THIRD SEMESTER

ORGANIC CHEMISTRY SPECIALISATION

Ch-301 OC: ORGANIC REACTION MECHANISMS

52 hours

UNIT-I

13h

Aliphatic nucleophilic and electrophilic substitution reactions

Nucleophilic substitution reactions:

Substitution at allylic carbon (allylic rearrangement), at a trigonal carbon (hydrolysis of esters and amides, use of DCC in the formation of anhydrides), substitution at a vinylic carbon. Neighboring group participation and S_Ni reactions.

Electrophilic substitution reactions:

SE2, SE1 and SEi mechanisms. Hydrogen exchange, migration of double bonds, α-halogenation of aldehydes, ketones and acids. Aliphatic diazonium coupling, nitrosation at carbon bearing active hydrogens, diazo transfer reaction, carbene and nitrene insertion, decarboxylation of aliphatic acids, haloform reaction, Haller-Bauer reaction.

UNIT-II

13h

Photochemistry

Physical and Chemical processes, Jablonski diagram. Photosensitization, quantum efficiency, quantum and chemical yields.

Photochemistry of functional groups:

i) *Olefins*: *Cis-trans* isomerism, [2 + 2]-cycloaddition, rearrangements. Reaction of conjugated olefins; di-π-methane rearrangements (including oxa- and aza- di-π-methane rearrangements).

ii) *Ketones*: Excited state of C=O. Norrish type-I and type-II cleavages. Paterno-Buchi reaction. α,β-unsaturated ketones. [2+2] addition. Rearrangement of cyclohexadienones (application in the synthesis of some important natural products).

iii) *Aromatic compounds*: Photorearrangement of benzene and its derivatives, cycloaddition of benzene.

iv) *Photochemical oxidations and reductions*: Cycloaddition of singlet molecular oxygen {[2+2], [4+2]-additions}. Oxidative coupling of aromatic compounds, photoreduction by hydrogen abstraction.

UNIT-III

13h

Pericyclic reactions

Molecular orbital symmetry, Woodward-Hoffmann correlation diagrams. FMO and PMO approaches. Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. *Electrocyclic reactions:* conrotatory and disrotatory motions, 4n, 4n+2 and allyl systems. *Cycloadditions:* antarafacial and suprafacial additions, $[_\pi m_s + {}_\pi n_a]$ and $[_\pi m_s + {}_\pi n_s]$-cycloadditions. $[_\omega 2_a + {}_\pi 2_s]$ and $[_\pi 4_s + {}_\omega 2_s]$-cheletropic reactions.

Regio, enantio- and endo- selectivities in Diels-Alder reactions. Hetero Diels-Alder reaction.

Sigmatropic rearrangements: suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties. [*i, j*]- sigmatropic rearrangements (including Walk, Claisen, Cope, oxy and aza-Cope rearrangements).

UNIT-IV **13h**

Free-radical chemistry

Generation of free-radicals: Thermal homolysis of peroxides, peresters and azo compounds, photochemical methods.

Free radical reactions: Free-radical mechanisms in general. Free-radical substitution mechanisms. Mechanisms at an aromatic substrate. Neighboring group assistance in free-radical reactions. Reactivity for aliphatic substrates, reactivity at a bridgehead, reactivity in aromatic substrates, reactivity in the attacking radical. Halogenation at an alkyl carbon and an allylic carbon, hydroxylation at an aliphatic carbon, hydroxylation at an aromatic carbon, oxidation of aldehydes to carboxylic acids, formation of hydroperoxides and peroxides, Gomberg-Bachmann reaction, Meerwein arylation, Sandmeyer reaction, Kolbe reaction and Hunsdiecker reaction.

Biochemical mechanisms

Introduction. The mechanistic role of the following in living systems.

i). Thiamine pyrophosphate (TPP) in decarboxylation of α-ketoacids and in the formation of α-ketols.

ii). Pyridoxal phosphate (PLP) in transamination, decarboxylation, dealdolisation and elimination reactions of amino acids.

iii). Lipoic acid in the transfer of acyl group reactions.

iv).Coenzyme A (CoASH) in the transfer of acyl group.

v). Biotin and Vitamin KH_2 coenzyme in carboxylation reactions.

vi).Tetrahydrofolic acid (H_4F) in one-carbon transfer reactions.

vii). Vitamin B_{12} coenzymes in molecular rearrangement reactions and in the synthesis of methionine and methane.

viii). Nicotinamide and Flavin coenzymes in biological redox reactions

SUGGESTED BOOKS

1. March's Advanced Organic Chemistry – Reactions, Mechanisms and Structure, M B Smith and J March, 8th Edition, John Wiley, 2019.
2. Modern molecular photochemistry of organic molecules, N J Turro, V Ramamurthy, J C Scaiano, Viva Books, New Delhi – 2017.
3. Textbook of pericyclic reactions – concept and application, K C Majumdar and P Biswas, Medtech, New Delhi – 2015
4. Organic Chemistry II edition, J Clayden, N Greeves and S Warren, Oxford Univ. Press, Oxford, 2012.
5. Frontier orbital and symmetry controlled pericyclic reactions, R K Kar, Books and Allied, Kolkata, 2010.
6. Advanced Organic Chemistry – Reactions, Mechanism and Structure, Jerry March, John Wiley, 2008.
7. Stereochemistry at a glance, J Eames and J M Peach, Blackwell, Oxford, 2003.
8. Advanced Organic Chemistry – Reaction Mechanisms, R. Bruckner, Harcourt/Academic Press, London, 2002.
9. Stereochemistry of Organic Compounds: Principles and Applications, D Nasipuri, New- Age

International, 1999.
10. Understanding organic reaction mechanisms, A. Jacob, Cambridge Univ. Press, 1997.
11. Radicals in organic synthesis, B. Giese, Pergamon Press, 1986.
12. Introduction to organic chemistry A. Streitweiser, Jr and C. H. Heathcock, Macmillan, 1985.
13. Stereoelectronic effects in organic chemistry, P. Deslongchamps, 1st Edn. Pergamon Press, 1983.
14. Frontier orbitals and organic chemical reactions, Oxford University Press primers, I Fleming, John Wiley, 1980.
15. Physical and mechanistic organic chemistry, R.A.Y. Jones, 1st Edn. Cambridge Univ. Press, 1979.
16. Mechanisms of molecular migrations, Vols I and II, B. S. Thiagarajan, 1st Edn. Pergamon Press, Oxford, 1979.
17. P. J. Garratt in Comprehensive organic chemistry, D. Barton and W. D. Ollis, 1st Edn. Pergamon Press, Oxford, 1979.
18. Organic photochemistry, J. M. Coxon and B. Halton, Cambridge Univ. Press, London, 1974.
19. Orbital symmetry, R. E. Lehr and A. P. Marchand, Academic Press, 1972.
20. Molecular reactions and photochemistry, C. H. Depuy and D. S. Chapman, 1st Edn. Prentice-hall India, New Delhi, 1972.
21. Molecular orbital theory for organic chemistry, A. Streitweiser, 1st Ed. Wiley & Sons, NY, 1969
22. Biochemistry, G. Zubey, Macmillan, NY, 1998.
23. Biochemistry, D. Voet and J. G. Voet, John Wiley & Sons, 2010.
24. Principles of Biochemistry, A. L. Lehninger, D. L. Nelson & M. M. Cox, Worth Publishers, NY, 2013.
25. Biochemistry illustrated, P N Campbell,m A D Smith, 3rd edition, Churchill Livingstone, Edinburgh, 1994.

Ch-302 OC: ORGANIC SYNTHESIS

52Hours

UNIT - I

13h

C-C and C-N bond forming reactions

Darzen's reaction, Use of acetylides in C-C bond formation reactions. Acid-catalyzed self condensation of olefins, Prins reaction, Shapiro reaction, Dieckmann cyclization, Robinson annulations, Hofmann-Loeffler-Freytag reaction. Hofmann-Martius reaction. Acyloin condensation. Houben-Hoesch reaction.

Stork-enamine synthesis. Meyer synthesis. Use of nucleophilic nitrogen and electrophilic carbon (NH_3, amines and nitrite as nucleophiles in substitution, NH_3 and amines in addition to ketones and aldehydes) and electrophilic nitrogen and nucleophilic carbon (nitration, nitrosation) for the bond formation reactions (including Chichibabin reaction, Skraup synthesis, Mitsunobu reaction, N-Nitroaromatic amine rearrangement, Fisher-Hepp reaction. Japp-Klingemann reaction).

UNIT-II

13h

Reagents in organic synthesis and functional group transformation

NBS, LDA, DCC, DDQ, Corey-Chaykovsky reagent, Raney-Nickel, diazomethane, TMS-chloride, 1,3-Dithiane (reactivity and umpolung) and PPA. Woodward and Prevost hydroxylation.

Oxidations

Cr (VI) oxidants, Mn (VII) oxidants, OsO_4, SeO_2, $Pb(OAc)_4$, HIO_4, Ag_2O, DMSO, Ozone, peroxides and peracids - as oxidizing agents. Oppenauer and Dess-Martin oxidation.

UNIT-III

Reductions **13h**

Complex metal hydrides, Birch, Clemmensen and diimide reduction. Catalytic hydrogenation (homogeneous and heterogeneous). Organoboranes as reducing agents. Wolf-Kishner and Meerwein-Pondorrf-Verley reduction. McMurry, Pummer, Willgerdot, Corey-Bakshi-Shibata and Tishchenko reactions.

UNIT-IV

13h

Asymmetric Synthesis

'*ee*' and methods of determination of '*ee*'.

Stereoselectivity: classification, terminology and principle. Asymmetric synthesis and asymmetric induction.

Double diastereoselection and double asymmetric induction.

Acyclic stereoselection: Addition of nucleophiles to carbonyl compounds (1,2- 1,3- and 1,4-asymmetric induction). Asymmetric aldol condensation. Addition of allylmetal and allylboranes to carbonyl group.

Diastereoselection in cyclic systems: Nucleophilic addition to cyclic ketones (formation of axial and equatorial alcohols, catalytic hydrogenation, alkylation, diastereoselective oxidations and stereoselective cyclization of poylenes).

Enantioselective synthesis: Reduction with chiral hydride donors [(S)-PBMgCl, (-)-$^{i}BOAlCl_2$, alpine-borane, (S)-BINAL-H, (R,R)-DIOP, and (S,S)-CHIRAPHOS).

Enantioselective alkylation of ketones *via* hydrazones. Enantioselective alkylation with chiral PTC. Enantioselective Michael addition. Enantioselective intramolecular aldol condensation. Use of (+)- and (–)- DET in asymmetric epoxidation. Polymer-bound chiral catalysts in asymmetric induction. Asymmetric amplification.

SUGGESTED BOOKS

1. March's Advanced Organic Chemistry – Reactions, Mechanisms and Structure, M B Smith and J March, 8th edition, John Wiley, 2019.
2. Essential reagents for organic synthesis, P L Fuchs, A B Charette, T Rovis, Wiley, NY, 2016.
3. Modern methods of organic synthesis, 4th edition, W. Carruthers and I Coldham, Cambridge Univ. Press, Cambridge, 2014.
4. Name reactions, 5th edition, J J Li, Springer, 2014.
5. Asymmetric synthesis II, more methods and applictions, M Christman, S. Brase, Wiley - VCH, 2013.
6. Organic chemistry Vol. II, I. L. Finar 6th edition Pearson, New Delhi - 2012.
7. Asymmetric synthesis: the essentials, 2nd edition, M Christman, S. Brase – Eds., Wiley - VCH, 2007.
8. Organic reaction mechanisms, 3rd Edn., V. K. Ahluwalia and R. K. Prashar, Narosa, New Delhi, 2005.
9. Name reactions and reagents in organic synthesis, 2nd edition, B P Mundy, M G Ellerd, F G Favalaro Jr. Wiley, NY – 2005.
10. M B Smith, Collective index for volumes 1-22 of Fiesers reagents for organic synthesis, Wiley-Interscience, NY, 2005.

11. Oxidation and reductions in organic synthesis, T J Donohoe, Oxford University Press primer, Oxford, 2000.
12. Understanding organic reaction mechanisms, A. Jacob, Cambridge Univ Press, 1997.
13. Introduction to organic chemistry, A. Streitweiser, Jr and C. H. Heathcock, Macmillan, 1985.
14. Comprehensive organic chemistry, D. Barton and W. D. Wallis, Pergamon Press, Oxford, 1983.
15. Physical and mechanistic organic chemistry, R. A.Y. Jones, 1st Edn. Cambridge University Press, 1979.
16. Modern synthetic reactions, H. O. House, W. A. Benjamin, California, 2nd edition. 1972.
17. Mechanisms of molecular migration, Vols I & II, B.S. Thyagarajan, Pergamon Press, Oxford, 1979.
18. Organic synthesis, R.E.Ireland, Prentice-hall India, New Delhi, 1975.
19. Oxidation and reduction of organic compounds, K L Rinehart Jr. Prentice – Hall, 1973.
20. Fiesers' reagents for organic synthesis, Volumes 1-22, 1967-2000

Ch-303 IC/OC/PC: ORGANIC SPECTROSCOPY
(Common to Inorganic/ Organic/ Physical chemistry)

52 Hours

UNIT-I

13h

Ultraviolet/ visible spectroscopy

Instrumentation. Classification of electronic transitions. Substituent and solvent effects.

UV spectral study of alkenes, polyenes, α,β-unsaturated carbonyl and aromatic compounds. Empirical rules for calculating λ_{max}.

Vibrational Spectroscopy: Infrared and Raman spectroscopy

Instrumentation. Sampling techniques, Group frequencies, factors affecting group frequencies, Bond order, Mass effect, Conjugation, Inductive, resonance, steric effects. Intramolecular interactions. Application of IR in the study of H-bonding, stereoisomerism and tautomerisam. Complementarity of IR and Raman. Identification of the following organic compounds by IR: alkanes, alkenes, alkynes, aromatic compounds, aldehydes, ketones, alcohols, acids, acid chlorides, amides, amines, esters, halides and nitro compounds etc. Problems using UV and IR.

UNIT-II

13h

Nuclear magnetic resonance spectroscopy-I

Introduction, Magnetic properties of nuclei- Resonance condition. Nuclear spin, population of nuclear spin levels and NMR isotopes, Relaxation methods. Instrumentation and sample handling, FT-NMR.

Chemical shift. Mechanism of shielding and deshielding in Alkanes, Alkyl halides, Alkenes, Aromatic compounds, Carbonyl compounds and Annulenes. Pascal's triangle-low and high resolution, spectrum of ethanol. Karplus Curve, Diamagnetic and paramagnetic effects and magnetic anisotropy. Equivalence of protons-chemical and magnetic equivalence. Spin-systems: First order and second order coupling of AB systems, Simplifications of complex spectras.

Problems.

Spin-spin interactions: AX,AX_2, AX_3, AMX,AB types. Vicinal, geminal and long range coupling-Spin decoupling. Chemical shift reagents and deuterium exchange. Stereochemistry and hindered rotations. Temperature effects.

UNIT-III

13h

Nuclear magnetic resonance spectroscopy-II

CIDNP, Nuclear Overhauser effect (NOE). Factors influencing coupling constants and Relative intensities. Protons attached to elements other than carbon.

^{13}C NMR Spectroscopy: Range and factors affecting chemical shifts of alkanes, alkyl halides, alkenes, alcohols, ethers, alkynes, carbonyl compounds and aromatics..

Multiple resonance spectroscopy: Introduction to 2D-techniques: DEPT, COSY, HETCOR, and INADEQUATE.

Explanation of the principle, applications to structure elucidation and stereochemistry of simple organic molecules.

Dynamic NMR.

NMR spectroscopy of other nuclei with spin I = ½. Introduction to ^{15}N, ^{19}F, ^{29}Si and ^{31}P NMR spectroscopies.

UNIT-IV

13h

Mass spectrometry and Composite Problems:

Basic principles-instrumentation – ion production-ion analysis-magnetic sector instruments Quadrapole mass spectrometers. Time of flight mass spectrometers-ion cyclotron resonance spectrometers- Mass spectrum-molecular ion-types of ions in mass spectra and effects of isotopes on mass spectra. Methods of ionization, EI, FAB MALDI and ESI methods. Fragmentation of of alkanes, alkenes, aromatics, alkyl halides, alcohols, aldehydes, ketones, acids, esters, ethers, amines, nitro and halo compounds peptides, Nitrogen rule, Factors affecting cleavage patterns. MeLafferty rearrangment. Determination of molecular formula. Problems.

Use of HRMS to determine exact molecular formulae of compounds.

Application of UV, IR, NMR and MS methods and chemical reactions in the structure elucidation of organic compounds – composite problems.

SUGGESTED BOOKS

1. Spectroscopic methods in organic chemistry, 7th edition, D Williams and I Fleming, Springer International Publishing, Berlin – 2019
2. Fundamentals of molecular spectroscopy5th edition, C N Banwell, E M McCash, H K Choudhury, Tata McGraw Hill, New Delhi - 2015
3. Spectrometric identification of organic compounds, R. M. Silverstien, F X Webster, D J Kiemle and D L Bryce, 8th Wiley student edition, New Delhi, 2015.
4. Organic spectroscopy, W. Kemp, Macmillan, London, 2011.
5. Introduction to spectroscopy, 4th edition, D. L. Pavia, G. M. Laupman and G. S. Kriz, Harcourt College Publishers, 2009.
6. Structure determination of organic compounds E Pretsch, P Buhlmann and M Badertscher, Springer-Verlag, Berlin – 2009.
7. Spectroscopic methods in organic chemistry, M Hesse, H Meier, B Zeeh, 2nd edition, Thieme, Stuttgart, 2008.

8. Organic Spectroscopy, LDS Yadav, Springer/Kluwer, 2005.
9. Organic Spectroscopic Analysis, R J Anderson, D J Bendell, P W Groundwater, RSC, Cambridge, 2004.
10. Mass spectrometry a foundation course, K Downard, RSC, Cambridge, 2004.
11. Structural analysis of organic compounds by combined application of spectroscopic studies, J T Clerc, E Pretsch, J Seibl, Elsevier, Amsterdam, 2001.
12. Biomolecular NMR Spectroscopy, J N S Evans, Oxford University, Oxford, 1995.
13. Modern NMR techniques and their Applications, Ed. A I Popov, Marcel Deckker, 1991.
14. Instrumental methods of analysis, H. H. Willard, L. L. Merritt, J. A. Dean and F.A. Settle, 7th edition, CBS Publishers and Distributors, 1989
15. Organic mass spectroscopy, K. R. Dass & E. P. James, IBH New Delhi, 1976.
16. The IR Spectra of complex molecules, Vols. I and II, L J Bellamy, Chapman and Hall, London, 1975.
17. Mass spectrometry of organic compounds, H. Budzkiewicz, Djerassi C. and D. H. Williams, Holden-Day New York, 1975.
18. Interpretation of organic mass spectra, F W McLafferty, W A Benjamin, London, 1973.
19. Organic spectroscopy, P. Laszlo and P. Stang, Harper & Row, New York, 1971.
20. Applications of absorption spectroscopy to organic compounds, J. R. Dyer, Prentice-Hall, New Delhi, 1969.
21. Interpretation of the UV spectra of natural products, A.I. Scott, Pergamon Press, Oxford, 1964.

Ch-304-[OPEN ELECTIVE, NON-CHEMISTRY PAPER]

OPEN ELECTIVE FOR NON-CHEMISTRY STUDENTS
Ch-304 OE: CHEMISTRY IN DAILY LIFE

52 Hours

UNIT-I **13h**

Dairy Products: Composition of milk and milk products. Analysis of fat content, minerals in milk and butter. Estimation of added water in milk.
Beverages: Analysis of caffeine in coffee and tea, detection of chicory in coffee, chloral hydrate in toddy, estimation of methyl alcohol in alcoholic beverages.
Food additives, adulterants and contaminants- Food preservatives like benzoates, propionates, sorbates, disulphites,
Artificial sweeteners: aspartame, saccharin, dulcin, sucralose and sodium cyclamate.
Flavours: Vanillin, alkyl esters (fruit flavours) and monosodium glutamate.
Artificial food colorants: Coal tar dyes and non-permitted colours and metallic salts. Analysis of pesticide residues in food.
Paints & Pigments: White pigments (white lead, ZnO, lithopone, TiO_2). Blue, red, yellow and green pigments. Paints and distempers: Requirement of a good paint. Emulsion, latex; luminescent paints. Fire retardant paints and enamels, lacquers. solvents and thinners for paints.
Dyes: Colour and constitution (electronic concept). Classification of dyes. Methods of applying dyes to the fabrics. A general study of azo dyes, Mordant brown, Congo red and methyl orange.

UNIT II **13h**

Air Pollution: Air pollutants, preventio and contraok, Green house gases and acid raid. Ozone hole and CFC's. Photochemical smog and PAN. Catalytic converters for mobile sources. Bhopal gas tragedy.
Hydrologic cycle, sources, criteria and standards of water quality – safe drinking water. Public health significance and measurement of water quality parameters- (Colour, turbidity, total solids, acidity, alkalinity, hardness, sulphate, flouride, phosphate, nitrite, nitrate, BOD and COD). Water purification for drinking and industrial purposes.
Toxic chemicals in the environment. Detergents- pollution aspects, eutrophication. Pesticides and insecticides-pollution aspects. Heavy metal pollution. Solid pollutants- treatment and disposal. Treatment of industrial liquid wastes. Sewage and industrial effluent treatment.
Composition of soil – inorganic and organic components in soil-micro and macronutrients.
Feritlisers: Classification of Fertilizers- Straight Fertilizers, Compound/Complex Fertilizers, Fertilizer Mixtures. Manufacture and general prosperities of Fertilizer products- Urea and DAP.

UNIT-III **13h**

Carbohydrates: Structure, function and Chemistry of some important monoand disaccharides.
Vitamins: Classification and Nomenclature. Sources, deficiency diseases and structures of Vitamin A, Vitamin B, Vitamin C, Vitamin D, Vitamin E & Vitamin K.
Drugs: Classification and nomenclature.
Structure and function of: *Analgesics* – aspirin, paracetamol;
Anthelmentic drug: mebendazole;
Antiallergic drug: Chloropheneramine maleate,
Antibiotics: Pencillin V, Chloromycetin, Streptomycin.
Anti-infalmmatory agent: Oxypheno-butazone,
Antimalarials: Primazuine phosphate & Chloroquine.
Oils and fats: Composition of edible oils, detection of purity, rancidity of fats and oil. Tests for adulterants like aregemone oil and mineral oils.
Soaps & Detergents: Structures and methods of use of soaps and detergents.

UNIT IV

13h

Chemical Thermodynamics: Concept of fugacity and free energy , Acitivity and activity coefficient, spontaneity of processes- entropy and free energy changes. Partial molar quantities, colligative properties, Le-Chatelier priniciple, phase equilibria. Enzyme catalysed reactions.
Principles of Reactivity: Basis kinetic concepts, rates of simple and complex chemical reactions, empirical rate equations. Temperature dependence of rates and activation parametrs. Branched chain reactions – explosion limits. Oscillatroy reactions.
Corrosion: Types and prevention, corrosion failure and analysis
Chemical energy system and limitations, principles and applictions of primatry & secondary batteries and fuel cell. Basics of solar energy, future energy storer.
Polymers : Types and classification of polymers. Source and general characteristics of natural and synthetic polymers. Typical examples of polymers used as plastics, in textiles, in electronic and automobile components, in the medical and aerospace materials. Problems of plastic waste management. Strategies for the development of environment friendly polymers.

SUGGESTED BOOKS

1. B. K. Sharma: introduction to Industiral Chemistry, Goel Publishing, Meerut (1998)
2. Medicinal Chemistry by Ashtoush Kar.
3. Drugs and Pharamaceutical Sciences Series, Marcel Dekker, Vol. II, INC, New York.
4. Analysis of Foods – H.E. Cox: 13. Chemical Analysis of Foods – H.E.Cox and pearson.
5. Foods: Facts and Principles. N. Shakuntala Many and S. Swamy, 4th ed. New Age International (1998)
6. Physical Chemistry – P I Atkins and J. de Paula – 7th Ed. 2002, Oxford University Press.
7. Handbook on Feritilizer Technology by Swaminathan and Goswamy, 6th ed. 2001, FAI.
8. Organic Chemistry by I. L. Finar, Vol. 1 & 2.
9. Polymer Science and Technology, J. R. Fired (Prentice Hall).

Ch-305, 306, 307 and 308 OC Practicals
Inorganic, Organic, Physical ~~and Analytical~~ Chemistry practicals (I Semester Syllabus) (4 days a week, 4 hours a day)