organic synthesis – Robert E Ireland
8. Strategic Applications of named reactions inorganic synthesis-Laszlo Kurti and Barbara Czako
9. Organic synthesis through disconnection approach-P.S. Kalsi

10. Heterocyclic Chemistry-T. Gilchrist
11. An introduction to the chemistry of heterocyclic compounds-R M Acheso
12. HeterocyclicChemistry-JAJoule andK Mills
13. Principles of modern heterocyclic chemistry-APaquette
14. Theessenceof Heterocyclic Chemistry- A. R. Parikh, Hansa Parikh, Ranjan Khunt
15. Hand book of Heterocyclic Chemistry- A R Katritzky ,A F Pozharskii
16. HeterocyclicChemistry- R.K.Bansal

PSCHO-232: Spectroscopic Methods in Structure Determination (48L+12 T) (4 Credit)

Learning objectives :

1. Spectroscopic techniques including the basic principles for recording of NMR, IR, UV, and MS spectra.
2. Identification and characteristics of functional groups using IR spectroscopy.
3. Principles of nuclear magnetic resonance spectroscopy of 1H, 13C (1D and 2D).
4. Fragmentation pattern, effect of isotopes in Mass spectroscopy.

Learning Outcomes :

On completion of the course, the student should understand:

1. Combine information from experimental NMR, IR, UV, and MS spectra and elucidate the structure of unknown organic compounds.
2. Suggested molecular structure from analysis of the spectral data.
3. Prediction of the NMR, IR, UV-Vis and MS spectra from a given molecular structure.

^{1}H NMR Spectroscopy (14)

Recapitulation of basic principle, Chemical shift, factors influencing chemical shift, deshielding, chemical shift values and correlation for protons bonded to carbons (aliphatic, olefinic, aldehydic, aromatic) and other nuclei(alcohols, phenols, enols, acids, amides and mercaptans), chemical exchange, effect of deuteration, spin-spin coupling, (n+1) rule, complex spin-spin interaction between two, three, four andfive nuclei (first order spectra), factors effecting coupling constant "*J*", Spin decoupling.
Factors affecting coupling constant, simplification of complex spectra, nuclear magnetic double resonance, spin decoupling, contact shift reagents, solvent effects, nuclear over-hausereffect (NOE), and resonance of other nuclei like ^{31}P

^{13}CNMRspectroscopy (8 L)

FT NMR, Types of ^{13}C NMR Spectra: un-decoupled, Proton decoupled, Off resonance, , DEPT with 3 different angles, chemical shift, calculations of chemical shifts ofaliphatic, olefinic, alkyne, aromatic, hetero aromatic and carbonyl carbons, factors affectingchemical shifts, chemical shifts of solvents, Homo nuclear (^{13}C-^{13}C) and Hetero nuclear (^{13}C-^{1}H)couplingconstants.

2D NMR Techniques (6L)

General idea about two dimensional NMR spectroscopy, Correlation spectroscopy (COSY)-Homo COSY (^{1}H-^{1}H), TOCSY, Hetero COSY (HMQC, HMBC), Homo and Hetero nuclear 2D resolved spectroscopy, NOESY and 2D-INADEQUATE experiments and their applications. Illustrative example of COSY, HSQC in carbohydrate characterization.

Mass Spectrometry (10L)

Instrumentation, various methods of ionization (fieldionization, field desorption, SIMS, FAB, MALDI, Californium plasma), different detectors (magnetic analyzer, ion cyclotron analyzer, Quadrapole mass filter, time of flight (TOF). Rules of fragmentation of different functional groups, factors controlling fragmentation

Problems based on joint application of UV, IR, PMR, CMR, and Mass. (10 L)

(Includingreactionsequences)

References:

1. IntroductiontoSpectroscopy D.L.Pavia,G.M .Lampman, G.S. Kriz, 3rdEd .(Harcourt college publishers).
2. Spectrometric identification of organic compounds R.M.Silverstein,F.X.Webster,6th Ed. JohnWileyand Sons.
3. Spectroscopic methods inorganic chemistry-D.H.Williams and I. Flemming McGraw Hill
4. Absorption spectroscopyoforganic molecules - V. M. Parikh
5. NuclearMagneticResonance-BasicPrinciples-Atta-Ur-Rehman,Springer-Verlag(1986)

PSCHO-233: Organic Stereochemistry-I and Organic Reaction Mechanism (48L+12 T) (4Credit)

Learning objectives :

1. To understand different conformations of substituted cyclohexane and their physical properties
2. To understand different conformations and reactivity of rings other than six membered
3. To understand stereochemistry of fused, bridged, caged ring system.
4. To learn reaction mechanism of reactions involving carbanion

4. Learning Outcomes :

On completion of the course, the student should understand

1. Nomenclature, synthesis; stereochemical aspects of Perhydrophenanthrene.
2. Perhydroanthracene, hydrindane, Steroids; Bridged system.
3. Conformations of substituted cyclohexanes.
4. Reaction mechanism of different name reactions involing carbanion, carbine and nitrene

1. Organic Stereochemistry-I

1. Stereochemistry of six member rings. Ref.1,3, 4, 5 **(11 L)**
2. Stereochemistry of rings other than six member Ref.1,3, 4, 5 **(7 L)**
3. Fused Bridged and caged rings Ref. 1,2, 3,4 **(6 L)**

2. Organic Reaction Mechanism

1. Carbanions: Formation, geometry,stability and related reactions- Aldol, α-halogenation ,haloform reaction, Michael reaction, Robinson annulations, Mannich, Stobbe, Cannizaro's, Darzons, Dieckmann, Knoevegel, Benzoin, Perkin, Benzoin condensation, Grignard, Claisen condensation, Baylis-Hilman, Appel reaction, Corey-Fuchs reaction Ref.6,7,8,10 **[12 L]**
2. Enamines: formation and applications of enamine in organic synthesis. Ref.9 **[4 L]**
3. NGP : Neighbouring group participation Ref.6 **[4 L]**
4. Synthesis and reactions of carbenes and nitrenes

   Hoffmann, Curtius, Lossen, Schmidt and Beckmann rearrangement reactions **[4 L]**

   Ref.9

References:

1. Stereochemistry of carbon compounds - E.L. Eliel
2. Stereochemistry of carbon compounds - E.L.Eliel and S. H. Wilen
3. Stereochemistry of organic compounds –Nasipuri
4. Stereochemistryof organiccompounds-Kalsi
5. Organic stereochemistry–Jagdamba Singh
6. Mechanism and structure in Organic Chemistry – E. S. Gould (Holt, Rinehart and Winston)
7. Advanced organicchemistrybyJ. March, 6th Ed.

8. Advanced organic chemistry. F. A. Carey and R. J. Sundberg, Part A 5th Ed. Springer (2007)
9. Advanced organic chemistry. F. A. Carey and R. J. Sundberg, Part B 5th Ed.Springer(2007)
10. Organic Chemistry–J.Clayden,N. Greeves,S.WarrenandP. Wothers

PSCHO -234:Photochemistry,Free radicals and Pericyclic Reactions and (48L+12 T)(4Credit)

Learning objectives :

1. To know the exact concept of pericyclic reactions and photochemical reactions.

To know the Stereochemistry, migratory aptitude of different reactions.

2. To learn photochemical and thermal reaction and their applications in organic synthesis
3. To understand reactions involving radical mechanism

Learning Outcomes :

On completion of the course, the student will be able to apply

1. To gain the knowledge of photochemical and pericyclic rearrangement
2. To understand the inter and intra molecular radical reaction
3. To construct the correlation diagram

1. Photochemistry (16 L)

Photo rearrangements of cyclopentanone , cyclohexanone, dienones, β-r unsaturated ketones, Aza-Di-**π**–Methane rearrangement, Di-**π**–Methane rearrangement, rearrangements in aromatic compounds, photo reduction and photo oxidation , photo substitution reaction at sp^3 carbon having one hydrogen - Barton reaction.
Photochemistry in nature- chemistry of vision, Application of photochemical reactions in synthesis – Isocomene Ref. 1,2,3,4

2. Free radicals: [16 L]

Radical initiators, Characteristic s reactions,- Free radical substitution ,addition to multiple bonds, free radical halogenations - chlorinationand bromination-NBS ,autoxidation, Thermal decomposition of hydroperoxides, Radicals in synthesis: Hunsdiecker reaction,Barton Nitrite Photolysis reaction ,Barton Decarboxylation, Inter and intramolecular C-C bond formation via mercuric hydride ,tin hydride, , Oxidative coupling. C-C bond formation in aromatics, SNAr reactions-Sandmeyer reaction Ref. 1, 3, 6

3. Pericyclic reactions [16 L]

Recapitulation of Molecular Orbitals, their symmetry properties, Woodward –Hoffmann's Conservation of orbital symmetry property rule.
Cycloaddition reactions, Chelotropic reactions, Sigmatropic reactions, and 1,3-dipolar additions, Analysis by correlation diagrams, Mobius Huckel theory and ATS concept. Application of pericyclic reactions: Ene reaction, Sommelet Hauser rearrangement, Claisen and Cope rearrangements, fluxional molecules, synthesis of Endiandric acid.
Ref.1, 3,5, 7,10-14

References:

1. Advanced Organic Chemistry, Part A – F. A. Carey and R. J. Sundberg, 5th Ed.Springer(2007)
2. Excitedstatesin Organic Chemistry-J.A.Barltrop andJ.D.Coyle, JohnWiley&sons
3. Photochemistryand Pericyclicreactions-Jagdamba Singh, Jaya Singh 3rdEd.

4. Organicphotochemistry:Avisualapproach-JanKopecky,VCHpublishers (1992).
5. Conservation of orbital symmetry – R. B. Woodward and R. Hoffmann; VerlagChemie,Academic press(1971).
6. RadicalsinOrganicSynthesisB.Giese,Pergamonpress(1986)
7. Orbital Symmetry : A problem solving approach- R. E. Lehr and A. P.Marchand;Academic (1972)
8. Classicsintotal synthesis-K. C.Nicolaouand E.J. Sorensen;VHC(1996)

9. P.A. Wenderand J. J. Howbert*J. Am.Chem. Soc.* **1981**,*103*, 688-690.
10. Organicreactionsandorbitalsymmetry,2nd Ed.T. L.GilchristandR.C.Storr
11. Organic Chemistry–J.Clayden,N. Greeves,S.WarrenandP. Wothers
12. Pericyclicreactions:Atextbook–S.Sankararaman
13. Pericyclicreactions-Gilland Willis
14. Frontierorbitals andorganicchemicalreactions-Ian Fleming,John Wiley& sons7

Practical course - I

PSCHO-235: Single stage preparations [4Credits]

At least nine single stage and two isolation of Natural products should carried out. The preparation should be carried out on micro scale.

Learning Objective:

1. Student will learn principle of isolation techniques.
2. Student will learn to handle reducing and oxidizing reagents in synthesis.
3. Student will be able to learn multicomponent reacrions

Learning Outcome:

4. Student will learn use of oxidizing and reducing reagents in different synthesis.
5. Student will get the knowledge of isolation of natural product.
6. Student will be able to perform multicomponent reacrions
7. Student will be able to perform rearrangement reactions

A) Advance organic practical (any 9)

Synthesis, purification and characterization

1) 2-phenyl indole by Fischer indole synthesis
2) Benzyl alcohol and benzoic acid from benzaldehyde (Canninzaro reaction)
3) 2-chlorobenzoic acid from anthranillic acid (Sandmeyer reaction)
4) Cyclohexanol from cyclohexanone ($NaBH_4$ reduction)
5) 4-Nitro Benzonitrile from 4-Nitrobenzaldehyde
6) Imidazole from orthophenylene diamine
7) Schiff base synthesis from substituted benzaldehyde
8) 4-amino benzoic acid from 4-Nitro benzoic acid
9) Synthesis of chalcone from substituted benzaldehyde
10) 2- amino 4-phenyl thiazole from acetophenone and thiourea
11) O-Benzoyloxyacetophenone from O-hydroxyacetophenone (Flavone)

B) Isolation of Natural products (Any2)

1) Piperine from pepper
2) Eugenol from clove
3) Cinnmaldehyde from cinnamon

Practical course II

PSCHO-236: Double e stage preparations [4credits]

At least 06 double stage and two multiple stage preparations should be carried out. The preparation should be carried out on micro scale.

Learning Objective:

1. Student will learn to handle two stage reaction.
2. To enhance practical skill of students.
3. Student will be able to apply spectroscopic concepts for structure of given organic compound

Learning Outcome:

1. Student will learn application of chemoselectivity in organic synthesis.
2. Student will be able to perform halogenations reaction
3. Student will be able to synthesize hetrocyclic compound reactions'

A) Double stage preparation (any 06)

1) Benzaldehyde to benzalacetophenone to epoxide
2) Cyclohexanone to phenylhydrazone to 1,2,3,4-tetrahydrocarbazole
3) Phthalic anhydride to phthalimide to anthranilicacid
4) Acetanilide to 4-nitroacetanilide to 4-nitroaniline
5) Benzyl cyanide to 4-nitro benzyl cyanide to 4-nitro phenyl acetic acid
6) Nitrobenzene to m-dinitrobanzene to m-nitro aniline
7) Benzanilide from benzophenone by Beckmann rearrangement.
8) P-nitro actanilide to p-nitroaniline to p-iodonitrobenzene
9) Phthalimide to n-benzyl Phthalimide to benzylamine
10) Preparation of P-amino benzoic acid
11) acetophenone to 2- amino 4-phenyl thiazole to substituted Schiff base
12) Preaparation of N-Bromosuccinamide
13) Structure elucidation by using given spectral data.