OC H 502: Synthetic Reagents and Spectroscopic Techniques

COURSE OUTCOME:

- Students will learn the preparation, properties, reactions and uses of organometallic reagents in organic synthesis.
- Students will know the uses of Gillman's reagent, LDA, DCC, 1,3-dithiane, TMSI, DDQ, SeO_2, Wikinson's catalyst, PTCs, Baker's yeast, PPA, TMS-CN, hydrosilane, chloramines-T, Woodward-Prevost hydroxylation, Zeigler-Natta catalyst, and crown ethers in organic synthesis and functional group transformation.
- Students will acquire the knowledge of utilization of principles of green chemistry by the use of crown ethers and ionic liquids in organic synthesis and microwave induced reactions.
- Students will demonstrate an understanding advanced aspects of IR, ^{1}H and ^{13}C NMR and Mass spectroscopy.
- Students will develop the ability to solve the composite problems involving the application of UV-Visible, IR, NMR (^{1}H &^{13}C) and Mass spectroscopic data, interpret the spectra to elucidate the structure of organic molecules.

UNIT- I: Reagents in Organic Synthesis-I **[15 Hours]**

Organometallic Reagents: Preparation and properties of Organolithium and organomagnesium compounds. Their uses in organic synthesis and in the preparation of Organometallic compounds.
Methods of preparation, properties, reactivity and reactions of Organozinc, Organocadmium, Organomercury Organoindium, Organoaluminium and Organotellurium reagents.

Silicon containing Reagents: Introduction, preparation reactions & stereochemistry, Peterson reaction.

Boron containing Reagents: Introduction, preparations, Hydroborations, reactions of Organoboranes- Isomerization, oxidation, protonolysis, carbonylation, cyanidation. Synthesis of esters, E and Z alkenes, conjugated dienes and alkynes.

Organotin Compounds: Synthesis of Organostannanes and their utility in C-C bond forming reactions. Tributyltin hydride, Barton decarboxylation reaction, Barton deoxygenation, Stelly-Kelly coupling reaction.

UNIT- II: Reagents in Organic Synthesis-II **[15 Hours]**

Use of the following reagents in Organic synthesis and functional group transformation: Gillman's reagent, Lithium diisopropylamide (LDA), Dicyclohexyl carbodiimide (DCC), 1,3-dithiane (reactivity-umpolong), Trimethyl silyliodide, DDQ, Selenium dioxide, Wilkinsons catalyst, Phase transfer catalysts, Baker's yeast, Polyphosphoric acid. Trimethyl silyl cyanide, Hydrosilanes, Chloramine-T, Aluminium*iso*-propoxide. Woodward and Prevost hydroxylation, Zeigler-Natta catalyst, Phase transfer catalysts, Crown ethers.

UNIT –III: **[15 Hours]**

IR, ^{1}H NMR and ^{13}C-NMR: Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. Detailed study of vibrational frequencies of carbonyl compounds (Ketones, aldehydes, esters, amides, acids, anhydrides, lactones, lactams and conjugated carbonyl compounds). Effect of H-bonding & solvent effect on vibrational frequencies.

Chemical shift of different class of organic compounds. Spin-spin coupling – illustrate with different examples. AB, AX-Spin system. Chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei. Stereochemistry, hindered rotation; Karplus-Curve. Variation of coupling constant with dihedral angle. Pulse techniques, Techniques for simplication of spectra, Heteronuclear coupling,INDOR,2D-NMR,FT-NMR.Applications of NMR Composite problems involving the application of UV, IR, ^{1}H NMR and ^{13}C-NMR and Mass spectroscopy technique in the structural elucidation of organic molecules.

Green Techniques:

Crown Ethers: Introduction, Nomenclature, Synthesis of Dibenzo[18]crown-6, Aza-crown, Cryptates, Synthetic applications like esterification, saponification, elimination reactions, superoxide anion, generation of carbenes.

Microwave induced reactions: Introduction, advantages, limitations, precautions, application like Deprotection, Hydrolysis, Condensation, ortho ester claisen rearrangement.

Ionic Liquids: Introduction, properties, types, preparation, applications like Epoxidation, Alkene Metathesis, Oxidation, Reduction and Enzyme catalysed synthesis.

References:

1. Advanced Organic chemistry 5th edition -J. March (John Wiley and sons).
2. Organic Chemistry- J. Clayden, N. Greeves, S. Warren and P. Wothers (Oxford University Press).
3. E. Eliel and S.H. Wilen, Stereochemistry of Organic compounds, John Wiley.
4. Organic Spectroscopy- William Kemp (Palgrave)2005.
5. Advanced Organic Chemistry – Part A& B, 3rd edition- F.A. Carey and Sundberg, (Plenum Press) 1990.
6. Advanced General Organic Chemistry-S.K. Ghosh (Book and Alleied (P) Ltd) 1998.
7. Organic Synthesis, special Techniques -V.K. Ahluwalia and Renu Agrawal (Narosa Publications).
8. Spectrometric Identification of Organic Compounds - Silverstein, Bassler & Monnill (Wiley)1981.
9. Spectroscopy of Organic Compounds-3rd Ed.-P.S.Kalsi (New Age, New Delhi) 2000.
10. Spectroscopic Methods in Organic Chemistry - Williams and Fleming, TMH.
11. Spectroscopy, Donald L.Pavia (Cengage learning India Pvt.Ltd., Delhi), 2007.
12. Organic Spectroscopy-3rd ed.-W.Kemp (Pagrave Publishers, New York), 1991.