JYOTI NIVAS COLLEGE AUTONOMOUS BANGALORE - 560095

M.Sc. Chemistry (Organic) Syllabi 2014-15

I Semester M.Sc. Chemistry (Organic)

JOC 101: Inorganic Chemistry - I **52 h**

Unit I

1. Chemical Bonding: **18 h**

Concepts of resonance and hybridization. VSEPR model, shapes of molecules, Bent's rules and energetics of hybridization. Electronegativity and partial ionic character, Bonds: ionic, covalent, co-ordinate, multicentre quadruple and synergic. Hydrogen bonds-types and detection, agostic bond.

Lattice energy, Born-Haber cycle and its use, Born-Lande equation, Fajan's rules, Slater's rules, radius-ratio rules, structures of crystal lattices (NaCl, CsCl and ZnS) and Zintl isoelectronic relationship in solids. M.O. Theory: σ, π and δ molecular orbitals, MOs of diatomic molecules (homo and heteronuclear), walsh diagrams of BeH_2 and H_2O.

Unit II

2. Compounds of non-metals: **12 h**

Periodicity and general trends in properties, Polymorphisms of carbon, phosphorus and sulphur: properties, structure and bonding in boranes, carboranes, metallo carboranes borazines, phosphazenes, sulphur-nitrogen compounds, oxyacids of nitrogen, phosphorus, sulphur and halogens; noble gas compounds.

Unit III

3. Silicates: **12 h**

Classification and structures, isomorphous replacement, pyroxenes, layered and vitreous silicates, silicates glasses, borosilicate glasses, glass ceramics, silica gel, zeolites and molecular sieves, silicones, condensed phosphates, polyhalides.

Unit IV

4. Concepts of Solvent systems and Acids-Bases: **06 h**

Solvent systems; Bronsted and Lewis acids and bases, pH and pKa, Hard and Soft acids and bases (HSAB) concept, acid-base concept in non-aqueous media, levelling effect, super acids, reactions in BrF_3, N_2O_4.

5. Isopoly and heteropoly acids of W, Mo and V **04 h**

Preparation properties structure and applicatons.

References

1. Basic Inorganic Chemistry, F.A.Cotton, G. Wilkinson and P.L. Gaus, John Wiley and sons (1995).
2. Advanced Inorganic Chemistry 3rd, 5th and 6th Editions, F. A. Cotton and G. Wilkinson.
3. Inorganic Chemistry, 4th Edition, J.E.Huheey, E.A.Keiterand R.L.Keiter, Addison Wesley (1993).
4. Inorganic Chemistry, 2nd Edition, D.F. Shriver, P.W. Atkins and C.H. Langford, ELBS (Oxford Univ. Press) (1994).
5. Concise Inorganic Chemistry, 5th Edition, J.D.Lee (1996).
6. Chemistry of the Elementals, N.N. Greenwood and A.E. Earnshaw, Butterworth Heinemann (1997).
7. Essential trends in Inorganic Chemistry, D.M.P.Mingos, Oxford Univ. Press (1998).
8. Materials Science, J.C.Anderson, K.D.Lever, J.M.Alexander and R.D. Rawlings, ELBS, (2000).
9. Structural Inorganic Chemistry, A.F.Wells, Oxford: Clarendon Press, 1984.
10. Inorganic Chemistry, James E. House, Latest ELBS edition.

JOC 102: Organic Chemistry - I **52 h**

Unit I

1.Nature of Bonding in Organic Molecules **05 h**

Delocalized chemical bonding: Conjugation, cross conjugation, resonance.

Aromaticity. Huckel's rule of aromaticity. Craig's rule. Aromatic systems with electron numbers other than six (including azulene, tropone, tropolone and annulenes). Antiaromaticity. Aromaticity in benzenoids, meso-ionic compounds. Homo-aromaticity. Alternant and nonalternant hydrocarbons, Energy levels in odd and even-alternant hydrocarbons, energy levels for the benzyl cation, benzyl free-radical and benzyl carbanion. Hyperconjugation. Tautomerism.

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2.Reaction Mechanisms: Structure and Reactivity **11 h**

Generation, structure, stability and reactivity of carbocations, carbanions, carbon free radicals, carbenes and nitrenes.

Classification of reactions and mechanisms. Thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond postulate, Curtin-Hammett principle. Potential energy diagrams, transition states and intermediates.

Methods of determining mechanisms: Based on the structure of products, determination of the presence of intermediates, isotopic labeling, isotope effects, from stereochemical evidence.

Acids and bases: Hard and soft acids and bases. Effect of structure on the strengths of acids and bases.

Effect of structure on reactivity: Resonance and field effects; steric effects. The Hammett equation and linear free energy relationship, substituent and reaction constants. Taft equation.

Nucleophilic substitution reaction at a saturated carbon: S_N1, S_N2, S_Ni and SET mechanisms. Effect of substrate structure, attacking nucleophile, leaving group. Ambident nucleophiles and substrates.

Unit II

3. Stereochemistry **09 h**

Fischer, Newman, Sawhorse and flying wedge projections and their interconversions. Optical isomerism: Elements of symmetry and chirality. D-L conventions. CIP rules,

R-S and M-P conventions. Chirality in compounds with a stereogenic centre, and in allenes, alkylidene cycloalkanes and spiranes (with a stereogenic axis).

Cram's and Prelog's rules.

Conformational analysis: Conformational analysis of cycloalkanes: cyclobutane, cyclopentane, cychexanes (monosubstituted e.g., methyl, *iso*-propyl, *tert*-butyl and di-substituted cyclohexanes e.g., dialkyl, dihalo, diols), and cycloheptane.

Nomenclature and conformations of fused rings and bridged ring systems.

Prochirality: Enantiotopic and diastereotopic atoms, groups and faces.

Unit III

4. Natural colouring compounds **07 h**

Anthocyanins: Methods of isolation, basic structural features of coumarins, chromones, flavones and isoflavones. Structural elucidation and synthesis of quercetin and wedelolactone.

Biosynthesis of quercetin, cyaniding and formononetin.

Carotenoids: Methods of isolation. Structural elucidation and synthesis of β- carotene. Structural relationship of α-, β- and γ-carotenes.

5. Heterocyclic compounds **06 h**

Nomenclature of heterocyclic compounds. Structure, reactivity, synthesis and reactions of pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, pyrimidine and purine. Preparation and reactions of quinoline, isoquinoline and indole.

Unit IV

6. Carbohydrates **07 h**

Determination of configuration of the monosaccharides. Conformational analysis of glucose and galactose. Structural elucidation of sucrose and maltose. Synthesis of aldonic, uronic, aldaric acids and alditols. Structures of trehalose, cellobiose, lactose, gentiobiose, meliobiose, starch, cellulose and chitin. Photosynthesis of carbohydrates.

7. Vitamins **07 h**

Biological importance and synthesis of vitamins A, B_1 (thiamine), B_6 (pyridoxine), C, E-(α-tocopherol), H (biotin), K_1, K_2, folic acid, pantothonic acid and riboflavin.

References

1. Advanced Organic Chemistry – Reactions, Mechanism and Structure, Jerry March, John Wiley (2008).
2. Advanced Organic Chemistry, F A Carey and R J Sundberg Plenum, (1990).
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman, (2000).
4. Structure and mechanism of Organic Chemistry, C K Ingold, Cornell University Press (1999).
5. Organic Chemistry, R T Morrison and R N Boyd, Prentice-Hall, (1998).
6. Modern Organic Reactions, H O House, Benjamin, (1972).
7. Principles of Organic Synthesis, R O C Norman and J M Coxon, Blackie Academic and Professional, (1996).
8. Stereochemistry of Organic Compounds, D Nasipuri, New-Age International, (1999).
9. Stereochemistry of Carbon Compounds, E L Eliel, S H Wilen and L N Mander, John Wiley, (1994).
10. Stereochemistry, Potapov, MIR, Moscow, 1984.
11. Organic Chemistry, Volumes I and II, I L Finar, Longman, (1999).
12. Peptides Chemistry: A practical text book, M. Bodansky, Springer-Verlag NY, 1988.
13. Solid-phase peptide synthesis: A practical approach-E. Artherton & R.C. Sheppard, I R L, Oxford Univ. Press, 1989.
14. Peptides: Chemistry and Biology, N Selwad and H.-D. Jakubke, Wiley-VCH, 2002.
15. Biochemical approach to medicinal and natural products, P. M. Dewick.
16. Advanced Organic Chemistry, Jagadamba Singh.
17. Advanced Organic Chemistry, Ahuwalia.

JOC 103: Physical Chemistry - I **52h**

Unit I

1. Classical Thermodynamics: **12 h**

Brief resume of concepts of laws of thermodynamics, Concept of free energy, chemical potential and entropies. Partial molar properties- Partial molar free energy, partial molar volume, partial molar heat content and their significance. Determination of these quantities. Phase Rule – Derivation of phase rule from the concept of chemical potential, application of phase rule to three component systems.

Concept of fugacity and its determination by graphical and compressibility factor methods. Non-ideal systems – Excess functions for non-ideal solutions. Activity and activity coefficients. Determination of activity coefficient by EMF and solubility methods. Relationship between mole fraction, molality, molarity and activity coefficients.

Unit II

2. Statistical Thermodynamics: 12 h

Concepts of distribution, thermodynamic probability and most probable distribution. Ensemble averaging – postulates of ensemble averaging. Canonical, grand canonical and micro canonical ensembles with corresponding distribution laws (using Lagranges method of undetermined multipliers). Partition functions: translational, rotational, vibrational and electronic partition functions. Calculation of thermodynamic properties in terms of partition functions. Chemical equilibrium and equilibrium constant in terms of partition functions. Fermi-Dirac statistics: distribution law and applications to metal. Bose-Einstein statistics – distribution law and application to Helium. Heat capacity behaviour of solids. Einstein's and Debye's equation. Characteristic temperature. Determination of heat capacity at low temperature.

Unit III

3. Non Equilibrium Thermodynamics: 05 h

Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow. Entropy balance equation for different irreversible processes (e.g. heat flow, chemical reaction etc.). Transformations of the generalized fluxes and forces, non-equilibrium stationary states, phenomenological equations, microscopic reversibility and Onsagar's reciprocity relations.

4. Macroscopic and Microscopic Kinetics: 05 h

Factors affecting reaction rates, methods of determination of order and rate laws, Collision theory of reaction rates, limitations, Transition state theory. Comparison of collision and transition state theory. Reaction between ions: influence of ionic strength – primary and secondary kinetic salt effects. Diffusion and activation controlled reactions in solutions.

5. Steady State Kinetics: 04 h

Chain reactions – general characteristics, chain length and chain inhibition. Mechanisms of thermal reactions (hydrogen-bromine, hydrogen-chlorine, pyrolysis of acetaldehyde, decomposition of ethane) and photochemical reactions (hydrogen-bromine and hydrogen-chlorine). Comparative study of thermal and photochemical hydrogen-halogen reactions.

Unit IV

6. Kinetics of Fast Reactions: 05 h

Study of fast reactions by relaxation method, flow method, flash photolysis and NMR method. Theories of unimolecular reactions, Perrin theory, Lindemann theory, Qualitative treatment of Hinshelwood theory & RRKM theory (no derivation), Slater treatment.

7. Enzyme Catalysis: **05 h**

Comparison of enzyme with chemical catalysts, mechanism (lock and key theory), Henri-Michaelis-Menten treatment, significance of Michaelis constant, Lineweaver-Burk plot, Effects of concentration, pH, temperature, activators and inhibitors on enzyme activity.

8. Surface Chemistry: **04 h**

Effect of temperature on adsorption, mechanical adsorption, BET and Gibbs adsorption isotherm, estimation of surface area using BET equation, surface tension and surface energy, Capillary action, Pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Surface film on liquids (electro-kinetic phenomena), Catalytic activity of surfaces.

References

1. Molecular Thermodynamics, Donald A.McQuarrie, John D. Simon, University Science Books, California (1999).
2. Thermodynamics for Chemists by S. Glasstone, Affiliated East-West Press, New Delhi (1960).
3. Statistical Thermodynamics, M.C. Gupta, Wiley Eastern Ltd. (1993).
4. Text Book of Physical Chemistry, Samuel Glasstone, 2nd Edition, Macmillan India Ltd. (1991).
5. Physical Chemistry, P.W. Atkins, Julio de Paula, ELBS, 7th Edition (2002).
6. Principles of Chemical Kinetics, House, J.E., W C Brown Publisher, Boston (1997).

JOC 104: Analytical Chemistry and Mathematics for Chemists **52 h**

Part A - Analytical Chemistry **[28 h]**

Unit I

1. Introduction to Analytical Methods: **05 h**

Classifications of analytical methods, types of instrumental analysis, factors influencing choice of analytical method, toxic chemicals sampling and handling hazards, Safety data sheets, Miniaturization of analytical methods and its significance in modern chemical analysis.

2. Separation Techniques: **09 h**

Solvent extraction: Types-batch, continuous, efficiency, selectivity, distribution coefficient, Nernst distribution law, derivation, applications and numerical problems.

Chromatography: Types, Terminology, principles and functioning of Paper, Thin layer, Column, Gas Chromatography, High Performance Liquid Chromatography, Reversed Phase Liquid Chromatography, Super Critical Fluid (SCF) Chromatography, 2D-Thin Layer Chromatography, Electrophoresis.

Unit II

3. Optical Methods of Chemical Analysis: 09 h

Interaction of electromagnetic radiation with matter, Beer-Lambert's law-derivation, verification, deviations. Molar extinction coefficient, choice of solvent, Sandel sensitivity, Ringbom's plot, Photometric titrations, Single and Double beam Uv-Visible spectrophotometer, application of quantitative and qualitative analysis, principles and applications of Fluorimetry, Turbidimetry and Nephelometry. Numerical problems on all these techniques.

4. Principles of Titrimetric Analysis: 05 h

Applications of acid-base titrations-Determination of nitrogen, sulphur, ammonium salts, nitrates and nitrites, carbonates and bicarbonates and organic functional groups like carboxylic acid, sulphuric acid, amines, ester, hydroxyl, carbonyl group, air pollutants like SO_2.

References

1. Analytical Chemistry, G.D. Christian, V Edition, John Wiley & Sons Inc. (1994).
2. Instrumental Methods of Analysis, H.H. Willard, L.L. Merrit, G.A. Dean and F.A. Set, CBS Publishers (1996).
3. Fundamentals of Analytical Chemistry, Skoog, West, Holler and Crouch, 8th Edition, Thomson Asia Pvt. Ltd. (2004).
4. Instrumental Methods of Chemical Analysis, G. W. Ewing, 5th edition, McGraw- Hill, New York, 1988

Part B - Mathematics for Chemists [24 h]

Unit III

5. Vectors: 03 h

Vectors, dot and cross products; scalar and vector triple products and their applications. Tensors and their applications.

6. Matrix Algebra: 04 h

Review of different types of matrices (including Hermitian and skew- Hermetian); matrix addition and multiplication; determinant of a square matrix, transpose, adjoint and inversre of a square matrix. Solution to system of linear equations (a) by matrix method & (b) by Cramer's Rule.

Characteristic equation of a square matrix, eigen values and eigen vectors.

7. Calculus: 02 h

Rule for differentiation; Chain Rule (for $f(x) = U^n$, sin u, log u etc.) implicit differentiation and parametric differentiation and successive differentiation of order 2 (for explicit functions only).

8. Applications of differentiation: **02 h**

Derivative as a slope of the tangent, derivative as a rate measure – velocity and acceleration, increasing and decreasing functions- maxima and minima- second derivative test- point of inflections- problems restricted to polynomials

Unit IV

9. Integration: **02 h**

Basic rules- simple substitution- Method of partial fractions- Integration by parts. Definite integral and application to areas of plane curves.

10.Functions of several variables: **03 h**

Partial derivatives; co-ordinate transformation from Cartesian co-ordinates to spherical and cylindrical co-ordinates and vice- versa.

11.Elementary Differential Equation: **04 h**

Variable separable, exact first order equations, linear and homogeneous equation**.**

Second order homogeneous differential equation with constant coeffecients; f(D)y=0. Solution of differential equations by power series method.

12.Fourier series: **02 h**

Simple problems.

13. Probability:

Review of permutations and combinations. Probability and addition theorem for mutually exclusive events and multiplication theorem for independent events.

14. Curve Fitting: **02 h**

Method of least squares.

References

1. Analytical Chemistry, G.D. Christian, V Edition, John Wiley & Sons Inc. (1994).
2. Instrumental Methods of Analysis, H.H. Willard, L.L. Merrit, G.A. Dean and F.A. Set, CBS Publishers (1996).
3. Fundamentals of Analytical Chemistry, Skoog, West, Holler and Crouch, 8th Edition, Thomson Asia Pvt. Ltd. (2004).
4. Instrumental Methods of Chemical Analysis, G. W. Ewing, 5th edition, McGraw- Hill, New York, 1988.
5. Electrochemical methods: A.J. Bard & I. R. Faulkner, 2nd edition, Wiley, New York, 2000.
6. Vogel's text book of Quantitative Chemical analysis 5th edition, Ed., Jeffery et. al ELBS/Longman, 1998

7. Calculus and analytical Geometry, Thomas, Finney. Narosa Publishing House.
8. Short Course in differential equations, Rainville and Bedient, IBH Publishers.
9. Theory and Problems in Mathematics, Vol II, S.S. Bosco,
10. Algebra- hall and Knight.
11. Mathematics for Chemistry, Doggett and Sucliffe, Longmann Publishers.
12. Mathematical preparation for Physical Chemistry, F. Daniels, McGraw Hill.
13. Chemical mathematics, D.M. Hirst, Longman publishers.
14. Basic mathematics for Chemists, Tebbutt, Wiley publishers.

JOC 106: Inorganic Chemistry Practical - I

A. Semi-micro qualitative analysis

Semi-micro qualitative analysis of mixtures containing two each of common cations and anions and one of the following less familiar elements: W, Mo, Ce, Th, Zr, V, U and Li.

B. Preparation and determination of yield of inorganic complexes:

1. Ferrous oxalate
2. Potassium tris-oxalatoferrate (III) trihydrate
3. Hexammine cobalt (III) chloride
4. Cis -potassium dioxalatodiaquochromium (III)
5. Mercury tetrathiocyanatocobaltate (III)

References

1. Inorganic Semi – micro Qualitative Analysis, Dr. V V Ramanujam, 3 rd Edition, The National Publishing Company 2008.
2. Vogel's Text Book of Qualitative Chemical Analysis, J. Bassett, G.H. Jeffery and J. Mendham, ELBS (1986).
3. Vogel's Text Book of Quantitative Chemical Analysis, J. Bassett, G.H. Jeffery, J. Mendham and R.C. Demmy, 5 th Edition, Longman Scientific and Technical (1999).
4. Practical Inorganic Chemistry by More and Racket.

JOC 107: Physical Chemistry Practical - I

A. Chemical Kinetics

1. Determination of the velocity constant, catalytic coefficient, temperature coefficient, t ½ and energy of activation for the acid hydrolysis of methyl acetate
2. Evaluation of Arrhenius parameters for the reaction between potassium persulphate and potassium iodide (1^{st} order).
3. Velocity constant for the saponification of ethyl acetate.

4. Determination of the order of reaction between hydrogen peroxide and potassium iodide (Clock reaction).

B. Colorimetry

5. Test for validity for Beer-Lambert's law and determination of the unknown concentration of solution. Calculation of molar extinction coefficient.
6. Titration of ferrous ammonium sulphate with potassium permanganate colorimetrically.
7. Simultaneous estimation of Mn and Cr in a solution of $KMnO_4$ and $K_2Cr_2O_7$.
8. Kinetics of reaction between $K_2S_2O_8$ -KI colorometrically.
9. Determination of concentration of Fe by spectrophotometric titration using EDTA.

C. Cryoscopy

10. Determination of molecular weight of a solute by cryoscopy.
11. Determination of degree of dissociation of an electrolyte and association of benzoic acid in benzene.

D. Partial Molar Volume

12. Determination of partial molar volume of ethanol by reciprocal density method.
13. Determination of PMV by apparent molar volume method, NaCl-H_2O system.

E. Phase Diagram

14. Construction of phase diagram of a two-component system and determination of eutectic temperature and eutectic composition.
15. Construction of phase diagram of a three-component system.

F. Adsorption

16. Adsorption of oxalic acid on charcoal. Verification of Langmuir adsorption isotherm.

References

1. Advanced Practical Chemistry by J.B. Yadav, Goel Publication House, Merrut (1989).
2. Experiments in Physical Chemistry by Shoemaker and Garland, McGraw Hill International edn. (1996).
3. Experimental Physical Chemistry, V.D. Athawale and Parul Mathur, New Age International, New Delhi (2001).

II Semester M.Sc. Chemistry (Organic)

JOC 201: Inorganic Chemistry - II (Co-Ordination Chemistry) 52 h

UNIT – I

1. Metal - Ligand Equilibria in Solution 08 h

Step-wise and overall formation constant and their relationship, trends in step-wise constant, kinetic and thermodynamic stability of metal complexes, factors affecting the stability of metal complexes with reference to the nature of the metal ion and ligand, chelate and macrocyclic effects and their thermodynamic origin , determination of binary formation constants by pH-metry, spectrophotometry, polarography and by ion exchange methods.

UNIT – II

2. Metal – Ligand Bonding 12 h

Crystal field theory-limitations, stereochemistry, coordination Nos,3 to 8, Evidences for metal-ligand orbital overlap, MO theory (including π bonding), Jahn-Teller distortion in metal complexes and metal chelates, Spectrochemical series,Nephelauxetic series, angular overlap model.

UNIT – III

3. Structure and Bonding 14 h

Hydride, dihydrogen, simple metal carbonyl, Nitrosyl, dinitrogen and tertiary phosphine complexes, metal complexes as liquid crystals, stereochemical non-rigidity, self-assembly in supramolecular chemistry. Stereoisomerism-chirality, optical activity, CD, ORD, Cotton effect and magnetic circular dichroism, absolute configurations.

UNIT – IV

4. Electronic Spectra of Transition Metal Complexes 12 h

Spectroscopic ground states, selection rules, term symbols for d^n ions, Racah parameters, Orgel correlation and Tanabe-Sugano diagrams, spectra of 3d metal aqua complexes of trivalent V,Cr, divalent Mn, Co and Ni, $[CoCl_4]^{2-}$, calculation of Dq, B and β parameters, charge transfer spectra.

UNIT – V

5. Magnetic Properties of Metal Complexes 06 h

Magnetic susceptibility, types of magnetic behaviour, diamagnetic corrections, orbital contribution, spin-orbit coupling, Ferro and antiferromagnetic coupling, spin crossover.

References

1. Basic Inorganic Chemistry, F.A. Cotton, G.Wilkinson and P.L.Gaus, John wiley & sons Inc,6th Edition (1999)
2. Inorganic Chemistry,4th Edition, J.E. Huheey, E.A.Keiter and R.L.Keiter,Addition-Wesley(1993)
3. Inorganic Chemistry,2nd Edition, D.F.Shriver, P.W.Atkins and C.H. Langford,ELBS (Oxford Uni. Press) (1994)
4. Chemistry of the Elementals, N.N.Greenwood and A.E. Earnshaw,Butterworth Heinemann(1997)
5. Inorganic Electronic Spectroscopy, A.B.P.Lever, Elsevier.
6. Essential trends in inorganic chemistry, D.M.P. Mingos, Oxford Univ. Press (1998) Magneto Chemistry, R.L.Carlin, Springer Verlag.
7. Electronic Absorption Spectroscopy and Related techniques, D.N. Sathyanarayana, Universities Press (2001).

JOC202: Organic Chemistry - II **52 h**

Unit I

1. Aromatic Substitution Reactions **10 h**

Electrophilic Substitution Reactions: The arenium ion mechanism. Orientation and reactivity. Energy profile diagrams. The *ortho*/*para* ratio, *ipso* attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Effect of leaving group. Amination, sulfonylation reactions; Diazonium coupling, Vilsmeier-Haack reaction, Gatterman reaction, Gatterman-Koch reaction and Hoesch reaction.

Nucleophilic substitution reactions: The S_NAr, S_N1, benzyne and SR_N1 mechanisms. Reactivity: effect of substrate structure, leaving group and attacking nucleophile. Goldberg reaction, Bucherer reaction and Schiemann reaction. Von Richter, Sommelet-Hauser and Smiles rearrangements.

Unit II

2. Addition Reactions **11 h**

Addition to carbon-carbon multiple bonds: mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals. Regio, stereo- and chemoselectivities. Orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Addition of alkenes and/or alkynes to alkenes and/or alkynes. Ene synthesis. Michael reaction.

Addition to carbon-heteroatom multiple bonds: Mechanism of metal hydride reduction (NaH, LiH, $LiAlH_4$, $NaBH_4$) of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagents and organolithium reagents to carbonyl compounds and unsaturated carbonyl compounds. Conversion of aldehydes to nitriles. Hydrolysis of nitriles and

addition of amines to isocyanates. Formation of xanthates. Wittig, Mannich and Stobbe reactions.

Unit III

3. Elimination Reactions **04 h**

The E_2, E_1 and E_1cB mechanisms and their spectrum. E_2C and E_2H mechanisms. Orientation of the double bond. Reactivity-effects of substrate structure, attacking base, the leaving group and the medium. Mechanism and orientation in pyrolytic elimination reactions (including Chugaev reaction).

4. Rearrangements **04 h**

Wagner-Meerwein, Pinacol-Pinacolone, Fries, Wolff, Beckmann, Hofmann, Curtiues, Lossen and Schmidt rearrangements.

5. Synthetic Molecular Receptors **06 h**

Definition and significance, Bonds weaker than covalent bonds, Structures and functions of receptors with: molecular clefts, molecular tweezers, macro cyclic polyethers, receptors with multiple hydrogen bonding sites, cyclophanes, calixarenes and cyclodextrins

Unit IV

6. Nucleic acids **06 h**

Introduction, protecting groups for hydroxyl group in sugar, amino group in the base and phosphate functions; Methods of formation of internucleotide bonds: DCC, phosphodiester and phosphotriester approaches, phosphoramidite and phosphoramide methods; Solid phase synthesis of oligonucleotides

7. Pepitdes **11 h**

Classification and nomenclature. Sanger and Edman methods of sequencing. Cleavage of peptide bond by chemical and enzymatic methods. Peptide synthesis- Protection of amino groups (Boc-, Z- and Fmoc-) and carboxyl group as alkyl and aryl esters. Use of DCC, 3reactions. Deprotection and racemisation in peptide synthesis. Solution and solid phase techniques. Synthesis of oxytocin, gramicidin, enkephalins, LH-RH. Introduction to peptidomimetics.

References

1. Advanced Organic Chemistry – Reactions, Mechanism and Structure, Jerry March,
1. John Wiley. (1999).
2. Advanced Organic Chemistry, F.A. Carey and R. J. Sundberg, Plenum (1990)
3. A Guide Book to Mechanism of Organic Chemistry, Peter Sykes, Longman (2000).
4. Structure and Mechanism of Organic Chemistry, C.K. Ingold, Cornell University Press.
5. Organic Chemistry, R.T. Morrison and R.N. Boyd, Prentice-Hall (1998).

6. Modern Organic Reactions, H.O. House, Benjamin (1972).
7. Principles of Organic Synthesis, R.O.C Norman and J.M. Coxon, Blackie Academic and Professional.
8. Stereochemistry of Organic Compounds, D. Nasipuri, New-Age International (1999).
9. Stereochemistry of Carbon Compounds, E.L. Eliel, S.H. Wilen and L.N. Mander, John Wiley (1994)
10. Organic Chemistry, Volumes I and II, I.L. Finar, Longman (1999).
11. Medicinal Chemistry, A. Kar, Wiley (2000)
12. Peptides Chemistry: A practical text book, M. Bodanzsky, Springer-Verlag NY (1988).
13. Solid-phase peptide synthesis: A practical approach-E.Artherton & R.C. Sheppard, R.L Oxford Univ. Press (1989)
14. Peptides: Chemistry and Biology, N Selwad and H.D. Jakubke, Wiley-VCH (2002).

JOC 203: Physical Chemistry- II **52 h**

UNIT – I

1. Classical Mechanics **10 h**

Dynamic variables-definition, dimension, units and dimensional analysis. Coordinate systems-rectangular, spherical-polar, Conversion of rectangular coordinates into spherical polar coordinates, volume element, symmetry of space and its relation to conservation laws, Conservation theorems, Conservation of linear momentum, angular momentum and energy. Equation of motion, Newtonian, Lagrangian and Hamiltonian forms and significance of Hamiltonian. Definition of Classical mechanics, Quantum mechanics and relativistic mechanics. Assumptions of classical mechanics, Planck's hypothesis, Failure of classical mechanics - Black body radiation, Photo electric effect, Compton Effect. Limitations of old quantum theory. Classical wave equation, de Broglie's Theory, Heisenberg's uncertainty principle, Schrödinger wave equation from classical wave equation. Eigen value equation. Hydrogen atom spectrum.

UNIT – II

2. Mathematics for Quantum Chemistry **07 h**

Functions - definition, classification. Linearly dependent and independent functions, odd and even functions, Inner product, normalization, orthogonality, ortho normal functions, Kronecker delta-proper function, Eigen functions, need for normalization. Operators-Linear and Hermitian and their properties, position, linear angular momentum, energy operators, Linear and non-Linear operators. Proof for Hermicity of linear momentum, angular momentum, position and Hamiltonian operators. Commutation of various operators - Commutation relation among angular momentum operators Lx, Ly, Lz and L^2.

UNIT – III

3. Quantum Chemistry Applications **10 h**

Wave-particle dualism - Postulates of quantum mechanics-Setting up Schrödinger Wave Equation and solving for particle in a 1D and 3D box, Harmonic oscillator, rigid rotor, Hydrogen atom –Hydrogen atomic orbitals, Analytical and graphical representations, Radial probability distribution function, Orthogonality of 1s,2s,2p orbitals. Stern Gerlach experiment. Concept of spin angular momentum. Coupling of spin angular momenta- Russel Saunders and JJ coupling schemes, Atomic term symbols, Pauli's exclusion principle, Slater determinant.

UNIT – IV

4. Electrochemistry **10 h**

Electrochemistry of solutions: Ionic atmosphere, Physical significance of k (kappa), Debye-Huckel theory to the problem of activity coefficient, Debye Huckel limiting law, Debye Huckel equation for appreciable concentration, The Huckel and Bronsted equation, Qualitative verification of Debye- Huckel equation, Debye-Huckel-Onsagar conductance equation, Bjerrum theory of ion association-triples ion-conductance minima.

UNIT – V

5. Electrical double layer **07 h**

Introduction to electrode-electrolyte interface. Diffuse double layer – Helmholtz-Perrin, Gouy Chappman, Stern Theory of double layer, Thermodynamics of electrified interfaces, concept of surface excess, its determination. Determination of charge density on the electrode. Derivation of electro capillary-Lipmann equation.

UNIT – VI

6. Irreversible electrode process **08 h**

Polarization and Over Voltage, types of Over Voltages. Electrolytic polarisation, dissolution and deposition potential. Determination of anode and cathode overpotential, concentration polarization, Variation of current with cell voltage, metal deposition over voltage, thickness of the diffusion layer, Derivation of Butler-Volmer equation, Exchange current density, factors affecting exchange current density. Influence of Current density, pH, temperature, rate of growth of deposits on Over Voltage.

Theories of Over Voltage: Bubble formation, Combination of atoms, Ion discharge and proton transfer as slow process.

References

1. R. K. Prasad, Quantum Chemistry, 1st Edition, New Delhi, Wiley Easter Ltd (1992)
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9. Text Book of Physical Chemistry- Samuel Glasstone, 2nd edition, Mac Millan India Ltd (1991)
10. Electrochemistry-Principles and Applications, Edmund, C. Potter, Cleaver Hume Press, London (1961)
11. Principles and Applications of Electrochemistry – D. R. Crow, 3rd Edition, Chapman hall, London (1988)

JOC 204: spectroscopy - I **52 h**

UNIT – I

1. Symmetry and Group Theory in Chemistry **07 h**

Principles of Group Theory – Symmetry elements, symmetry operations, Properties of group, Abelian, non-Abelian and cyclic group, Multiplication Tables, Classes, subgroups, Molecular point groups, Schoenflies symbols, Matrices for symmetry operations, Reducible and irreducible representations, Statement of Great Orthogonality theorem, Construction of character tables, C_{2v}, C_{2h}, C_{3v}-Explanation of a character table.

2. Applications of Group Theory **08 h**

Standard reduction formula relating reducible and irreducible representations-Hybridization schemes for atoms in molecules of different geometry, AB tetrahedral, AB triangular planar, AB Linear molecules. Symmetries of vibrational modes in non-linear molecules (H_2O, NH_3 and BF_3), Symmetries of vibrational modes in linear molecules(HCN,CO_2,C_2H_2), Integration method, Selection rules in spectroscopy, Mutual exclusion rule-Symmetry in crystals, Hermann-Mauguin symbols. Space groups of crystals, Translational elements of symmetry, Comparison of crystal symmetry with molecular symmetry.

UNIT – II

4. Microwave Spectroscopy **06 h**

Rotations of molecules, rigid diatomic molecule, rotational energy expression, energy level diagram, rotational wave functions and their symmetry, selection rules, expression for the energies of spectral lines, computation of intensities, effect of isotopic substitution, centrifugal distortion and spectrum of a non-rigid rotor. Rotational spectra of poly atomic molecule-linear, symmetric top and asymmetric top molecules. Stark effect, techniques and instrumentation.

UNIT – III

5. Infrared Spectroscopy **12 h**

Vibrations of molecules, harmonic and anharmonic oscillators-vibrational energy, selection rules, expression of energies of spectral lines, computation of diatomic vibrating rotor, Born-Oppenheimer approximation, vibrational rotational spectra of diatomic molecules, P, Q and R branches, breakdown of the Born-Oppenheimer approximation.

Vibrations of poly atomic molecules: Normal coordinates, translations, vibrations and rotations, vibrational energy levels and wave functions, fundamentals, overtones and combinations.

Vibration-rotation spectra of poly atomic molecules, parallel and perpendicular vibrations of linear and symmetric top molecules, Techniques and instrumentation, FTIR.

6. Raman Spectroscopy **07 h**

Classical theory of the Raman effect, polarizability as a tensor, polarizability ellipsoids, quantum theory of the Raman effect, Pure rotational Raman Spectra of Linear and asymmetric top molecules, vibrational Raman Spectra, Raman activity of vibrations, rule of mutual exclusions, rotational fine structure, O and S branches, Polarization of Raman scattered photons. Structure determination from Raman and IR spectroscopy - AB_2 and AB_3 molecules. Techniques and instrumentation.

UNIT – IV

7. Electronic Spectroscopy **12 h**

Born-Oppenheimer approximation, vibrational coarse structure, intensities by Franck-Condon principle, Dissociation energy, rotational fine structure, Fortrat diagram, pre-dissociation

Electronic structure of diatomic molecules- basic results of MO theory, classification of states by electronic angular momentum-σ,π,δ, and ϕ molecular orbitals, selection rules, spectrum of singlet and triplet molecular hydrogen

Electronic spectra of polyatomic molecules- localized MOs, spectrum of HCHO, change of shape on excitation

Decay of excited states- radiative (fluorescence and phosphorescence) and non-radiative decay, internal conversion

References

1. Group Theory and its applications to chemistry, K.V. Raman, New Delhi, TATA McGraw Hill Co (1990)
2. Chemical Applications of Group theory, F. A. Cotton, Wiley Eastern (1976)
3. Molecular Symmetry, D. S. Schonland, Van Nostrand (1965)
4. Introduction to Molecular Spectroscopy, C. N. Banwell, TMH Edition (1994)
5. Introduction to Molecular Spectroscopy, G. M. Barrow, McGraw Hill, Int. Studens Edition (1988)
6. Molecular Spectroscopy, J. D. Graybeal, McGraw Hill, Int. Studens Edition (1990)

7. Basic principles of spectroscopy, R. Chang, New Jersy, Englewood Cliffs (1978)
8. Spectroscopy vol. 1,2,3 B. P. Straughan and S. Walter, New York and London (1976)
9. Vibrational Spectroscopy , D.N. Satnarayana, New Age Publishers , Latest edition
10. Group theory, D.N. Sathnarayana

JOC 206: Inorganic Chemistry Practical - II

1. Gravimetric analysis

a) Gravimetric determination of Fe in an iron ore as Fe_2O_3.
b) Gravimetric determination of Ni in Cu and Ni solution.
c) Gravimetric estimation of Cu in Cu and Fe solution.
d) Gravimetric estimation of Cu in Cu and Zn solution.
e) Gravimetric estimation of Ni in Ni and Zn solution.

2. Volumetric Analysis

a) Volumetric estimation of Cu in Cu and Ni solution.
b) Volumetric estimation of Fe in Cu and Fe solution.
c) Volumetric estimation of Zn in Cu and Zn solution.
d) Volumetric estimation of Zn in Ni and Zn solution.

3. Analysis of alloys

a) German silver
b) Steel
c) Solder

4. Colorimetry

a) Colorimetric determination of nickel.

References

1. Vogel's Text Book of Qualitative Chemical Analysis, J. Bassett, G.H. Jeffery and J. Mendham, ELBS (1986).
2. Vogel's Text Book of Quantitative Chemical Analysis, J. Bassett, G.H. Jeffery, J. Mendham and R.C. Demmy, 5 th Edition, Longman Scientific and Technical (1999).

JOC 207: Physical Chemistry Practical - II

A. Conductometry

1. Determination of solubility of sparingly soluble salt.
2. Titration of mixture of strong and weak acids against strong base.
3. Titration of mixture of strong acid, weak acid and salt (Copper sulphate) against strong base

4. Titration of weak acid against weak base.
5. Precipitation titration: lithium sulphate against barium chloride.
6. Dissociation constant of weak electrolyte (weak base-NH_4OH; weak acid-CH_3COOH).
7. Verification of Onsagar's equation – determination of λ_0 of an electrolyte.

B. Potentiometry

8. Determination of single electrode potential of Cu^{2+}/Cu and Zn^{2+}/Zn and testing the validity of Nernst equation.
9. Determination of pH of buffers by using quinhydrone electrode and comparison of the pH values obtained with glass electrode.
10. Determination of mean ion activity coefficient of HCl by emf method.
11. Potentiometric titration of ferrous ammonium sulphate against potassium dichromate - calculation of formal redox potential of Fe^{3+}/Fe^{2+}.
12. Potentiometric titration of potassium iodide against potassium permanganate.
13. Titration of silver nitrate against potassium chloride.
14. Determination of EMF of a concentration cell and calculation of solubility product of AgCl.
15. Titration of weak acid against strong base using quinhydrone electrode and calculation of pKa value of the weak acid.
16. Titration of a mixture of HCl and CH_3COOH potentiometrically and determination of the composition of the mixture.

References

1. Advanced Practical Chemistry by J.B. Yadav, Goel Publication House, Merrut (1989).
2. Experiments in Physical Chemistry by Shoemaker and Garland, McGraw Hill International edn. (1996).
3. Experimental Physical Chemistry, V.D. Athawale and Parul Mathur, New Age International, New Delhi (2001).

III Semester M.Sc. Chemistry (Organic)

JOC 301: Organic Reaction Mechanisms **52 h**

UNIT I

1. Aliphatic Nucleophilic and Electrophilic Substitution Reactions **11 h**

Nucleophilic substitution reactions- Substitution at allylic, vinylic and trigonal carbon atoms. Hydrolysis of esters- mechanisms. Use of DCC in the formation of anhydrides. Neighbouring group participation. Selected reactions: Von Braun reaction, Dieckmann condensation and Williamson reaction.

***Aliphatic electrophilic substitution reac*tions**-S_E1, S_E2 and S_Ei mechanisms- Effect of structure, leaving group, attacking nucleophile and solvent- Selected reactions- Migration of double

bonds- Halogenation of aldehydes, ketones and acids- Aliphatic diazonium coupling, nitrosation at carbon and nitrogen, diazo transfer reactions, carbene and nitrene insertion, decarboxylation of aliphatic acids, haloform reactions, Haller-Bauer reaction.

UNIT II

2. Free-radical Chemistry **08 h**

Generation of free-radicals: Thermal homolysis of peroxides, peresters and azo compounds, photochemical methods.

Hydrogen abstraction, chain process- Stability – Steric, resonance and hyperconjugative effects and stereochemistry of free radicals.

Free radical reactions- Addition, Substitution, elimination, rearrangement and electron transfer reactions. Neighbouring group assistance in free radical reactions. Reactivity for aliphatic substrates, reactivity at a bridgehead, reactivity in aromatic substrates. Use of free radicals in organic synthesis.

Orton reaction, Gomberg-Bachmann reaction, Meerwein arylation, Sandmeyer reaction, Kolbe reaction and Hunsdiecker reaction.

UNIT III

3. Photochemistry **12 h**

General consideration- Activation in thermal and photochemical reactions. Light absorption and excitation- Singlet and triplet states. Morse curve, Frank – Condon principle.

Deexcitation: Physical process, Jablonski diagram, Photosensitization (donor acceptor concept, resonance and collision transfer)-Chemical process, quantum efficiency- quantum and chemical yields.

Photochemistry of functional groups:

i) ***Olefins:***Cis-trans isomerism,[2+2] Cycloaddition, rearrangements. Reactions of conjugated olefins, di-π methane rearrangement.

ii) ***Ketones*****:** Excited state of C=O. *Norrish type-I* and *type- II* cleavages. Paterno-Buchi reaction. α,β-unsaturated ketones. [2+2] addition, cis-trans isomerisation, rearrangements of cyclohexadienones.

iii) ***Aromatic compounds*****:** Photo rearrangement of benzene and its derivatives and cycloaddition of benzene.

iv) ***Photochemical oxidations and reductions*****:** Cycloaddition of singlet molecular oxygen. Oxidative coupling of aromatic compounds and photoreduction by hydrogen absorptions.

UNIT IV

4. Pericyclic reactions **11 h**

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. FMO and PMO approach.

Electrocyclic reactions: conrotatory and disrotatory motions. 4n, 4n+2 and allyl systems.
Cycloadditions: antarafacial and suprafacial additions[$_{\pi}m_s + {}_{\pi}n_a$] and [$_{\pi}m_s + {}_{\pi}n_s$]-cycloadditions. [$_{\omega}2_a + {}_{\pi}2_s$] and [$_{\pi}4_s + {}_{\omega}2_s$]-cheletropic reactions. Regio, enantio and Endo selectivities in Diels-Alder reactions. Hetero Diels-Alder reaction.
Sigmatropic rearrangements: suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties. [*i, j*]- sigmatropic rearrangements (including Walk, Claisen, Cope, oxy and aza-Cope rearrangements).

UNIT V

6. Biochemical mechanisms **10 h**

Introduction- The mechanistic role of the following in living systems:

i) Thiamine pyrophosphate (TPP) in decarboxylation of α-ketoacids and in the formation of α-ketols
ii) Pyridoxal phosphate (PLP) in transamination, decarboxylation, dealdolisation and elimination reactions of amino acids
iii) Lipoic acid in the transfer of acyl group reactions
iv) Coenzyme A (CoASH) in the transfer of acyl group
v) Biotin in the carboxylation reactions
vi) Tetrahydrofolic acid (H4F) in one- carbon transfer reactions
vii) Vitamin B_{12} coenzymes in molecular rearrangement reactions and in the synthesis of methionine and methane
viii) Nicotinamide in biological redox reactions
ix) Flavin coenzymes in biological redox reactions
x) Vitamin KH_2 coenzyme in carboxylation reactions

References

1. Understanding Organic Reaction Mechanisms, A.Jacob, Cambridge Univ.Press, 1997.
2. Introduction to Organic Chemistry, A.Streitweiser.Jr. and C.H.Heathcock, Macmillan 1998.
3. Physical and Mechanistic Organic Chemistry, R.A.Y. Jones, 1st Edn.Cambridge Univ. Press, 1979.
4. P.J.Garratt in Comprehensive Organic Chemistry, D.Barton and W.D.Ollis 1st Edition, Pergamon Press, Oxford, 1979.
5. Mechanisms of Molecular Migrations, Vol I and II, B.S.Thiagarajan, 1st Edition, Pergamon Press, Oxford, 1979.
6. Radicals in Organic Synthesis, B.Giese, Pergamon Press, 1986.
7. Stereoelectronic effects in Organic Chemistry, P.Deslongchamps, 1st Edition, Pergamon Press, 1983.
8. Frontier Orbitals and Organic Chemical Reactions, Ian Fleming, John Wiley, 1980.
9. Molecular Orbital Theory for Organic Chemistry, A.Streitweiser, 1st Edition, Wiley & sons, NY 1969.

10. Organic photochemistry, J.M.Coxon and B.Halton, 1st Edition, Cambridge Univ.Press, London 1974.
11. Orbital symmetry, R.E.Lehr and A.P.Marchand, Academic Press, 1972.
12. Molecular reactions and photochemistry, C.H.Deputy and D.S.Chapman, 1st Edition, Prentice-Hall India, New Delhi, 1972.
13. Advanced Organic Chemistry, Jerry, March 4th Edn, John Wiley and sons, 1999.
14. Bio chemistry, G.Zubey, Macmillan, NY, 1998.
15. Bio chemistry, D.Voet and J.G.Voet, John Wiley and sons, 1998.
16. Principles of Biochemistry, A.L.Lehninger, D.L.Nelson and M. M.Cox, 2nd Edition, Worth Publishers, NY 1999.

JOC 302: Organic Synthetic Methods - I **52 h**

UNIT I

1. C-C and C-N bond forming reactions **13 h**

Friedel-Crafts reactions, Diels-Alder reaction, Chichibabin reaction, Darzen's reaction, use of acetylides in C-C bond formation reactions. Acid catalysed self-condensation of olefins, Skraup synthesis, Prins reaction, Shapiro reaction, Reformatsky reaction, Robinson annulation, Hofmann-Loeffler-Freytag reaction.

Stork-enamine synthesis, Meyer synthesis. Use of nucleophilic nitrogen and electrophilic carbon (NH_3, amines and nitrite as nucleophiles in substitution; NH_3 and amines in addition to ketones and aldehydes) and electrophilic nitrogen and nucleophilic carbon (nitration) in bond formation reactions.

UNIT II

2. Reagents in Organic Synthesis **11 h**

Use of the following in Organic synthesis and functional group transformations:

LDA, DCC, DDQ, TMS-iodide, 1.3-Dithiane (reactivity and umpolung), Merrified resin, Baker's yeast. Woodward and Prevost hydroxylation, Diazomethane, Raney nickel, Aluminum isopropoxide, N-bromo succinamide, Me_3SiCl, Fenton's reagent

UNIT III

3. Oxidations **09 h**

CrO_3, $K_2Cr_2O_7$, $KMnO_4$, OsO_4, SeO_2, $Pb(OAc)_4$, HIO_4, Oxygen (singlet & triplet), Ozone, peroxides and peracids as oxidizing agents. Jones reagent and Chromyl chloride

Dess Martin Reaction

UNIT IV

4. Reductions **09 h**

Complex metal hydrides, dissolving metal reductions, diimide reduction, catalytic hydrogenation (homogenous and heterogenous), tri-n-butyltin hydride, organoboranes, LAH, Na/NH_3, NAH, $NaBH_4$, hydrazine as reducing agents. Meerwein-Ponndorf-Vereley, Wolf-Kishner and Clemmensen reductions

UNIT V

5. Molecular Rearrangements **10 h**

Benzil-Benzilic acid rearrangement, Arndt-Eister reaction, Tiffeneau-Demjanov reaction, Fritsch-Buttenburg-Wiechell rearrangement; Stevens, Wittig, Favorski and Fries rearrangements; Baeyer-Villiger Oxidation, Neber rearrangement, Fischer indole synthesis and Benzidine rearrangement

References

1. Advanced Organic Chemistry, J. March, 4th Edition, John Wiley, 1999
2. Organic Synthesis, R.E.Ireland, Prentice-hall India, New Delhi, 1975
3. Understanding Organic reaction mechanisms, A.Jacob, Cambridge Univ Press, 1997
4. Introduction to Organic Chemistry, A.Streitwiser Jr. and C.H.Heathcock, Macmillan, 1985
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7. Some Modern Methods of Organic synthesis, W.Carruthurs, Cambridge Univ. Press, London, 2nd Edition, 1978
8. Mechanism of Molecular Migration, Vol I & II, B.S.Thyagarajan, Pergamon Press, Oxford, 1979
9. Comprehensive Organic Chemistry, D.Barton and W.D.Wallis, Pergamon Press, Oxford, 1983
10. Organic Chemistry, Vol II, I.L.Finar 6th Edition, Longman, 1992

JOC 303: Spectroscopy – II **52 h**

UNIT I

1. Ultraviolet and visible spectroscopy **03 h**

Classification of electronic transitions, Terminology, Substituent and solvent effects, UV spectral study of alkenes, polyenes, enones and aromatic compounds. Empirical rules for calculating λ_{max}

UNIT II

2. Vibrational Spectroscopy: spectroscopy 09 h

Sampling techniques, Group frequencies, factors affecting group frequencies, Bond order, Mass effect, Conjugation, Inductive, resonance, steric effects and Intramolecular interactions. Application of IR in the study of H-bonding, stereoisomerism and tautomerism. Complementarity of IR and Raman.

Identification for the following organic compounds by IR: Alkanes, Alkenes, Alkynes, Aromatic compounds, Aldehydes, Ketones, Alcohols, Acids, Acid chlorides, Amides, Amines, Esters, Halides, Nitro compounds, etc., problems using UV and IR.

UNIT III

3. Nuclear magnetic resonance spectroscopy 15 h

Introduction, Magnetic properties of nuclei-Resonance condition. Nuclear spin, population of nuclear spin levels and NMR isotopes, Realization methods. Instrumentation and sample handling, FT-NMR.

Chemical shift- Mechanism of shielding and deshielding in alkanes, alkyl halides, alkenes, aromatic compounds, carbonyl compounds and annulenes. Pascal's triangle-low and high resolution, spectrum of ethanol. Karplus Curve, Diamagnetic and paramagnetic effects and magnetic anisotropy. Equivalence of protons-chemical and magnetic equivalence. Spin-systems: First order and second order coupling of AB systems, Simplifications of complex spectras. Problems.

Spin-spin interactions- AX, AX_2, AX_3, AMX, AB types. Vicinal, geminal and long range coupling-Spin decoupling. Chemical shift reagents and deuterium exchange. Stereochemistry and hindered rotations. Temperature effects.

CIDNP, Nuclear Overhauser Effect (NOE). Factors influencing coupling constants and Relative intensities. Protons attached to elements other than carbon.

4. ^{13} C NMR and Correlation Spectroscopy 10 h

^{13} C NMR Spectroscopy- Types of CMR spectra-undecoupled, proton decoupled and off-resonance decoupled. Selectivity decoupled and gated decoupled spectra. ^{13}C chemicals shifts of Alkanes, Alkyl halides, Alkenes, Alcohols, Ethers, Carbonyl compounds and aromatic compounds, Factors affecting the chemical shifts. Applications of ^{13}C NMR Spectroscopy in confirmation of structure; Introduction to 2D-NMR Pulse sequences. FT-Methods. Classification of 2D Experiments. 2D-J-resolved spectroscopy. HOMO and HETERO-2D-J-Resolved spectra. Correlation Spectroscopy (COSY). Homonuclear (^{13}C-^{13}CJ), and heteronuclear (^{13}C-^{1}H,^{13}C-^{2}HJ) couplings, DEPT. Explanation of the principle, applications to structure elucidation of simple organic molecules.

UNIT IV

5. Mass spectrometry and Composite Problems 08 h

Basic principles-instrumentation – ion production-ion analysis-magnetic sector instruments-Quadruple mass spectrometers; Time of flight mass spectrometers-ion cyclotron resonance spectrometers- Mass spectrum-molecular ion-types of ions in mass spectra and effects of isotopes on mass spectra. Methods of ionization, EI, FAB mass and MALDI methods; Fragmentation of: Alkanes, Alkenes, alkyl halides, alcohols, aldehydes, ketones, acids, esters, ethers, amines, nitro and halo compounds Nitrogen rule, Factors affecting cleavage patterns McLafferty and McLafferty +1 rearrangement. Determination of molecular formula. Composite problems. Use of HRMS to determine exact molecular formulae of compounds

UNIT V

6. Problems based on Spectral Data 07 h

Application of NMR and MS methods and chemical reactions in structure elucidation of organic compounds.

References

1. Applications of Absorption Spectroscopy to Organic compounds, J.R.Dyer, Prentice- Hal, New Delhi, 1969.
2. Organic Spectroscopy, P. Laszlo and P.Stang, Harper &Row, New York, 1971.
3. Organic Spectroscopy, W.Kemp, ELBS London, 2000.
4. Spectrometric Identification of Organic Compounds, R.M.Silverstein and W.P.Weber, 2005.
5. Introduction to Spectroscopy, 3rd Edition, D.L.Pavia, G.M.Laupman and G.S.Kriz, Harcourt College Publishers, 2001.
6. Organic Mass Spectroscopy, K.R.Dass & E.P.James, IBH New Delhi, 1976.
7. Interpretation of Organic Mass Spectra, F.W.McLafferty, W.A.Benjamin, London, 1973.
8. Practical Organic Spectroscopy, 2nd Edn. J.R.Chapman, John Wiley, NY, 1993.
9. The IR Spectra of Complex Molecules, Vol. I & II, L.J.Bellamy, Chapman and Hall, London 1975.
10. Spectroscopic Techniques for Organic Chemists, J.W.Cooper, John Wiley, NY, 1980.
11. Biomolecular NMR Spectroscopy, JNS Evans, Oxford Univ, 1995.
12. Mass Spectrometry-a foundation course, K.Downard, RSC, Cambridge, 2004.
13. Mass Spectrometry of Organic Compounds, H.Budzkiewicz, Djerassic and D.H.Williams, Holden Day, NY, 1975.
14. Modern NMR Techniques and Their Applications, Ed.A.I.Popou, Marcel Dekker, 1991.
15. Modern Structural Theory of Organic Compounds, L.N.Ferguson, Prentice-Hall, New Delhi, 1973.
16. Instrumental Methods of Analysis, H.H.Williard, L.L.Merrit, I.A.Dean and F.A.Settle, CBS Publishers and Distributors, 1986.

17. Fundamentals of Molecular Spectroscopy, 4th Ed., C.N.Banwell and E.M.McCash, Tata McGraw – Hill, New Delhi, 1999.

JOC 304: Chemistry of Natural Products **52 h**

UNIT I

1. Terpenoids **11 h**

Classification, nomenclature, occurrence and isolation. Isoprene rules – stereochemistry of Citral, farnesol, limonene, 1,8-cineole, menthols and borneols - Correlation of configuration of terpenoids.

Structural elucidation of α- pinene, camphene, β-caryophyllene, α – santonin and gibberrillic acid.

Synthesis and biosynthesis of the following:

Linalool, α-terpeneol, fenchone, eudesmol and abietic acid. Commercial synthesis of camphor- Biosynthesis of squalene and cyclisation of squalene into α-lanosterol and friedelene.

UNIT II

2. Steroids **12 h**

Occurrence, Nomenclature, basic skeleton, Diels hydrocarbon and stereochemistry – Isolation, structure and structural elucidation of sterols and bile acids. Sex hormones, Cortico-steroids. Synthesis of Cholestrol, estrone, progesterone, epiandrosterone, testosterone – Photo products of ergosterol- Vitamin D. Barton reaction for the synthesis of aldosterone.

Marker degradation. Brief discussion of (dl) norgestrel and ethinyl oestradiol – Manufactures as applicable.

UNIT III

3. Alkaloids **10 h**

Definition, Nomenclature, Occurrence, isolation, classification-General methods of structural elucidation.

Synthesis and biosynthesis of the following alkaloids:

Ephedrin, hygrine, coniine, cocaine, cinchonine and morphine – structural elucidation of papaverine, reserpine and ergotamine.

Photochemical synthesis of Nuciferine, coradyline and tylophorine.

UNIT IV

Porphyrins and Vitamin B_{12} **07 h**

Structure and synthesis of haemin and chlorophyll – a, Vitamin B_{12} – structure elucidation and synthesis from cobyric acid only

UNIT V

4. Prostaglandins, Prostacyclins and thromboxanes **07 h**

Introduction, Nomenclature, classification and biological role of prostaglandins, prostacyclins and thromboxanes. Structural elucidation and stereochemistry of PGE_1 PGE_2 and PGE_3. Synthesis of PGE_1 and $PGE_2$by Corey's and Stork's approaches, $PGE_3$by Upjohn's approach – synthesis of prostacyclin $I_2$and thromboxane B_2.

UNIT VI

5. Insect Pheromones: **05 h**

Introduction, Classification, Pheromones in pest control.

Synthesis of i) Grandisol (component of boll weevil pheromone)
ii) Farenal (trail pheromone of pharaoh's ants)
iii) Brevicomin (pheromone from Dendroitis brevicomis)
iv) (+) – Disparlure (gypsy moth sex pheromone)
v) 3,11-Dimethyl-1,2-nonacosanone (pheromone of GermanCockroaches)
vi) Bombykol (sex pheromone of silkworm moth)
vii) Multistriatin (Elm bark beetle sex pheromone)

One synthesis should be stereoselective.

References

1. Natural Products: Their Chemistry and Biological Significance- J.Mann, R.S.Davidson, J.B.Hobbs, D.V.Banthorpe & J.B.Harbone, Longman, UK, 1994.
2. Terpenes, J.Verghese, Tata McGraw- Hill, New Delhi, 1982.
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4. Handbook of Naturally Occurring Compounds Vol II: Terpenes, T.K.Davon, A.I.Scott, Academic Press NY, 1972.
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6. Total Synthesis of Natural Products Vol I & VI, Apsimon, John Wiley, NY, 1973-1981.
7. Organic Chemistry Vol II, I.L.Finar, 6^{th} edn. Longman,1992
8. Chemistry of Natural Products Vol I & II, O.P.Aggarwal, Goel Publishing house, 6^{th} edn. 1982.
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10. Medicinal Natural products: A biosynthetic approach, P.M.Dewick, John Wiley, Chichester, 1997.
11. The Colours of Life, An introduction to the chemistry of porphyrins and related, L.R.Milgrom, Wiley Chichester, 1995.
12. Interpretation of the UV Spectra of Natural Products, A.I.Scott, Pergamon Press, Oxford, 1964.

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14. Chemistry of Natural Products: A Unified Approach, N.R.Krishnaswamy, University Press, India, 1999.
15. Organic Chemistry Vol I & II, I.L.Finar Longman, 1999.

JOC 305: Organic Chemistry Practical – I

A. Preparation (Single stage):

1. Cannizarro reaction: Benzaldehyde.
2. Claisen-Schmidt reaction: acetone and benzaldehyde.
3. Sandmeyer reaction: p- Chlorotoluene from p-toluidine.
4. Pechmann reaction: Resorcinol and ethylacetoacetate.
5. Oxidation of cyclohexanol.
6. Preparation of S-benzylisothiuronium chloride.
7. Synthesis of p-iodonitrobenzene.
8. Synthesis of N-phenyl-2,4-dinitroaniline.
9. Synthesis of 2,4,6-tribromoaniline.
10. Synthesis of 2,4-dichlorophenoxyacetic acid.
11. Fries rearrangement: Phenyl acetate.
12. Friedel –Crafts reaction: Benzene and Acetyl chloride.

B. Qualitative analysis:

Separation and systematic analysis of a binary mixture of organic compounds

JOC 306: Organic Chemistry Practical - II

A. Preparation (Two and Three stages):

1. p-nitroaniline from acetanilide.
2. p-bromoaniline from acetanilide.
3. m-nitrobenzoic acid from methyl benzoate.
4. Anthranilic acid from phthalic acid.
5. 2,4-dinitrophenylhydrazine from chloronitrobenzene.
6. Benzanilide from benzophenone.
7. Benzilic acid from benzoin.
8. Synthesis of acridone.
9. Synthesis of hydantoin.

B. Quantitative analysis:

1. Determination of equivalent weight of mono/dicarboxylic acids.

2. Estimation of glucose (Fehling's method).
3. Estimation of keto group.
4. Estimation of amines by acylation method.
5. Estimation of phenols by acylation method.
6. Saponification value of oil.
7. Iodine value of oil (chloramine-T method).

References

1. Laboratory Manual of Organic Chemistry - B. B. Dey, M. V. Sitaraman and T. R. Govindachari, Allied Publishers, New Delhi, (1996).
2. Practical Organic Chemistry-Mann and Saunders, (1980).
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4. Test Book of Quantitative Organic Analysis-A.I.Vogel, (1996).
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7. Comprehensive Practical Organic Chemistry: Qualitative analysis, V.K.Ahluwalia, S.Dhingra, Universities Press (India), 2000.
8. An Advanced Course in Practical Chemistry, A.Ghoshal, B.Mahapatra and A.Kr.Nad, New central book agency, Calcutta, 2000.
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11. Laboratory Techniques in Organic Chemistry, V.K.Ahluwalia, Pooja Bhagat and Renu Aggarwal, I.K.International Publishing House, New Delhi, 2005.
12. Intermediates for Organic Synthesis, V.K.Ahluwalia, Pooja Bhagat, Ramesh Chandra and Renu Aggarwal, I.K.International Publishing House, New Delhi, 2005.

IV Semester M.Sc. Chemistry (Organic)

JOC 401: Stereochemistry and Reactivity **52 h**

Unit I

1. Stereochemistry I **10 h**

Optical activity in the absence of chiral atoms

Chirality in biphenyls, adamantanes, ansa compounds, cyclophanes, *trans*-cyclooctene, catenanes, rotaxanes and helicenes. Assignment of R, S - configuration to these classes of compounds.

Optical activity due to the presence hetero atoms

Chirality of organic compounds due to the presence of silicon, nitrogen, phosphorous, arsenic and sulphur atoms. Determination of R, S - configuration of these compounds using CIP rules.

Unit II

2. Stereochemistry II **12 h**

Methods of determining absolute configuration

i) Chemical correlation: a) without affecting bonds attached to a stereo centre and b) affecting bonds attached to a stereo centre in a predictable manner and c) involving diastereomers.

ii) Optical rotatory dispersion: α-axial haloketone rule and octant rule, application of these rule in the determination of absolute configuration of cyclohexanones, decalones and cholestanones.

iii) Study of quasi-racemates.

iv) Anomalous X- ray scattering technique.

Transannular reactions

Conformational analysis of medium rings. Trasnannular reactions: Hydrolysis of medium ring epoxides and bromination of C_8–C_{10} cyclic dienes.

Unit III

3.Retrosynthetic Analysis I **17 h**

Disconnection approach

Introduction to synthons, and synthetic equivalents, disconnection approach. Basic principles and terminologies used in disconnection approach. One group C-X and two group C-X disconnections. Chemoselectivity, reversal of polarity, cyclisation reactions.

Protecting groups

Principle of protection of alcohols, amines, acids and carbonyl groups

C-C one group and C-C two group disconnections

Alcohols, carbonyl compounds, alkenes. Use of acetylides and aliphatic nitro compounds in organic syntesis. Diels-Alder reaction, 1,3-difunctionalised compounds, α,β-unsaturated compounds, carbonyl compounds condensations, 1,5- difunctionalised compounds. Michael addition and Robinson annelation.

Unit IV

4. Retrosynthetic Analysis I **13 h**

Ring Synthesis

Saturated heterocycles, synthesis of 3-, 4-, 5- and 6-membered rings.

Synthesis of some complex molecules

Application of the above in the synthesis of following compounds.

Camphor, longifloene, cortisone, reserpine, vitamin-D, juvabione, aphidicolin and fredericamycin-A.

References

1. Stereochemistry of carbon compounds, E. L. Eliel, S. H. Wilen and L. N. Mander, John Wiley & Sons, 1994.
2. Stereochemistry, Potapov, MIR, Moscow, 1984.
3. Stereochemistry, Nasipuri, D, New Age, 1999.
4. Advanced organic chemistry, J. March, 4th Edn. John Wiley, 2008.
5. Organic Chemistry, R. E. Ireland Prentice-Hall India, New Delhi, 1975.
6. Some modern methods of Organic Synthesis, W. Caruthers, Cambridge Uni. Press London, 2nd Edn., 1998.
7. Stereochemistry of organic compounds- Principle and applications, D. Nasipuri, 2nd Edn., New Age International Publishers, 2001.
8. Organic synthesis: The synthon approach, S. Warren, John Wiley & Sons, New York, 1st. Edn. 1983.
9. Designing organic synthesis: A disconnection approach, S. Warren, John Wiley & Sons, New York, 2nd Edn. 1987.
10. Organic synthesis, C. Willis and M. Wills, Oxford University Press, 1995.
11. Organic synthesis: Concepts, methods and starting materials, J. Furhfop and G. Penzillin, Verlag VCH.
12. Principles of organic synthesis, R. Norman and J. M. Coxon, Blackie Academic & Professional.
13. Advanced organic chemistry Part B, F. A. Carrey and J. Sundberg, Plenum Press, 1999.
14. Organic chemistry Vol. 2, 6th Ed., I. L. Finar, Longman, 1992.

JOC 402: Organic Synthetic Methods - II **52 h**

Unit I

1. Asymmetric Synthesis **20 h**

'*ee*' and methods of determination of '*ee*'.

Stereoselectivity

Classification, terminology and principle. Asymmetric synthesis and asymmetric induction

Double diastereoselection and double asymmetric induction

Acyclic stereoselection

Addition of nucleophiles to carbonyl compounds (1,2- 1,3- and 1,4-asymmetric induction), Asymmetric aldol condensation, addition of allylmetal and allylboranes to carbonyl group.

Diastereoselection in cyclic systems

Nucleophilic addition to cyclic ketones (formation of axial and equatorial alcohols, catalytic hydrogenation, alkylation, diastereoselective oxidations and stereoselective cyclization of poylenes)

Enantioselective synthesis

Reduction with chiral hydride donors [(S)-PBMgCl, (-)-^{i}BOAlCl$_2$, alpine-borane, (S)-BINAL-H, (R,R)-DIOP, and (S,S)-CHIRAPHOS)

Enantioselective alkylation of ketones via hydrazones. Enantioselective alkylation with chiral PTC. Enantioselective Michael addition. Enantioselective intramolecular aldol condensation. Use of (+)- and (–)- DET in asymmetric epoxidation.
Polymer-bound chiral catalysts in asymmetric induction. Asymmetric amplification.

Unit II

2. Organic Synthesis under the Influence of Ultrasound and Microwaves **06 h**

Use of ultrasound

Introduction, instrumentation, the phenomenon of cavitation Sonochemical esterification, substitution, addition, alkylation, oxidation, reduction and coupling reactions

Use of Microwaves

Introduction, concept, reaction vessel, reaction medium, specific effects, atom efficiency (% atom utilization), advantages and limitations. N-alkylation and alkylation of active methylene compounds, condensation of active methylene compounds with aldehydes. Diels-Alder reaction, Deprotection of esters and silyl ethers, reductive amination of ketones, oxidation of alcohols and sulfides

3. Ionic-liquids **02 h**

Introduction, structure, synthesis and applications of some important ionic liquids in organic synthesis

Unit III

4. Polymer supported reagents and synthesis **06 h**

Introduction- properties of polymer support, advantages of polymer supported reagents and choice of polymers. Application: Substrate covalently bound to the support-synthesis of oligosachcharides, intramolecular cyclization reactions (Dieckmann cyclization), solid-state Edman degradation, Preparation of polymer bound aldehyde and application in aldol and Wittig reactions. Synthesis of polystyryl boronic acid and use in diol protection reaction

Reagent linked to a polymeric material: sulfonazide polymer in diazotransfer reaction, polymeric n-butyl- triphenylphosphonium bromide in Wittig reaction, polymer bound per acid and its applications. Polymer supported catalytic reactions- acetal from polymer supported $AlCl_3$ and application in etherification and acetal formation reactions

5. Phase transfer catalysis and Crown ethers **06 h**

***Phase transfer catalysis*:** Introduction, definition, mechanism of phase transfer catalysis, advantages and types of phase transfer catalysts. Preparation of catalysts and applications: substitution, elimination, addition, alkylation, oxidation and reduction reactions.

Crown ethers: Introduction, nomenclature, features, nature of donor site. General synthesis of crown ethers. Synthetic applications: alkylation, anhydride formation, generation of carbenes,

aromatic substitution and displacement reactions, generation and application of superoxide anions, cation deactivation reaction.

Unit IV

6. Nonbenzenoidand Polycyclic Aromatic Compounds **06 h**

***Nonbenzenoid aromatic compounds*:** Introduction, synthesis of cyclopropenyl cations, cyclobutadienyl dications, cyclopentadienyl anions, cycloheptatrienium cation, cyclooctatetraenyl dication, [10]-, [14], and [18]-annulenes, azulene and their reactions.

***Polycic aromatic compounds*:** Introduction, nomenclature, preparation of anthracene, phenenthrene, naphthacene, chrysene, picene, pyrene, perylene, coronene and lapachol. Reactions of anthracene and phenanthrene.

7. Pesticides and Insecticides **06 h**

Introduction, classification

***Naturally occurring insecticides*:** Rotenones, pyrethrins, precocenes

***Synthetic insecticides*:** Introduction, classification, mode of action and synthesis of chlorinated insecticides (DDT, chlordane, heptachlor and hexachlorocyclohexane)

Organophosphorous insecticides: Malathion, parathion, DDVP, diazenon.

Carbamate insecticides: Sevin, carbofluron, aldicab, beygon.

Introduction to the use of the following in the control of pests and insects: Fumigants, nematicides, acaricides, hormones (juvenile hormone), insect repellents, molluscicides and rodenticides.

References

1. Polymer science, V.R. Gowariker, N.V.Vishwanathan & J. Sreedhar, Wiley Eastern Ltd. 1986.
2. Polymers: Chemistry & physics of modern materials J. M. G. Cowie, International Text Books Co Ltd 1973.
3. Chemical process industrial chemistry, 3rd Edn. McGraw-Hill, 1967.
4. Riegels handbook of industrial chemistry, James A. Kent, 7th Edn. 1974.
5. Basic organic chemistry Part-V: Industrial products, J. M. Tedder, A. Nechuvatal & A. H. Jubb, John Wiley & Sons, 1975
6. A textbook of organic chemistry, V. K. Ahluwalia and M. Goyal, Narosa Publishing House, New Delhi, 2000.
7. Organic synthesis: Special techniques, V K Ahluwalia and R Aggarwal, Narosa, New Delhi, 2001.
8. Green Chemistry, environment friendly alternatives, R. Sanghi and M M Srivastava, Narosa, New Delhi, 2003.
9. Green Chemistry-an introduction text, Royal Society of Chemistry, UK, 2002,

10. Stereochemistry of carbon compounds, E. L. Eliel, S. H. Wilen and L. N. Mander, John Wiley & Sons, 1994.
11. Stereochemistry, Potapov, MIR, Moscow, 1984.
12. Stereochemistry, Nasipuri, D, New Age, 2001.
13. Advanced organic chemistry, J. March, 4th Edn. John Wiley, 2008
14. The text book of polymer science, F. W. Billmeyer, Jr, Wiley Interscience, 1984.
15. Principles and applications of asymmetric synthesis, G D Lin, Y M Li and A S C Chan, Wiley Interscience, 2001.

JOC 403: Organometallic and Heterocyclic Chemistry **52 h**

Unit I

1. Organometallic compounds in organic synthesis - I **05 h**

Chemistry of Organotransition metal complexes

General introduction, 18- and 16-Electron rules, Green rules

Complexation and De-complexation Reactions

s-bonded systems including η_1 ligands, p-bonded systems involving η_2 to η_3 ligands such as-olefins, acetylenes, allyl moieties, butadiene, cyclobutadiene, cyclopentadienyl, arenes, cycloheptatrienyl and cyclooctatetraene moieties

Unit II

2. Organometallic compounds in organic synthesis - II **12 h**

Organotransition metal complexes as protecting and stabilizing groups Protection of olefins, acetylenes, diene; Stabilization of cyclobutadienes and norbornadienones

Organometallics as electrophiles and nucleophiles

Nucleophilic addition to η_2, η_5 and η_6 complexes; Electrophilic addition to η_4, η_6 and carbene complexes

Organometallics in coupling and cyclization reactions

Coupling and cyclization of organic nucleophiles with olefins (Heck reaction) and coupling of olefins with acetylenes (Felkin's reaction)

Organometallics in isomerization, oxidation and reduction reactions

Isomerization of olefins, allylic alcohols and allylic ethers; Oxidation of olefins (Wacker's process and epoxidation); reduction of olefins and α,β-unsaturated compounds (Wilkinson's reaction)

Carbonylation reactions

Use of zirconium complexes in the synthesis of esters, acids, aldehydes or acyl halides from alkyl halides and in the hydroformylation of olefins and dienes

Use of iron complexes for the insertion of CO group into organic molecules such as dienes, alkyl halides, and vinyl epoxides

Use of cobalt complexes in the synthesis of ketones from epoxides, lactones from allylic alcohols and in the hydroformylation of olefins

Use of palladium complexes for the carbonylation of alkyl halides, dienes and allenes

Unit III

3. Organometallic compounds in organic synthesis - III 13 h

Application of the following organometallics in Organic Synthesis

***Organozincs*:** Preparation, reaction with compounds containing acidic protons, C-C multiple bonds, trans-metallation, addition reactions of zinc reagents with carbonyl compounds; Simmons Smith and Reformatsky reactions

***Organolithiums*:** Preparation, deprotonation reactions, nucleophilic addition reactions, reactions with imines, nitriles and isonitriles

Organocopper reagents (Gilman reagents - lithium dialkyl cuprates): Preparation, reactions with alkyl, allyl, vinyl, benzyl and aryl halides, aldehydes, ketones (including α,β-unsaturated carbonyl compounds) and epoxides

***Organoseleniums*:** Preparation, Use in the synthesis of alkenes from alkyl halides, α,β-unsaturated carbonyl compounds from carbonyl compounds

Organotelluriums:Debromination of vic-dibromides, deoxygenation of epoxides, oxidation of hydroquinone and synthesis of biaryls

***Organoaluminiums*:** Preparation, hydroalumination and carboalumination of alkenes, nucleophillic addition reactions with carbonyl compounds, hydrocyanation, preparation of alkenyldialkylalanes and their reactions

***Organosilicons*:** Introduction, preparation and general reactions of trialkylsilyl halides, Peterson olefination

***Organotins*:** Preparation and reactions of tri-*n*-butyltin hydride, Barton decarboxylation and Barton- McCombie reaction

***Organocerates*:** Preparation and reactions of organocerates

***Organomercurials*:** Preparation, electrophilic substitution reactions, solvomercuration, de-mercuration and cyclopropanation of alkenes

Unit IV

4. Heterocyclic chemistry I 11 h

***Small ring heterocycles*:** Properties and reactions of 3- and 4- membered heterocycles: oxiranes, thiranes, aziridines, azetidines, oxetanes and thietanes.

***Benzo-fused heterocycles*:** Synthesis and reactions of benzofurans, benzothiophenes, benzoxazoles, benzothiazoles and benzimidazoles.

***Six-membered heterocycles with two or more heteroatoms*:** Synthesis of Diazines, triazines, tetrazines and thiazines.

Unit V

5. Heterocyclic chemistry II **11 h**

***Seven and large membered heterocycles*:** Synthesis and reactions of azepanes, oxepines, thiepines, diazepines, thiazepines, azocines, diazocines, dioxocines and dithiocines.

***Heterocycles containing P, As, Sb and B*:** Synthesis of 5- and 6-membered heterocycles with P, As, Sb and B.

***Mesoionic compounds*:** General classification, chemistry of some important meso-ionicheterocycles of type-A and type-B and their applications.

References

1. Organometallic Chemistry, R. C. Mehrotra and A. Singh, Wiley Eastern, 1991.
2. The Organometallic Chemistry of the transition metals, R. H. Crabtree, 1988.
3. Principles and application of the organotrnsition metal chemistry, J. P. Collman, L. S.Hegedus, University Science books, 1980.
4. An introduction to Organometallic Chemistry, A. W. Parkins and R. C. Poller,Macmillan, 1986.
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6. Organometallics, Vol. 1 & 2, M. Bochmann, Oxford Chemistry primers, OxfordUniversity Press, 1994.
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8. Organotransition metal chemistry, S. G. Davies, Pergamon Press, Oxford, 1982.
9. Heterocyclic Chemistry, Vols. 1-3, R. R. Gupta, M. Kumar and V. Gupta, SpringerVerlag.
10. The Chemistry of Heterocycles, T. Eicher and S Hauptimann, Thieme.
11. Heterocyclic Chemistry, J. A. Joule, K. Mills and G. F. Smith, Chapman and Hill.
12. Heterocyclic Chemistry, T. L. Gilchrist, Longman Scientific Tech.
13. Contemporary Heterocyclic Chemistry, G. R. Newkome, and W. W. Paudler, Wiley-Inter Science.
14. An introduction to Heterocyclic Compounds, R. M. Acheson, John Wiley.
15. Comprehensive Heterocyclic Chemistry, A. R. Katritzky and C. W. Rees, Eds. Pergamon Press.

JOC 404: Medicinal Organic Chemistry **52 h**

Unit I

1. Introduction **07 h**

Chemotherapy, pharmacokinetics and pharmacodynamics, metabolites and antimetabolites, Prodrugs and soft drugs, agonists and antagonists, Generics and analogues; Concept of drug receptors; Elementary treatment of drug receptor interactions; Quantitative Structure Activity Relationship (QSAR); Theories of drug activity: Occupancy theory, rate theory and induced fit

theory; Computer- aided drug design and molecular modeling; General principles of dosage form design and drug administration

Unit II

Mechanism of drug action and the synthesis of the following classes of drugs (interconversions as applicable)

2. Antipyretics, analgesics and Anti-inflammatory Drugs **03 h**

Aspirin, paracetamol, phenacetin, novalgin, phenylbutazone, ibuprofen, naproxen

3. Antibiotics **08 h**

Penicillins (structure elucidation, stereochemistry); cephalosporin C, tetracyclins - aureomycin and terramycin, streptomycin. Interconversion of penicillin to cephalosporin, aureomycin to tetracycline, synthesis of ampicillin, amoxicillin, chloramphenicol

4. Antidiabetics **03 h**

Structure of insulin, glibenclamide, metformin, glitazone and pioglitazone

5. Antihistamines **02 h**

Methapyrilene, chlorpheniramine

6. Antineoplastic agents **04 h**

Introduction, cancer chemotherapy, special problems, role of alkylating agents and antimetabolites in treatment of cancer, Mention of carcinolytic antibiotics and mitotic inhibitors, Mechlorethamine, cyclophosphamide, melphalan, uracil mustards and 6-mercaptopurine, recent development in cancer chemotherapy, Hormone and natural products

Unit III

7. Antivirals **02 h**

Acyclovir, amantidine, rimantidine and zidovudine

8. Cardiovascular drugs **05 h**

Introduction, cardiovascular diseases, direct acting arteriolar dilators, amyl nitrite, sorbitrate, quinidine, verapamil, methyldopa

9. Local antiinfective drugs **07 h**

Sulphonamides, furazolidone, nalidixic acid, ciprofloxacin, norfloxacin, dapsone, aminosalicylic acid, isoniazid, ethionamide, ethambutal, griseofulvin, chloroquin, primaquine, flucanozole and econozole

Unit IV

10. Psychoactive drugs- the chemotherapy of the mind **11 h**

Phenobarbital, pethidine, methadone, chlordiazepoxide, diazepam, meprobamate, phenytoin, chloropromazine, alprazolam, ethosuximide, trimethadione, barbiturates, thiopental sodium, glutethimide and caffeine; Brief account of β-LPH and its relation to β-endorphin, MSH and ACTH

Brief discussion of the recent developments chemotherapy, lead compounds and their isolation from natural and synthetic sources; Green Chemistry in the manufacture of drugs

References

1. Introduction to Medicinal Chemistry, A.Gringuage, Wiley-VCH.
2. Wilson and Gisvold's Text book of Organic Medicinal and Pharmaceutical Chemistry, Ed Robert F.Dorge.
3. An Introduction to Drug Design, S.S.Pandey and J.R.Dimmock, New Age International.
4. Burger's Medicinal Chemistry and Drug Discovery, Vol-1 (Chapter-9 and Ch-14), Ed.M.E.Wolff, John Wiley.
5. Goodman and Gilman's Pharmacological Basis of Therapeutics, McGraw-Hill.
6. The Organic Chemistry of Drug Design and Drug Action, R.B.Silverman, Academic Press.
7. Strategies for Organic Drug Synthesis and Design, D.Lednicer, John Wiley.
8. Medicinal Chemistry, A.Kar, Wiley, 2000.
9. Synthetic Drugs, G.R.Chatwal, Himalaya, New Delhi, 1995.
10. Comprehensive Organic Chemistry, Vol.5 (Antibiotics), D.H.R.Barton, W.D.Ollis, Pergamon Press, NY, 1979.
11. Instant Notes on Medicinal Chemistry, P.Graham, viva, New Delhi, 2002.

JOC 405: Organic Chemistry Practicals - III

1. Preparations:

1. Preparations of NBS from succinic acid and its application in allylic bromination reactions.
2. Preparation of benzpinacolone from benzophenone.
3. Synthesis of 1-bromo-2-naphthol from 2-naphthol.
4. Preparation of 2-phenylindole from phenylhydrazine.
5. Anthrone from anthracene.
6. Synthesis of stilbene.
7. Synthesis of benzocaine from 4-nitrobenzoic acid.
8. Synthesis of methyl red.
9. Preparation of 2,4,5-triphenyloxazole from benzoin.
10. Biosynthesis of ethanol from sucrose.
11. Synthesis of hippuric acid.

2. Instrumental methods in organic analysis:

Recording of spectra using UV, IR, NMR and GC-MS techniques for the compounds prepared in JOC 305 (Organic Practical-I), JOC 306 (Organic Practical-II), JOC-405(Organic Practical-III).

3. Extraction:

1. Extraction of piperine from pepper.
2. Extraction of caffeine from tea leaves.
3. Isolation of lactose from milk.
4. Isolation of (+) limonene from citrus rinds.

4. Separations:

1. Separation of p-rosaniline and methyl red by column chromatography.
2. Separation of amino acids by paper chromatography.
3. Separation of carbohydrates by thin layer chromatography.

References

1. Semi-Micro Qualitative Organic Analysis, Cheronis, Entrikin and Hoanett
2. Preparation of Organic Intermediates, D.A.Hirley, John Wiley
3. Text book of Practical Organic Chemistry, A.I.Vogel, Pearson, 5th Ed. Delhi, 2004
4. A Laboratory Manual of Qualitative Organic Analysis, H.T.Openshaw, Univ.Press, 1999
5. Organic Synthesis, Collective Vols. I to X, 1956-1999
6. Natural Products, Laboratory Manual, Ikan, 2000
7. Organic Experiments, L.F.Fieser, 2 nd Edition, D.C.Heath & Co.USA, 1974-2000
8. Practical Organic Chemistry F.G.Mann and B.C.Saunders, 4 th Edition, Longman, 2002
9. Comprehensive Practical Organic Chemistry: Preparation and quantitative analysis, V.K.Ahluwalia, R.Aggarwal, Universities Press (India), 2000
10. Comprehensive Practical Organic Chemistry: Qualitative analysis, V.K.Ahluwalia, S.Dhingra, Universities Press (India), 2000
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15. Intermediates for Organic Synthesis, V.K.Ahluwalia, Pooja Bhagat, Ramesh Chandra and Renu Aggarwal, I. K.International Publishing House, New Delhi, 2005

JOC 406: Project and Review

Students carry out a 45 days (1.5 months) industrial internship or in-house projects.