Subject Code : N3B8

Paper – VIII – Organic Chemistry – III

Unit I Organic Photochemistry :

Fundamental concepts Joblonski diagram – energy transfer – characteristics of photoreaction an photoxidation – photoreactions of ketones and enones – Norrish type I and II reactions. Photochemistry of alkenes, dienes and aromatic compounds. Photosensitisaion –photoadditions – Barton reaction – Paterno – Buchi reaction.

Pericylic reactions :

Concerted reactions – stereochemistry – orbital symmetry and correlation diagram – Fronteir molecular orbital approach – Wooeward Hoffmann rules – electrocylic reactions – Cycloadditions selection rules, sigmatropic rearrangements – selection rules with simple examples – 1,3 and 1,5 – hydrogen shifts – Cope and Claisen rearrangement.

Unit II
A. Ultraviolet and visible spectroscopy :

Basic principles of electronic transitions – correlation of energy change with electronic transitions – instrumentation and sample handling techniques. Applications of UV – visible spectroscopy – Woodward – Fieser – Scott rules – applications to conjucated dienes, trienes, polyenes, - unsaturated carbonyl compounds, conjugated cyclic ketones and acetophenones – benzene and its substituted derivatives, other aromatic hydrocarbons and hetrocylcic systems – differentiations of position isomers. Stereochemical factors affecting electronic spectra of biphenyl and binaphthyls – cis and trans isomers – angular distortion and cross conjugation.

Infrared spectroscopy :

Instrumentation and sampling techniques – types of stretching and bending vibrations – characteristics group frequencies – both internal and external – quantitative studies – organic structure determination. Finger print region – identification of functional groups – hydrogen bonding (intermolecular and intramolecular) – conformational aspects in cyclic 1,2-diols and 13-diols transannular interactions in UV and IR – Determination of reaction rates and mechanisms of reactions employing IR and UV spectroscopy (basic aspects).

Unit III
Proton NMR Spectroscopy :

Chemical and magnetic nonequivalence – chemical shift – coupling constant – first and second order proton, spin – spin splitting, dependence of J on dihedral angel, vicinal and geminal coupling constants – Karolus equation. Long range coupling constants. Influences of streochemical factors on chemical shift of protons – simplification of complex spectral – double resonance techniques, shift reagents. Chemical spin decoupling of rapidly exchangeable protons (DH, SH, COOH, NH, HN2) an elementary treatment of NOE phenonmenon – 2D techniques (COSYm NOSEY and ROSY).

13C NMR Spectroscopy :

Basic principles : FT/NMR/Relaxation – broad decoupling – off resonance decoupling. Calculation of chemical shifts for simple aliphatic and aromatic compounds –

Conformation and chemical shift correlations – peak assignments. Importance of NOE phenomenon in C13 NMR spectroscopy.

Unit IV

Mass spectroscopy : Basic principles – resolutions – EI and CI methods – base peaks, isotopic peaks, metastable peaks, parent peaks, determination of molecular formula – recognition of molecular ion peak, FAR, fragmentation – general rules. Nitrogen rule – pattern of fragmentation of various classes of compounds. McLafferty rearrangement, importance of metastable peaks.

B. Electron spin resonance spectroscopy :

Basic principles – comparison between ESR and NMR spectra, hyperfine splitting – factors affecting the magnitude of G values. Calculation of unpaired electron density on an atom in a delocalized system. Applications to organic free radicals.

C. Optional rotatory dispersion and circular dichorism :

Introduction to theory and terminology. Cotton effects and ORD curves. Axial haloketone rule and its applications – octant rule and is applications. Applications of ORD to determine absolute configuration of simple monocyclic ketones – comparison between ORD and CD and their interrelationship.

Unit V

Steroids :

Classification – structural elucidation of cholesterol (synthesis not required - structure elucidation and synthesis of vitamin D – estrone, progesterone, ergosterol, stigmasterol, equilenin, androsterone and cortisone. Classification and functions of prostaglandins. Conformation of steroids – Biosynthesis of cholesterol.

Heterocyclics : Synthesis and reactions of azoles – pyrazole, imidazole, oxazole and thiazole – synthesis and reactions of azepine, oxazine, thiazine, pyridazine, pyrimidine and pyrazine.

References:

1. M.G. Arora Organic photo chemistry and pericylic reactions.
2. C.H.Depuy and O.S. Chapman, Molecular Reactions and Photochemistry Prentice Hall 1975.
3. R.B.Woodward and R.Hoftmann, The conservation of orbital symmetry, Verlag Chemil 1970.
4. G.B.Grill, M.R. Willis, Pericylcic reactions Chapman & Hall 1974.
5. Willima Kepmp Organic Spectroscopy ELBS Macmillan 1991.
6. P.M.Silvertein, G.C.Bassber and T.C.Morrill, Spectroscopic Identification of organic compounds. 3rd edition 1974.
7. J.R.Dyer Application of absorption Spectroscopy of organic compounds Prentice Hall 1964.
8. P.S.Kalsi, Spectroscopy of organic compounds Wiley 1993.
9. I.L.Finar, Organic Chemistry Vol II 5th Edition ELBS 1975
10. L.A.Pacquette, Principles of moden hetrocyclic chemistry. W.A.Benzamin 1968.
11. Raj.K>Bansal, Hetrocylci chemistry Synthesis Reactions and Mechanisms, Wiley – 1990.
12. V.R.Sharma Elementary organic spectroscopy Principle and chemical applications S.Chand 1992.