

T.Y.B.Sc, CHEMISTRY (Six Units)

SEMESTER V

ORGANIC CHEMISTRY

COURSE CODE: USCH503

CREDITS: 02

LECTURES: 60

Unit I

1.1 Mechanism of organic reactions (10 L)

- 1.1.1 The basic terms & concepts: bond fission, reaction intermediates, electrophiles & nucleophiles, ligand, base, electrophilicity vs. acidity & nucleophilicity vs basicity.
- 1.1.2 Neighbouring group participation in nucleophilic substitution reactions: participation of lone pair of electrons, kinetics and stereochemical outcome.
- 1.1.3 Acyl nucleophilic substitution (Tetrahedral mechanism): Acid catalyzed esterification of carboxylic acids ($A_{AC}2$) and base promoted hydrolysis of esters ($B_{AC}2$).
- 1.1.4 Pericyclic reactions, classification and nomenclature
 - 1.1.4.1 Electro cyclic reactions (ring opening and ring closing), cycloaddition, sigma tropic Rearrangement, group transfer reactions, cheletropic reaction (definition and one example of each type)
 - 1.1.4.2 Pyrolytic elimination: Cope, Chugaev, pyrolysis of acetates

References:

1. A guidebook to mechanism in Organic Chemistry, 6th edition, Peter Sykes, Pearson education, New Delhi
2. Organic Reaction Mechanism, 4th edition, V. K. Ahluwalia, R. K. Parashar, Narosa Publication.
3. Organic reactions & their mechanisms, 3rd revised edition, P.S. Kalsi, New Age International Publishers.
4. M.B.Smith and J. March, Advanced organic chemistry- reactions mechanism and structure, 5th edition.

1.2 Photochemistry (5 L)

- 1.2.1 Introduction: Difference between thermal and photochemical reactions. Jablonski diagram, singlet and triplet states, allowed and forbidden transitions, fate of excited molecules, photosensitization.
- 1.2.2 Photochemical reactions of olefins: photoisomerization, photochemical rearrangement of 1,4-dienes (di- π methane)
- 1.2.3 Photochemistry of carbonyl compounds: Norrish I, Norrish II cleavages. Photo reduction (e.g. benzophenone to benzpinacol)

References:

1. Organic Chemistry, 7th Edition, R.T. Morrison, R. N. Boyd & S. K. Bhattacharjee, Pearson.
2. Organic chemistry, 8th edition, John Mc Murry

Unit II

2.1 Stereochemistry I (5 L)

- 2.1.1 Molecular chirality and elements of symmetry: Mirror plane symmetry, inversion center, rotation -reflection (alternating) axis.

2.1.2 Chirality of compounds without a stereogenic center: cummulenes and biphenyls.

References:

1. L. Eliel, stereochemistry of carbon compounds, Tata McGraw Hill
2. Stereochemistry P.S.Kalsi, New Age International Ltd., 4th Edition
3. Stereochemistry by Nassipuri.

2.2 Agrochemicals (4 L)

- 2.2.1 General introduction & scope, meaning & examples of insecticides, herbicides, fungicide, rodenticide, pesticides, plant growth regulators.
- 2.2.2 Advantages & disadvantages of agrochemicals
- 2.2.3 Synthesis & application of IAA (Indole Acetic Acid) & Endosulphan,
- 2.2.4 Bio pesticides – Neem oil & Karanj oil.

References:

1. Insecticides & pesticides: Saxena A. B., Anmol publication.
2. Growth regulators in Agriculture & Horticulture: Amarjit Basra, CRC press 2000.
3. Agrochemicals and pesticides: A.Jadhav and T.V.Sathe.

2.3 Heterocyclic chemistry: (6 L)

- 2.3.1 Reactivity of pyridine-N-oxide, quinoline and iso-quinoline.
- 2.3.2 Preparation of pyridine-N-oxide, quinoline (Skraup synthesis) and iso-quinoline (Bischler-Napieralski synthesis).
- 2.3.3 Reactions of pyridine-N-oxide: halogenation, nitration and reaction with $\text{NaNH}_2/\text{liq.NH}_3$, $n\text{-BuLi}$.
- 2.3.4 Reactions of quinoline and isoquinoline; oxidation, reduction, nitration, halogenation and reaction with $\text{NaNH}_2/\text{liq.NH}_3, n\text{-BuLi}$.

References

1. Name Reactions in Heterocyclic Chemistry, Jie-Jack Li, Wiley-Interscience publications, 2005.
2. Handbook of Heterocyclic Chemistry, 2nd Edition, Alan R. Katritzky and Alexander F. Pozharskii, Elsevier Science Ltd, 2000.
3. Heterocyclic Chemistry, 5th Edition, John A. Joule and Keith Mills, Wiley publication, 2010.
4. Heterocyclic chemistry, 3rd Edition, Thomas L. Gilchrist, Pearson Education, 2007.

Unit III

3.1 IUPAC (5 L)

IUPAC Systematic nomenclature of the following classes of compounds (including compounds upto two substituents / functional groups):

- 3.1.1 Bicyclic compounds – spiro, fused and bridged (upto 11 carbon atoms) – saturated and unsaturated compounds.
- 3.1.2 Biphenyls
- 3.1.3 Cummulenes with upto 3 double bonds
- 3.1.4 Quinolines and isoquinolines

References

1. Nomenclature of Organic Chemistry: IUPAC recommendations and preferred Names 2013, RSC publication.
2. IUPAC nomenclature by S.C.Pal.

3.2 Synthesis of organic compounds (10L)

3.2.1 Introduction: Linear and convergent synthesis, criteria for an ideal synthesis, concept of chemo selectivity and regioselectivity with examples, calculation of yields.

3.2.2 Multicomponent Synthesis: Mannich reaction and Biginelli reaction. Synthesis with examples (no mechanism)

3.2.3 Green chemistry and synthesis:

Introduction: Twelve principles of green chemistry, concept of atom economy and E-factor, calculations and their significance, numerical examples.

- i) Green reagents: dimethyl carbonate.
- ii) Green starting materials : D-glucose
- iii) Green solvents : supercritical CO₂
- iv) Green catalysts: Bio catalysts.

3.2.4 Planning of organic synthesis

- i) synthesis of nitroanilines. (*o&p*)
- ii) synthesis of halobenzoic acid.(*o&p*)
- iii) Alcohols (primary / secondary / tertiary) using Grignard reagents.
- iv) Alkanes (using organo lithium compounds)

Reference:

1. Green chemistry an introductory text : Mike Lancaster.
2. Green chemistry: V. K. Ahluwalia (Narosa publishing house pvt. ltd.)
3. Green chemistry an introductory text : RSC publishing.
4. New trends in green chemistry V. K. Ahluwalia , M. Kidwai, Klumer Academic publisher
5. Green chemistry by V. Kumar.
6. Organic chemistry: Francis Carey
7. Organic chemistry: Carey and Sundberg.

Unit IV

4.1 Spectroscopy I (5 L)

4.1.1 Introduction: Electromagnetic spectrum, units of wavelength and frequency

4.1.2 UV – Visible spectroscopy: Basic theory, solvents, nature of UV-Visible spectrum, concept of chromophore, auxochrome, bathochromic and hypsochromic shifts, hyperchromic and hypochromic effects, chromophore-chromophore and chromophore-auxochrome interactions.

4.1.3 Mass spectrometry: Basic theory. Nature of mass spectrum. General rules of fragmentation. Importance of molecular ion peak, isotopic peaks, base peak, nitrogen rule, rule of 13 for determination of empirical formula and molecular formula. Fragmentation of alkanes and aliphatic carbonyl compounds.

References:

1. Organic spectroscopy (Second edition), Jag Mohan ,Narosa publication
2. Spectroscopy, Pavia, Lampman, Kriz, Vyvyan.

3. Elementary organic spectroscopy (Third edition), Y.R.Sharma, S.Chand publication..
4. Introduction to spectroscopy (third edition), Pavia ,Lampman,Kriz,John vonDeling,Emily Barrosse.
5. Organic chemistry Paula Y. Bruice, Pearson education.
6. Spectral identification of organic molecules by Silverstein.
7. Absorption spectroscopy of organic molecules by V.M.Parikh.

4.2 Natural Products: (10L)

4.2.1. Terpenoids: Introduction, Isoprene rule, special isoprene rule and the gem-dialkyl rule.

4.2.2 Citral:

- a) Structural determination of citral.
- b) Synthesis of citral from methyl heptenone
- c) Isomerism in citral. (cis and trans form).

4.2.3. Alkaloids Introduction and occurrence.

Hofmann's exhaustive methylation and degradation in: simple open chain and N – substituted monocyclic amines.

4.2.4 Nicotine:

- a) Structural determination of nicotine. (Pinner's work included)
- b) Synthesis of nicotine from nicotinic acid
- c) Harmful effects of nicotine.

4.2.5 Hormones:

Introduction, structure of adrenaline (epinephrine), physiological action of adrenaline.

Synthesis of adrenaline from

- a) Catechol
- b) p-hydroxybenzaldehyde(Ott's synthesis)

References:

1. Chemistry of natural products by Chatwal Anand – Vol I and Vol II
2. Chemistry of natural products by O.P. Agarwal
3. Chemistry of natural products by Meenakshi Sivakumar and Sujata Bhat.
4. Organic chemistry by Morrison and Boyd, 7th edition.
5. I.L.Finar, Vol-I and Vol-II, 5th edition.

PRACTICALS

SEMESTER V

ORGANIC CHEMISTRY

COURSE CODE: USCHP09

CREDITS: 02

A) SEMESTER V: Separation of Binary solid-solid mixture (2.0 gms mixture to be given).

1. Minimum Six mixtures to be completed by the students.
2. Components of the mixture should include water soluble and water insoluble acids (carboxylic acid), water insoluble phenols(2-naphthol, 1-naphthol), water insoluble bases

(nitroanilines) , water soluble neutral (thiourea) and water insoluble neutral compounds (anilides , amides, m-DNB, hydrocarbons)

After correct determination of chemical type, the separating reagent should be decided by the student for separation.

4. Follow separation scheme with the bulk sample of binary mixture.

5. After separation into component A and component B, one component (decided by the examiner) is to be analyzed and identified with m.p..

References:

1. Practical organic chemistry – A. I. Vogel
2. Practical organic chemistry – H.Middleton.
3. Practical organic chemistry – O.P.Aggarwal.

SEMESTER VI

ORGANIC CHEMISTRY

COURSE CODE: USCH603

CREDITS: 02

LECTURES: 60

Unit I

1.1 Stereochemistry II

(10 L)

1.1.1 Stereoselectivity and stereospecificity: Idea of enantioselectivity (ee) and diastereoselectivity (de) , Topicity : enantiotopic and diasterotopic atoms, groups and faces.

1.1.2 Stereochemistry of –

- i) Substitution reactions : S_{Ni} (reaction of alcohol with thionyl chloride)
- ii) Elimination reactions: E_2 -Base induced dehydrohalogenation of 1-bromo-1,2-diphenylpropane.
- iii) Addition reactions to olefins:
 - a) bromination (electrophilic anti addition)
 - b) syn hydroxylation with O_3 and $KMnO_4$
 - c) epoxidation followed by hydrolysis.

References:

Refer Stereochemistry –I (Sem-V, Unit-II)

1.2 Amino acids & Proteins

(5 L)

1.2.1 α -Amino acids: General Structure, configuration, and classification based on structure and nutrition. Properties: pH dependency of ionic structure, isoelectric point and zwitter ion. Methods of preparations: Strecker synthesis, Gabriel phthalamide synthesis.

1.2.2 Polypeptides and Proteins: nature of peptide bond. Nomenclature and representation of polypeptides (di- and tri-peptides) with examples Merrifield solid phase polypeptide synthesis. .Protiens:general idea of primary,secondary,tertiary & quaternary structure

References:

1. Biochemistry, 8th Ed., Jeremy Berg, Lubert Stryer, John L. Tymoczko, Gregory J. Gatto Pub. W. H. Freeman Publishers
2. Lehninger Principles of Biochemistry 7th Ed., David Nelson and Michael Cox, Publisher W. H. Freeman
3. Name Reactions – Jie Jack Li, 4th Edition, Springer Pub.

Unit II

2.1 Molecular Rearrangements (5 L)

Mechanism of the following rearrangements with examples and stereochemistry wherever applicable.

- 2.1.1 Migration to the electron deficient carbon: Pinacol-pinacolone rearrangement.
- 2.1.2 Migration to the electron deficient nitrogen: Beckmann rearrangement.
- 2.1.3 Migration involving a carbanion : Favorski rearrangement.
- 2.1.4 Name reactions: Michael addition, Wittig reaction.

References:

Refer Mechanism of organic reaction (Sem-V, Unit-I)

2.2 Carbohydrates (10 L)

- 2.2.1 Introduction: classification, reducing and non-reducing sugars, DL notation
- 2.2.2 Structures of monosaccharides: Fischer projection (4-6 carbon monosaccharides) and Haworth formula (furanose and pyranose forms of pentoses and hexoses)
Interconversion: open chain and Haworth forms of monosaccharides with 5 and 6 carbons.
Chair conformation with stereochemistry of D-glucose, Stability of chair form of D-glucose
- 2.2.3 Stereoisomers of D-glucose: enantiomer, diastereomers, anomers, epimers.
- 2.2.4 Mutarotation in D-glucose with mechanism
- 2.2.5 Chain lengthening & shortening reactions: Modified Kiliani-Fischer synthesis (D-arabinose to D-glucose and D-mannose), Wohl method (D-glucose to D-arabinose)
- 2.2.6 Reactions of D-glucose and D-fructose:
(a) Osazone formation (b) reduction: H_2/Ni , NaBH_4 (c) oxidation: bromine water, HNO_3 , HIO_4
(d) acetylation (e) methylation: (d) and (e) with cyclic pyranose forms
- 2.2.7 Glycosides: general structure

References:

1. Organic chemistry (fourth edition), G. Marc Loudon, Oxford University press.
2. Introduction to Organic Chemistry (Third edition), Andrew Streitwieser, Jr. Clayton H. Heathcock, Macmillan publishing.
3. Organic chemistry fourth edition, Morrison and Boyd.
4. Introduction to Organic chemistry, John McMurry.
5. Organic chemistry volume-1&2 (fifth and sixth edition) I.L. Finar.

Unit III

3.1 Spectroscopy II (10 L)

- 3.1.1 IR Spectroscopy: Basic theory, nature of IR spectrum, selection rule, fingerprint region.
- 3.1.2 PMR Spectroscopy: Basic theory of PMR, nature of PMR spectrum, chemical shift (δ unit), standard for PMR, solvents used. Factors affecting chemical shift: (1) inductive effect (2) anisotropic effect (with reference to $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$ and benzene ring). Spin-spin coupling and

coupling constant. application of deuterium exchange technique. application of PMR in structure determination.

3.1.3 Spectral characteristics of following classes of organic compounds, including benzene and monosubstituted benzenes, with respect to IR and PMR: (1) alkanes (2) alkenes (3) alkynes (4) haloalkanes (5) alcohols (6) carbonyl compounds (7) ethers (8) amines (broad regions characteristic of different groups are expected).

Problems of structure elucidation of simple organic compounds using individual or combined use of UV-Vis, IR, Mass and NMR spectroscopic technique are expected. (Index of hydrogen deficiency should be the first step in solving the problems).

References:

Refer spectroscopy –I, (Sem-V, Unit-IV)

3.2 Nucleic Acids (5 L)

Controlled hydrolysis of nucleic acids. sugars and bases in nucleic acids. Structures of nucleosides and nucleotides in DNA and RNA. Structures of nucleic acids (DNA and RNA) including base pairing.

References:

1. Organic chemistry R.T.Morrison and R.N.Boyd, 6th edition, pearson education
2. S.H.Pine, organic chemistry 4th edition. McGraw Hill

Unit IV

4.1 Polymer (8 L)

- 4.1.1 Introduction: terms monomer, polymer, homopolymer, copolymer, thermo plastics and thermosets.
- 4.1.2 Addition polymers: polyethylene, polypropylene, teflon, polystyrene, PVC, Uses.
- 4.1.3 Condensation polymers: polyesters, polyamides, polyurethanes, polycarbonates, phenol formaldehyde resins.Uses
- 4.1.4 Stereochemistry of polymers: Tacticity, mechanism of stereochemical control of polymerization using Ziegler Natta catalysts.
- 4.1.5 Natural and synthetic rubbers: Polymerisation of isoprene: 1,2 and 1,4 addition (cis and trans), Styrene butadiene copolymer.
- 4.1.6 Additives to polymers: Plasticisers, stabilizers and fillers.
- 4.1.7 Biodegradable polymers: Classification and uses. polylactic acid structure, properties and use for packaging and medical purposes.

(Note : Identification of monomer in a given polymer & structure of polymer for a given monomer is expected. condition for polymerization is not expected)

References:

1. Polymer chemistry by M.G.Arora, K.Singh.
2. Polymer science – a text book by Ahluwalia and Mishra
3. Introduction to polymer chemistry - R.Seymour, Wiley Interscience.

4.2 Catalysts and Reagents (7 L)

Study of the following catalysts and reagents with respect to functional group transformations and selectivity (no mechanism).

4.2.1 Catalysts: Catalysts for hydrogenation:

- a. Raney Nickel

- b. Pt and PtO₂ (C=C, CN, NO₂, aromatic ring)
- c. Pd/C : C=C, COCl→CHO (Rosenmund)
- d. Lindlar catalyst: alkynes

d.2.2 Reagents:

- a. LiAlH₄ (reduction of CO, COOR, CN,NO₂)
- b. NaBH₄ (reduction of CO)
- c. SeO₂ (Oxidation of CH₂ alpha to CO)
- d. mCPBA (epoxidation of C=C)
- e. NBS (allylic and benzylic bromination)

References:

1. Organic chemistry by Francis Carey – McGrawHill .
2. Organic chemistry by Carey and Sundberg, Part A & B

PRACTICALS

SEMESTER VI

ORGANIC CHEMISTRY

COURSE CODE: USCHP10

CREDITS: 02

A) SEMESTER VI: Separation of Binary liquid-liquid and liquid- solid mixture.

1. Minimum Six mixtures to be completed by the students.
2. Components of the liq-liq mixture should include volatile liquids like acetone, methylacetate, ethylacetate, isopropylalcohol, ethyl alcohol, EMK and non volatile liquids like chlorobenzene , bromobenzene, aniline, N,N dimethylaniline, acetophenone, nitrobenzene, ethyl benzoate.
3. Components of the liq- solid mixture should include volatile liquids like acetone, methylacetate, ethylacetate, ethyl alcohol, IPA, EMK and solids such as water insoluble acids, phenols, bases, neutral.
4. A sample of the mixture one ml to be given to the student for detection of the physical type of the mixture.
5. After correct determination of physical type, separation of the binary mixture to be carried out by distillation method using microscale technique.
6. After separation into component A and component B, the compound to be identified can be decided by examiner.

References:

4. Practical organic chemistry – A. I. Vogel
5. Practical organic chemistry – H.Middleton.
6. Practical organic chemistry – O.P.Aggarwal.
