

**PG -SEMESTER I  
SEMESTER-III  
ORGANIC CHEMISTRY – III**

**(90 Hrs) 4 Credits**

**Core Paper – 9**

This course mainly focuses on the structural determination of organic molecules using UV, IR, NMR Spectroscopy and Mass spectrometry as tools. In addition, aromaticity, organic photochemistry, pericyclic reaction, the synthesis of Anthocyanins, Flavones, Isoflavanones, Carotenoids and Steroids will be discussed in detail.

**UNIT 1: –Physical Methods for the Structural Determination of Organic compounds :  
UV-IR and MASS Spectrometry, ORD, CD, Axial Haloketone Rule and Octant Rule  
(20 HOURS)**

- 1.1** Organic structure determination. Principles, applications of UV- Visible spectroscopy - Woodward Fischer Rule-(Derivation of Beer- lambart's law is not required) - IR spectroscopy-quantitative applications and organic structure determination.
- 1.2** Mass spectrometry-Instrumentation- nitrogen rule- odd and even electron rule- fundamentals- molecular ion peak, base peak, isotopic peak and meta stable ions- Mass fragmentation of functional groups- aliphatic alkanes and hydrocarbons, alcohol, phenol, carbonyl compounds- carboxylic acid, esters - McLafferty rearrangement- amines, nitro compounds - Retro Diel's Alder reaction in Mass Spectrometry- Hydrogen transfer reaction- Tandem Mass Spectrometry – GC-MS - Analysis of Biomolecules.
- 1.3** Optical rotatory dispersion and Cotton effect – applications-plain curves -specific rotation Vs wavelength, Molecular rotation Vs Wavelength-Non plain curves- applications-Location of methyl group at C<sub>2</sub> or C<sub>4</sub> in 3-cholestanone,ring size ,

conformational changes in menthone and degree of ketal formation.  
Application of ORD and CD to stereochemistry of cyclohexanone.

- 1.4** Axial haloketo rule and octant rule. Problem solving approach.  
(Applicable to 3-methylcyclohexanones and cis and trans-10-methyl-2-decalone).

**UNIT 2: NMR Spectroscopy (<sup>1</sup>H AND <sup>13</sup>C): (18 HOURS)**

- 2.1.** <sup>1</sup>H Nuclear Magnetic resonance spectroscopy - Chemical shift, spin-spin coupling - geminal, vicinal, long-range-1J, 2J, 3J, 4J and 5J coupling in NMR, Spin systems: Two interacting nuclei: A<sub>2</sub>, AB, AX, AA'BB', dd, pair of doublet, AB quartet, and higher- Pople nomenclature- coupling constants, NMR and symmetry, second order effects in coupled systems, virtual coupling and shift reagents. Factors affecting coupling constant: cis, trans, gem, ortho, meta, para coupling – exchange with deuterium.
- 2.2** Applications to organic structure determination. FT-NMR, NOE studies, 2D NMR (COSY, HETCOR) and stereochemistry - Differentiating enantiomers and diastereomers
- 2.3.** <sup>13</sup>C NMR spectroscopy– Sensitivity, natural abundance, sample requirement, PFT, proton noise or broadband decoupling, Decoupling technique: SFORD and Off Resonance decoupled spectrum identification of various types of carbon using <sup>13</sup>C NMR. Quaternary carbons, chemical shifts, spin-spin coupling. Homo nuclear and heteronuclear coupling.
- 2.4.** Applications and examples, conjoint problems (solving the structure of a compound using UV, IR, NMR spectroscopy and MASS spectrometry)

### UNIT 3: AROMATICITY AND ORGANIC PHOTOCHEMISTRY (16 HOURS)

- 3.1.** Aromaticity of benzenoid, heterocyclic and non-benzenoid compounds- Huckel's rule- Aromatic systems with pi electron numbers other than six, non-aromatic and anti-aromatic systems -systems with more than 10 pi electrons – Annulenes up to C<sub>18</sub>, fulvenes, fulvalenes and azulenes – craig's rule (preparation, physical and chemical properties of all these compounds is not expected).
- 3.2.** Photochemistry of ketones, Norrish Type I and II, photo reduction, photo addition of alpha, beta unsaturated ketones, photo cycloaddition, photo oxidation, Paterno - Buchi reaction, Di-pi methane rearrangement (bicyclic systems not required) - Barton reaction, photo- Fries reaction.

### UNIT 4: Pericyclic reactions: (18 HOURS)

- 4.1.** Pericyclic reaction – classification (Electrocyclic, Cycloaddition, Sigmatropic, cheletropic reactions - one example each) - Orbital symmetry-Woodward Hoffman rules.
- 4.2.** Electrocyclic reactions -FMO and correlation diagram –Interconversion of butadiene – cyclobutene- hexatriene to cyclohexadiene.
- 4.3.** Cycloaddition FMO and correlation diagram  $-(\pi^{2s} + \pi^{2s}), (\pi^{4s} + \pi^{2s})$  –Diels alder reaction
- 4.4** Sigmatropic reactions- FMO method only – (1,3), (1,5), (1,7) and (3,3) sigmatropic rearrangements – oxy cope, aza cope and Claisen rearrangements. Structure of bulvalene - fluxional molecule.

**UNIT 5 Anthocyanins, Flavones, Isoflavanones, Carotenoids and Steroids:  
(18 HOURS)**

**5.1 Anthocyanins-Robinson synthesis of Cyanin (Properties and reactions not required).**

Flavones – general method of synthesis - Reaction with KOH- Quercetin- Robinson Method - Baker Venkatraman and Robinson syntheses. Isoflavones- Reaction with KOH -daidzein only-Spath and Baker Ollis synthesis- Carotenoids –Weedon et al synthesis of Lycopene.

**5.2 Elucidation of structure of cholesterol (by chemical degradation). Conversion of cholesterol to progesterone, estrone and testosterone.**

**TEXT BOOKS**

1. R.M. Silverstein, G.C. Bassler and Morrill, 1991, Spectrometric identification of Organic Compounds, 5<sup>th</sup> Edition, John Wiley and Sons, New York.
2. I.L. Finar, 1986, Organic Chemistry – Vol.II, 5<sup>th</sup> edition, ELBS Publication.
3. P.S. Kalsi, 2002, Spectroscopy of Organic Compounds, Wiley Eastern Ltd, Chennai.
4. H. Depuy and Orville, Molecular reaction and Photochemistry Charles, L.Chapman, Prentice Hall of India Pvt. Ltd., New Delhi
5. L.A.Pacquette, 1978, Principles of Modern Heterocyclic Chemistry, Benjamin Cummings Publishing Co., London.
6. J. March, 1992, Advanced Organic Chemistry, 7<sup>th</sup> Edition, Singapore
7. F.A. Carey and R.J. Sundberg, 1990, Advanced Organic Chemistry, 4<sup>th</sup> Edition, Plenum Press, New York.
8. Neil S. Issacs, 1987, Physical Organic Chemistry, ELBS Publication.
9. P.S. Kalsi, 1999, Textbook of Organic Chemistry, Mcmillan India Ltd.

## REFERENCES

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- 2 L.D.Field, S.Sternhell and J.R.Kalman, 2013, Organic structures from spectra, Wiley.
- 3 F.C.Nachod(ed), 2012, Determination of Organic structures by physical methods Vol.3, Elsevier science.
- 4 R.M. Silverstein, F.X.Webster, D.J.Kiemle and D.L.Bryce 2014, Spectrometric identification of Organic Compounds, John Wiley and Sons.
- 5 D.L.Pavia, G.M.Lampman, G.S.Kriz and J.A.Vyvyan 2014, Introduction to Spectroscopy, Cengage learning.
- 6 L.D.SYadav, 2013, Organic Spectroscopy, Springer science and business media
- 7 J.B.Lambert, .S.Gronert, H.F.Shruvell, D.Lightner and R.G.Cooks, 2013, Organic structural spectroscopy, Pearson Education limited.
- 8 Yong-cheng Ning, 2011, Interpretation of organic spectra, John Wiley and Sons.
- 9 Y.R.Sharma, 2010, Elementary organic spectroscopy: Principles and chemical applications, S.Chand
- 10 Jagmohan, 2009, Organic Spectroscopy: Principles and applications, Narosa book distributors
- 11 William kemp, 2008, Organic spectroscopy, Palgrave Macmillan.
- 12 D.H.Williams, 2007, Spectroscopic methods in Organic Chemistry, McGraw-Hill Higher education
- 13 P.S. Kalsi, 2007, Spectroscopy of Organic Compounds New age International.
- 14 I.L. Finar, 1986, Organic Chemistry – Vol.II, 5<sup>th</sup> edition, ELBS Publication.
- 15 P.Crabbe, 2012, ORD and CD in chemistry and biochemistry, Elsevier.
- 16 E.L.Eliel and S.H.Ebook, 2015

- 17 G.R.Chatwal and S.K.Anand, 2011, Instrumental methods of chemical analysis, Himalaya publishing house.
- 18 B.K.Sharma,2009, Instrumental methods of chemical analysis, Krishna prakashan media
- 19 H.Willard, L.L.Meritt, J.A.Dean and F.A.Settle, 2004, Instrumental methods of analysis, CBS publishers and distributors.
- 20 S.F.Sun, 2004, Optical rotator dispersion and Circular dichroism, Wiley on line library.
- 21 D.A.Lightner and J.E.Gurst, 2000, Organic conformational analysis and stereochemistry from circular dichroism spectroscopy-methods in stereochemical analysis-book 23, Wiley-VCH.
- 22 J.M.Coxon and B.Halton, 2015, Organic photochemistry 2<sup>nd</sup> edition, Cambridge India
- 23 J.Kagan, 2012, Organic photochemistry: Principles and applications, Academic press
- 24 Dr. Sapana gupta,2014, Practice problems of photochemistry, Lulu.com
- 25 N.J.Turro, J.C.Scaiano and V.Ramamurthy, 2010, Modern molecular photochemistry of organic molecules, University science books.
- 26 P.Clan and J.Wirz, 2009, Photochemistry of organic compounds-From concepts to practice, Wiley.
- 27 A.G.Griesbeck and J.Mattay, 2004, Synthetic organic photochemistry, CRC press.
- 28 R.Gleiter, G.Haberhaur and R.Hoffmann, 2012, Aromaticity and conjugation effects, Wiley-VCH.
- 29 J.D.Hepworth, D.R.Waring, M.J. Waring, 2003, Aromatic chemistry, Wiley-RSC
- 30 S.Kumar, V.Kumar and S.P.Singh, 2015, Pericyclic reactions: A mechanistic and problem solving approach, Academic press.
- 31 S.M.Bachrach, 2014, Computational organic chemistry, John Wiley & sons.

- 32 I. Fleming, 2015, Pericyclic reactions, Oxford university primers
- 33 S.Jena, 2014, Pericyclic reactions through solved problems, Create space independent publishing platform.
- 34 J.Singh, 2012, Photochemistry and pericyclic reactions, New age.
- 35 S.Sankararaman, 2005, Pericyclic Reactions – A textbook: Reactions, applications and theory, Wiley-VCH.
- 36 Organic Chemistry , Jonathan Clayden, Nick Greeves & Stuart Warren, Second Edition, Oxford University press.

#### **WEBSITES :**

1. <http://www.asdlib.org/>
2. <http://www.chemdex.org/>
3. <https://courses.stu.qmul.ac.uk/NatSci/sbcs/info/home.htm%20>
4. <http://www.iupac.org/>
5. <http://www.rsc.org/periodic-table>
6. <http://www.rsc.org/learn-chemistry>
7. <https://courses.stu.qmul.ac.uk/NatSci/sbcs/info/webmaths.htm>
8. <http://webbook.nist.gov/chemistry/>
9. <http://www.organic-chemistry.org/>
10. <http://www.orgsyn.org/>
11. <http://www.ilpi.com/organomet/index.html>
12. <http://www.spectroscopynow.com/>
13. <http://www.chem.qmul.ac.uk/surfaces/>
14. <http://scienceworld.wolfram.com/chemistry/letters/>
15. <http://www.rsc.org/>
16. <https://www.acs.org/content/acs/en.html>
17. <http://www1.iucr.org/cww-top/crystal.index.html>
18. <http://iupac.org/>

## ORGANIC CHEMISTRY - IV (90 Hrs) 4 Credits

### CORE PAPER -13

This course aims to explain the importance of bio-organic chemistry in DNA and RNA Synthesis, Alkaloids and Terpenoids chemistry, proteins and vitamin synthesis. In addition, synthetic application of various organic reagents, protection and deprotection of functional groups are discussed in detail, followed by the synthetic importance of organo metallic reagents using naming reactions and a detailed note on retro synthesis and its synthetic application.

#### UNIT 1: Bio-Organic Chemistry (18 HOURS)

- 1.1 Pyrimidines-(1,3-diazines)- hybridisation, basicity, orientation in nucleophilic substitution –preparation of Purines and pyrimidines from barbituric acid and urea- preparation of cytosine from malondialdehyde and 2,4 dichloropyrimidine- thiamine – preparation from urea and  $\alpha$  –cyanoester- uracil –preparation by Davidson method and Wheeler and Liddle method
- 1.2 Purines-tautomerism in adenine and guanine –Preparation of adenine by Fischer and Brederick method –Guanine – preparation by Fischer and Traub method-(Preparation of other substituted pyrimidines and purines not required)-
- 1.3. Structure and functions of nucleic acids- Nucleoside and nucleotide - Nucleo bases and hydrogen bonding - Chargof rule- Replication of DNA –Transcription and Translation process- Genetic code. Types and Structure of RNA –biological roleof DNA and RNA- Protein synthesis and Deciphering of Genetic code.

## **UNIT 2 Alkaloids and Terpenoids: (18 HOURS)**

**2.1** Structural elucidation by chemical degradation and synthesis of Cocaine , Morphine and reserpine

**2.2** Synthesis of cocaine -Conversion of 2, 6 dihydroxy naphthalene to bridged lactam stage of morphine –conversion of bridged lactam to codeine/morphine – conversion of parabenzoquinone to bromo keto lactone stage of reserpine-conversion of bromoketo lactone to reserpine (Total synthesis of morphine and reserpine is not required).

**2.3** Terpene chemistry- limonene, Menthol , camphor, and  $\alpha$ -pinene –Chemical synthesis.

## **UNIT 3 Proteins and vitamins: (18 HOURS)**

**3.1** Peptides and their synthesis - Synthesis of tetrapeptide-general methods - Merrified synthesis of tripeptide-using Glycine, Alanine, Phenyl alanine, aspartic acid, Lysine, Cysteine, Glutamic acid and Arginine.

**3.2** Vitamins: Structure and chemical synthesis of vitamin, A<sub>1</sub>- Weeden et.al via Reformatsky pathway, Vitamin A<sub>2</sub>- Isler et. al method, B<sub>2</sub>- Tishler et.al, B<sub>6</sub>-Harris and Folker et.al.

**3.3** Biosynthesis of Cholesterol synthesis of mevalolate from acetate, conversion of mevalonate from isoprene, condensation of isoprene to squalene, conversion of squalene to cholesterol- Biosynthesis of bile acids - fatty acids.

## **UNIT 4 Modern Synthetic Methodology And Named Reactions In Organometallic (Sn, Pd, Cu, Ru, Si, B, Mn, Ti, Ni, Ce, Cr) Chemistry Involving Single Step Organic Functional Group Transformations Without Mechanism (18 HOURS)**

- 4.1.** Basic principles of disconnection approach to organic synthesis- synthon and synthetic equivalents.
- 4.2** Retrosynthesis of 3-Methyl-1-pentane, Methyl-3-phenyl butanoate, Aspirin, cis-1-isopropyl-2-benzyl ethylene, Geraniol, 1-phenyl-1-pentane dione, cyclopenta1,2-dione, 5,5-dimethylcyclohexane-1,3-dione and 2,6-dibromoaniline.
- 4.3** Ficini et al., synthesis analysis of Juvabione, Corey et al., synthesis of Longifolene, cubane and Z jasmone
- 4.4** Barton-McCombie reaction. Buchwald-Hartwig cross coupling reaction. Heck reaction Sonogashira coupling. Chan-Lam coupling. Elington reaction. Negishi coupling . Kumada and Suzuki coupling- (with mechanism)
- 4.5** Glaser, Hay, Cladiot-Chodkiewicz, Nozaki-Hiyama, Stille, Hiyama, Hiyama-Denmark,. Fukuyama reduction- Corey-Bakshi-Shibata reduction. Jacobsen-Katsuki, Prilezhaev, Kullinkovich cyclopropanation, Kullinkovich-de meijere and Kullinkovich-Szymoniak reactions. Luche reduction. Mc Murry reaction. (Without mechanism)

**UNIT 5: Protection Of Functional Groups, Reagents and its applications In Organic Synthesis And Free Radical Reactions (18 HOURS)**

- 5.1** Protection and deprotection of functional groups (R-OH, RCHO, R-CO-R, R-NH<sub>2</sub> and R- COOH).
- 5.2** Uses of the following reagents: 9BBN, Trimethylsilyl chloride and iodide, 1,3-dithiane (Umpolung), diisobutylaluminumhydride(DIBAL),DMSO,PCC,DCC,DMAP, DEAD, TEMPO, LDA, n-butyl lithium, Dess-Martin reagent, Catechol Boranes, Enamines-alkylations and acylations. Application of synthetic methodology for the synthesis of target molecules - through 1,3 dithianyl derivative.

**5.3** Long lived and short lived free radicals, sources - methods of generation and detection of free radicals by Paneth and ESR techniques. The following aromatic radical substitution reactions are to be studied: decomposition of diazocompounds, phenol-coupling - Sandmeyer reaction – Gomberg-Bachmann reaction, Pschorr reaction, Ulmann reaction, Hunsdicker reaction.

#### **TEXT BOOKS**

1. R.M. Silverstein, G.C. Bassler and Morrill, 1991, Spectrometric identification of Organic Compounds, 5<sup>th</sup> Edition, John Wiley and Sons, New York.
2. I.L. Finar, 1986, Organic Chemistry – Vol.II, 5<sup>th</sup> edition, ELBS Publication.
3. P.S. Kalsi, 2002, Spectroscopy of Organic Compounds, Wiley Eastern Ltd, Chennai.
4. H. Depuy and Orville, Molecular reaction and Photochemistry Charles, L.Chapman, Prentice Hall of India Pvt. Ltd., New Delhi
5. L.A.Pacquette, 1978, Principles of Modern Heterocyclic Chemistry, Benjamin Cummings Publishing Co., London.
6. J. March, 1992, Advanced Organic Chemistry, 7<sup>th</sup> Edition, Singapore
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## REFERENCES

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3. F.C.Nachod(ed), 2012, Determination of Organic structures by physical methods Vol.3, Elsevier science.
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5. R.K.Bansal, 2015, Heterocyclic chemistry, 5<sup>th</sup> ed., New age International pvt ltd publishers.
6. M.Sainsury, 2014, Heterocyclic chemistry, Wiley.
7. T.Eicher, S.Hauptmann, A.Speicher, 2013, The chemistry of heterocycles: Structure, reactions, synthesis and applications 3<sup>rd</sup> ed., John wiley& sons.
8. A.F.Pozharskii, A.Soldatenkov and A.R.Katritzky, 2011, Heterocycles in life and society, Wiley.
9. R.K.Parashar,2010, Heterocyclic chemistry, ANE books.
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## **WEBSITES :**

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22. <http://www.iupac.org/>
23. <http://www.rsc.org/periodic-table>
24. <http://www.rsc.org/learn-chemistry>
25. <https://courses.stu.qmul.ac.uk/NatSci/sbcs/info/webmaths.htm>
26. <http://webbook.nist.gov/chemistry/>
27. <http://www.organic-chemistry.org/>
28. <http://www.orgsyn.org/>

## ORGANIC CHEMISTRY PRACTICAL II

(60 Hrs) 4 Credits

### a) Organic Preparation

#### Grey Synthesis

1. Preparation of m-Nitro benzoic acid from methyl benzoate.  
(Aromatic electrophilic substitution)
2. Preparation of 2-phenyl indole from benzaldehyde
3. Comparison of green and grey method (phthalimide from phthalic anhydride).
4. Preparation of Benzoin from benzaldehyde – benzil from benzoin.  
(Benzoin Condensation), Benzilic acid from benzaldehyde (Benzoin condensation, oxidation and Benzil-benzilic acid rearrangement)
5. Benzophenone oxime from benzophenone- benzophenone oxime to benzanilide  
(Beckmann rearrangements).
6. Preparation of Isatin Via Indigo from Anthranilic acid (3 stage preparation)

#### Green Synthesis

7. Acetylation of primary amine using zinc dust
8. Nitration of phenol using calcium nitrate
9. Radical coupling reaction – preparation of 1,1 – bis -2- naphthol

### b) Organic Estimation

1. Estimation of aniline by bromination (Bromate- Bromide) method
2. Estimation of phenol by bromination (Bromate- Bromide) method
3. Estimation of glucose (Bertrand's Method)
4. Estimation of glycine by Sorensen's Formol method
5. Estimation of formaldehyde (formalin)
6. Estimation of acetic acid in commercial vinegar.
7. Estimation of Vitamin C (Reduced)

**\*c) Any two exercises in the extraction of Natural Products:**

1. Caffeine from tea leaves
2. Lactose from milk
3. Citric acid from lemon
4. Piperine from black pepper
5. Lycopene from tomato paste

**d) Spectral Interpretation Of Organic Compounds - Any Ten from the following  
(UV, IR, PMR AND MASS SPECTRA)**

1. 1, 3, 5-Trimethylbenzene
2. Pinacolone
3. n-Propyl amine
4. p-Methoxybenzyl alcohol
5. Benzyl bromide
6. Phenyl acetone
7. 2-Methoxyethyl acetate
8. Acetone
9. Isopropyl alcohol
10. Acetaldehyde diacetate
11. 2-N, N-Dimethylamino ethanol
12. Pyridine
13. 4-Picoline
14. 1, 3 dibromo-1, 1-dichloropropene
15. Cinnamaldehyde.
16. Sucrose
17. Citral

**References:**

1. Arthur I. Vogel, A Text Book of Practical Organic Chemistry.
2. Spectrometric identification of organic compounds by R.M.Silverstein, G.C.Basseller and Monsil, John Wiley and sons, Newyork.
3. Spectroscopy of organic compounds by P.S.Kalsi, Wiley Eastern Ltd., Chennai.
4. Raj K. Bansal, Laboratory Manual of Organic Chemistry, Wiley Eastern Limited.
5. Mann and Saunders, Laboratory manual of Organic Chemistry