

Course Code	Course Title	C	H	I	E	T
17P3CMC7	ORGANIC CHEMISTRY-III	4	4	25	75	100

**UNIT 1 SPECTROSCOPY-I** 12 Hrs

(a) *UV Spectroscopy*: Principle- types of electronic excitation, Woodward-Fieser rules for conjugated polyenes, enones, Scott rules for some substituted aromatic compounds; factors affecting the position and intensity of  $\lambda$ -structure, solvent and shift reagents

(b) *IR Spectroscopy*: Vibrational frequency- Factors affecting the group frequencies - hydrogen bonding, electronic and steric effect, Fermi resonance –finger print region, FT-IR

(c) *ORD and CD*: Definition, deduction of absolute configuration, octant rule for ketones.

**UNIT II SPECTROSCOPY-I** 12 Hrs

a)  $^1\text{H}$  *NMR spectroscopy*: Principle - TMS as internal standard-Relaxation process - Chemical shift-nmr scales; Number, intensity & position of signals - Factors affecting the chemical shift ; spin-spin coupling, coupling constant; spin-spin splitting-lanthanide shift reagents, Proton exchange, deuterium exchange and the influence of restricted rotation.

(b)  $^{13}\text{C}$  *NMR spectroscopy* : Basic principle of FT technique - Relaxation time, assignment of signals; Off-resonance decoupling- double resonance-spin tickling, Nuclear-Overhauser Effect and CIDNP; DEPT  $^{13}\text{C}$  spectra,  $^{13}\text{C}$ -  $^{13}\text{C}$  CORRELATION, INADEQUATE, COSY, HETCOR, ROESY, NOESY and TOCSY.

(c) *Mass Spectrometry*: Principle-types of ions –molecular, isotopic, metastable; Base peak; Nitrogen rule; Fragmentation modes; Retro Diels-Alder reaction, McLafferty rearrangement.

**UNIT III PERICYCLIC REACTIONS** 12 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3- butadiene, 1,3,5 –hexatriene and allyl system. Classification of pericyclic reactions. Woodward-Hoffmann correlation diagrams.  $4n$  and  $4n+2$  systems, FMO and PMO approach. Electrocyclic reactions – *con* rotatory and *dis* rotatory ring closure - 2+2 addition of ketenes, 1,3- dipolar cycloadditions and cheletropic reactions.

Sigmatropic rearrangements - suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties, 3,3- and 5,5- sigmatropic rearrangements. Claisen, Cope and aza-Cope rearrangements. Fluxional tautomerism, ene reaction.

**UNIT IV PHOTOCHEMISTRY** 12 Hrs

Photochemistry:  $n$  to  $\pi^*$  and  $\pi$  to  $\pi^*$  transitions - allowed and forbidden,

Intramolecular reactions of the olefinic bond - geometrical isomerism, cyclisation reaction, rearrangement of 1,4 and 1,5 dienes.

Photochemistry of carbonyl compounds - intramolecular reactions of carbonyl compounds: Norrish type I & type II, Paterno-Buchi reaction, saturated cyclic and acyclic -  $\alpha$ ,  $\beta$  and  $\beta$ ,  $\gamma$ -unsaturated compounds.

Photochemistry of aromatic compounds - Isomerization, addition and substitution.

Miscellaneous photochemical reactions - Barton reaction, photo-Fries rearrangement, Hofmann Freytag reaction.

## UNIT V REAGENTS

12 Hrs

Principle, preparations, properties and applications of the following in organic synthesis:

Organometallic reagents: Organolithium compounds (PhLi & BuLi), Organocopper compounds (Lithiumorgano cuprates), Organocadmium compounds, Organomercury compounds (Mercuric acetate),

Phosphorous containing reagents: (Phosphorous ylides), Sulfur containing reagents: (dimethyl anion, diphenyl sulfide, dithioacetals, Julia reaction), Silicon containing reagents: (Peterson reaction, trimethylvinyl silane, Trimethylsilyl chloride, aryl and alkenyl silanes), Boron containing reagents: (diborane, organoborane, 9-BBN, Corey-Nicolaou reagent)

Transition metal compounds: Titanium reagents: (Tebbe reagent, Ziegler's catalyst), Organochromium compounds, Iron compounds: (Acyl iron complexes), Cobalt compounds: (Hydroformylation, Pauson-Khand reaction), Rhodium compounds: (Wilkinson catalyst), Palladium compounds: (Pd II complexes).

Other reagents: DDQ, DCC, NBS, OsO<sub>4</sub>.

### Text Book(s):

1. Kemp, W., "Organic Spectroscopy", Third Edition, Replica Press Pvt. Ltd., New Delhi, 2008.
2. Silverstein, R.M., Bassler, G.C. and Morrill, T.C., "Spectroscopic Identification of Organic Compounds", Sixth Edition, Wiley Ind. Ltd., Singapore, 2006.
3. Depuy, E.C.H. and Chapman, O.S., "Molecular Reactions and Photochemistry", Prentice Hall, New York, 1988.
4. Norman, R. O. C., Coxon, J. M. Principles of Organic Synthesis, and Blackie Academic & Professional, 1988.
5. March, J., "Advanced Organic Chemistry", Sixth Edition, John Wiley & Sons, New York, 2007.

### Reference Books:

1. Mohan, J., "Organic Spectroscopy (Principles and Applications)" Second Edition, Narosa Publishing House, New Delhi, 2004.
2. Kalsi, P. S., Spectroscopy of Organic Compounds, Wiley Easternj Ltd., New Delhi, 1993.
3. Singh, J. and Singh, J., "Photochemistry and Pericyclic Reaction", First Edition, New Age International, New Delhi, 2004.
4. Ahluwalia, V.K. and Parashar, R.K., "Organic Reaction Mechanism" Fourth Edition, Narosa Publishing House, New Delhi, 2011.
5. Kalsi, P. S. Organic Reactions and their Mechanisms, New Age International Publishers, New Delhi, 1996.