ANDHRA UNIVERSITY
SEMESTER – III SYLLABUS
M.SC., CHEMISTRY (Organic Chemistry Specialization)
(From the batch admitted during the academic year 2019-2020)

Paper I - Organic Reaction Mechanisms, Pericyclic Reactions and Photochemistry

UNIT-I

A) Radical substitution Mechanism: Reactivity for aliphatic substrates, reactivity at bridgehead, Reactivity in aromatic substrates, neighbouring group assistance in free radical reactions, reactivity in the attacking radical, effect of solvent on reactivity, halogenation at an alkyl carbon and allylic carbon, hydroxylation at aromatic carbon by means of Fenton's reagent, oxidation of aldehydes to carboxylic acids, formation of cyclic ethers with Pb(OAC)4, Reed reaction, sandmayer reaction, kolbe reaction and Hunsdiecker reaction.

B) Elimination reactions: - mechanisms of E2, El, and E1CB, reactivity-effects of substrate, attacking base, leaving group and medium, Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations - Saytzeff and Hoffman elimination and pyrolytic elimination.

UNIT-II

Addition Elimination Mechanisms:

(a) **Addition to carbon-carbon multiple bonds**- Addition reactions involving electrophiles, necleophiles and free radicals, cyclic mechanisms, Orientation and reactivity-stereochemical orientation. Hydrogenation of double and triple bonds, hydroboration, Birch reduction. Michael reaction, addition of oxygen and N_2O_4.

(b) **Addition to carbon-hetero atom multiple bonds**: Mechanism and reactivity, Mannich reaction, reductions of carbonyl compounds, carboxylic acids, esters, nitrites, addtion of Grignard reagents, Reformatsky reaction, Tollen's reaction, witting reaction, Prins reaction.

UNIT-III

Pericyclic reactions:

Molecular orbital symmetry, frontier orbitals of ethylene, 1,3 Butadiene, 1,3,5- Hexatriene, allyl system, classification of pericyclic reactions. Woodward- Hoffman correlation diagram method. FMO and perturbation of molecular (PMO) approach for the explanation of pericyclic reactions under thermal and photochemical conditions.

Electrocyclic Reactions: Conrotatory and disrotatory motions. 4n and 4n+2 π electrons systems.

Cycloadditions: Antarafacial and suprafacial additions, notation of cycloadditions, 2+2, 4+2 additions and chelotropic reactions.

Sigma tropic rearrgements-suprafacial and antarafacial shifts of H, Sigmatropic shift involving carbon moieties, (3.3) and (5.5) sigmatropic rearrangements. Claisen, Cope, Oxy-cope and aza-Cope rearrangements. Ene reaction

UNIT-IV

Organic Photochemistry:

Photochemistry of carbonyl compounds- n-$\pi^*$and π-π^* transitions. Norrish type I and Norrish type II cleavages, Patterno-Buchi reactions, Photoreduction, photochemistry of enones-Hydrogen abstraction, rearrangement of α,β-unsaturated ketones and cyclohexadienones, photochemistry of unsaturated systems (Olefins)-cis-trans isomerisation, dimerization and hydrogen abstractions and additions, acetylenes-dimerisation, Dienes - Photochemistry of 1,3 butadienes, di-π-methane rearrangement. Photochemistry of aromatic compounds - Excited state of benzene and its 1,2-, 1,3-, 1,4- additions. Photo-Fries rearrangement, Photo-Fries reactions of anilides, photosubstitution reactions of benzene derivatives.

Reference Books:

1) Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
3) Pericyclic reactions by S.N. Mukharji, Mcmilan.
4) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Rich gardson.
5) The modern structural theory in Organic Chemistry by L.N.Ferguson, Pretice Hall

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Paper II- Organic Spectroscopy

UNIT-I

UV SPECTROSCOPY: a) UV spectra of aromatic and heterocyclic compounds, α-diketones , β-diketones, enediones and quinines) Applications of UV Specroscopy-study of isomerism, determination of strength of hydrogen bonding and conformations of α-substituted cyclohexanones. Steric effect in biphenyls.

Infrared Spectroscopy: characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols, amines, carbonyl compounds, esters, amides, carboxylic acids, anhydrides, lactones, lactums, nitriles and conjugated carbonyl compounds. Effect of hydrogen bonding and solvent on vibrational frequencies.

UNIT-II

Nuclear Magnetic Resonance Spectroscopy (1H NMR): Nuclear spin, resonance, satuaration, shielding of magnetic nuclei, chemical shifts and its measurements, factors affecting chemical shift, chemical and magnetic equivalence of spins, spin-spin coupling, intergration, the coupling constant, types of spin-spin couplings, factors influencing coupling constants, first-order and non-first order spectra, spin system notations (ABX, AMX, ABC, A_2B_2 etc.). Simplification of non-first order spectra- use of higher magnetic fields, nuclear magnetic double resonance and contact shift reagents. Deuterium exchange, nuclear overhauser effect difference spectra, Study of dynamic processes by Variable temperature (VT) NMR, restricted rotation DMF, cyclohexane ring inversion.

UNIT-III

Mass spectroscopy: Basic Principles, instrumentation, isotope abundance, the molecular ion, metastable ions, base peak, fragment ions, even-electron rule and nitrogen rule. McLafferty rearrangement, ortho effect. *retro*-Diels- Alder reaction, Fragmentation processes-fragmentation associated with various functional groups (alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, phenols, ethers, aldehydes , ketones, esters , carboxylic acids, amides, amines, alkyl chlorides and alkyl bromides.

UNIT-IV

Structural elucidation of Organic compounds by a combined application of the UV, IR, NMR and MASS spectral data.

Reference books:

1. Spectroscopic identification of organic compounds by RM Silverstein, G C Bassler and T B Morrill
2. Organic Spectroscopy by William Kemp
3. Spectroscopic methods in Organic chemistry by DH Williams and I Fleming
4. Modern NMR techniques for chemistry research by Andrew B Derome
5. NMR in chemistry - A multinuclear introduction by William Kemp
6. Spectroscopic identification of organic compounds by P S Kalsi
7. Introduction to organic spectroscopy by Pavia
8. Carbon-13 NMR for organic chemists by GC Levy and O L Nelson
9. Nuclear Magnetic Resonance Basic principles by Atta-ur-Rahman

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Paper III – Organic Synthesis

UNIT-I

Formation of Carbon-Carbon (C-C) single bonds:
A) Alkylations via enolate anions-1,3-dicarbonyl and related compounds, direct alkylation of simple enolates, imine and hydrozone anions, enamines. The aldol reaction, umplong (dipole inversion).

B) Via organometallic reagents- organ palladium, organo nickel and organo copper reagents

UNIT-II

Formation of carbon-carbon double bonds:
β- Elimination reactions, Pyrolytic *syn* eliminations, alkenes form hydrazones, 1,2-diols, sulfones, sulphoxide-sulphonate rearrangement, the Wittig and related reactions

UNIT-III:

Organic polymers & Reactions of unactivated carbon-hydrogen bonds

A) Introduction to organic polymers, general properties and classification of polymers. Methods of polymerization: (a) Addition polymerization-Definition, synthesis and applications, vulcanization. (b) Condensation polymerization- Definition, synthesis and applications. Radical polymerization- Definition, synthesis and applications. Ziegler-Natta polymerization
(With atleast two examples in each category)

B) Unactivated carbon-hydrogen bonds: Definition, mechanism and synthetic applications- The Hoffmann-Loeffler- Freytag reaction-the Barton reaction-Photolysis of organic hypohalites.

UNIT-IV:

Asymmetric Synthesis

Topocity – Prochirality – Substrate selectivity – Diastereoselectivity and enantioselectivity – Substrate controlled methods – use of chiral substrates – examples

Auxiliary controlled methods – Use of chiral auxiliaries – Chiral enolates – alkylation of chiral imines – Stereoselective Diels – Alder reaction

Reagent controlled methods – Use of chiral reagents – Asymmetric oxidation – Sharpless epoxidation – Asymmetric reduction – Use of lithium aluminium hydride and borate reagents.

Textbooks:

1. Some Modem Methods of Organic Synthesis W. Carothers, Third Edition, Cambridge University Press, Cambridge, 1988.
2. Modern Synthetic Reactions, Herbert O. House, Second Edition, W.A. BenzamineInc. Menio Park, California, 1972.
3. Principle of Organic Synthesis- R.O.C. Norman and J. M. Coxon.(ELBS)
4. Advanced organic chemistry part A & B; Fourth edition; Francis A Cary and Richard J. Sundberg; Kluwer Academic/Plenum Publisher New York, 2000.
5. Organic chemistry Jonathan Clayden, Nick Geeves, Stuart Warren, 2nd Edition, 2012, Oxford University Press
6. Stereochemistry of organic compounds — Principles & Applications by D Nasipuri
7. Stereochemistry of Carbon compounds by Ernest L Eliel & Samuel H. wilen
8. Stereochemistry: Conformation & Mechanism by P S Kalsi
9. The third dimension in organic chemistry, by Alan Bassendale
10. Stereo selectivity in organic synthesis by R S Ward.
11. Asymmetric synthesis by Nogradi
12. Asymmetric organic reactions by J D Morrison and H S Moschcr
13. Principles in Asymmetric synthesis by Robert E. Gawley & JEFFREY AUBE

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Paper IV – Chemistry of Natural Products

UNIT-I

Isolation, structure elucidation, stereochemistry, synthesis and biological properties of Pencillin G. Cephalosphorin-C, streptomycin, chloramphenicol and tetracyclins

UNIT-II

Isolation, structure elucidation, stereochemistry, synthesis and biological properties of Terpenes: Forskolin, taxol and β-amyrin

UNIT-III

Isolation, structure elucidation, stereochemistry, synthesis, and biological properties of Alkaloids: Morphine, reserpine and vincristine

UNIT-IV

Natural Pigments: Flavones-Apigenin, flavanones-Hesperetin, Isoflavones-Genistein, Flavonol-qurcetin, xanthone-Euxanthone, quinones-Polyporic acid, chlorophyll and haemin.

Reference Material:

1) Organic Chemistry, Volume 2, Stereochemistry and chemistry of natural products, I.L. Finar, 5th Edition. ELBS.
2) 2) Chemical A spects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996
3) Chemistiy of Natural Products. A Unified Approach, N.R. Krishnaswamy, Universe.y Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999.
4) Chemistry of natural products, S. V. Bhat, Narosa Publishing House, 6th reprint 2010