

#### UNIVERSITY OF LUCKNOW LUCKNOW M.Sc. Pharmaceutical Chemistry (Core) Physical Chemistry Semester I, Paper I, PH1CO1

#### UNIT I

- 1. Bioenergetics: coupled reactions, ATP and its role in bioenergetics, high energy bond, free energy and entropy change in ATP hydrolysis, thermodynamic aspects of metabolism and respiration, glycolysis, biological redox reactions.
- 2. Acid-base catalysis: specific and general catalysis, Skrabal diagram, Bronsted catalysis law, prototropic and protolytic mechanism with examples, acidity function.

#### UNIT II

- 3. Enzyme catalysis and its mechanism, Michaelis-Menten equation, effect of pH and temperature on enzyme catalysis.
- 4. Kinetics of enzyme inhibition, protein folding and pathological misfolding, Muscle contraction and molecular mo

### UNIT III

- 5. Adsorption and various types of adsorption isotherms. The Langmuir theory, kinetic and statistical derivation, multilayer adsorption-BET theory, Use of Langmuir and BET isotherms for surface area determination. Adsorption of liquids by solids, positive and negative adsorption, Gibbs adsorption equation., flash desorption
- 6. Colloids: Zeta potential, Electrokinetic phenomena, Sedimentation potential and Streaming potential, Donnan membrane equilibrium.

### UNIT IV

- 7. Theories of unimolecular reactions. Reactions in solution: factors determining reaction in solutions, effect of dielectric constant and ionic strength, cage effect, Bronsted-Bjerrum equation, primary and secondary kinetic salt effect, influence of solvent on reaction rates, significance of volume of activation,
- 8. Kinetics of Fast reactions: relaxation, flow and shock methods, flash photolysis, NMR and ESR methods of studying fast reactions.



#### UNIVERSITY OF LUCKNOW LUCKNOW M.Sc. Pharmaceutical Chemistry (Core) Organometallic and nuclear Chemistry Semester I, Paper II, PH1CO2

# Unit I

 Reactions of Organometallic Compounds Substitution reactions-nucleophilic ligand substitution, nucleophilic and electrophilic attack on coordinated ligands. Addition and elimination reactions-1,2 additions to double bonds, carbonylation and decarbonylation, oxidative addition and reductive elimination, insertion (migration) and elimination reactions. Rearrangement reactions, redistribution reactions, fluxional isomerism.

# Unit II

 Catalysis by Organometallic Compounds . Homogeneous and heterogeneous organometallic catalysis-alkene hydrogenation using Wilkinson catalyst, Tolman catalytic loops. the Fischer-Tropsch reaction(synthesis of gasoline). Hydroformylation of olefins using cobalt or rhodium catalyst. Carbonylation reactions-Monsanto acetic acid process

### Unit III

3. Bioinorganic Compounds Essential and trace elements in biological systems, structure and functions of biological membranes, mechanism of ion transport across membranes, sodium pump, ionophores, valinomycin and crown ether complexes of Na+and K+, ATP and ADP. S II. Role of calcium in muscle contraction, blood clotting mechanism and biological calcification. Oxygen carriers and oxygen transport proteins-haemoglobins, myoglobins and haemocyanin, haemerythrins and haemevanadins, cooperativity in haemoglobin. Iron storage and transport in biological systems-ferritin and transferrin. Redox metalloenzymes-cytochromes, peroxidases and superoxide dismutase and Nonredox metalloenzymes-CarboxypeptidaseA-structure catalases. and functions. Nitrogen Fixation-nitrogenase, vitamin B12 and the vitamin B12 coenzymes. Metal-Nuclei acid interaction

Metals in medicine-therapeutic applications of cis-platin, radio-isotopes and MRI agents. Toxic effects of metals(Cd, Hg, Cr and Pb).

# Unit IV

4. Analytical applications of radioisotopes-radiometric titrations, kinetics of exchange reactions, measurement of physical constants including diffusion constants, Radioanalysis, Neutron Activation Analysis, Prompt Gama Neutron Activation Analysis and Neutron Absorptiometry.

Applications of radio isotopes in industry, medicine, radiopharmacology, radiation safety precaution, nuclear waste disposal.



### UNIVERSITY OF LUCKNOW LUCKNOW M.Sc. Pharmaceutical Chemistry (Core) Organic Chemistry Semester I, Paper III, PH1CO3

### UNIT I

# 1. Physical Organic Chemistry

a. Energy profiles. Kinetic versus thermodynamic control of product formation, Hammond postulate, kinetic isotope effects with examples, Linear free energy relationship Hammet equation, Taft equation.

# 2. Modern Synthetic Methods

a. Baylis-Hillman reaction, Henry reaction, Nef reaction, Kulinkovich reaction, Ritter reaction, Sakurai reaction, Ugi reaction. Brook rearrangement. Tebbe olefination. Metal mediated C-C and C-X coupling reactions: Heck, Suzuki, Negishi and Sonogashira, Nozaki-Hiyama,

# UNIT II

# 3. Oxidation

- a. Metal based and non-metal based oxidations of
  - i. alcohols to carbonyls (chromium, manganese, aluminium, and silver based reagents)
  - ii. Phenols (Fremy salt, silver carbonate)
- b. Alkenes to epoxides (peroxides/peracids based), Sharpless asymmetric epoxidation.
- c. Alkenes to diols (Manganese, Osmium based), Sharpless asymmetric dihydroxylation, Prevost reaction.
- d. Alkenes to carbonyls with bond cleavage (manganese, osmium, ruthenium and lead based, ozonolysis)
- e. Alkenes to alcohols/carbonyls without bond cleavage (hydroborationoxidation, Wacker oxidation)
- f. ketones to ester/lactones (Baeyer-Villiger).

# 4. Reduction

- a. (a) Catalytic hydrogenation (Heterogeneous: Pd /Pt /Rh /Ni etc; Homogeneous: Wilkinson). Noyori asymmetric hydrogenation.
- b. (b) Metal based reductions using Li/Na/Ca in liquid ammonia, Sodium, Magnesium and Zinc (Birch, Pinacol formation, McMurry, Acyloin formation, dehalogenation and deoxygenations)
- c. (c) Hydride transfer reagents
  - i. NaBH<sub>4</sub> triacetoxyborohydride; LiAlH4 and DIBAL-H, Meerwein Pondorff-Verley reduction)
  - ii. Stereo/enantioselective reductions (Chiral Boranes, Corey-Bakshi-Shibata).



### UNIVERSITY OF LUCKNOW LUCKNOW M.Sc. Pharmaceutical Chemistry (Core) Organic Chemistry Semester I, Paper III, PH1CO3

# Unit III

# 5. Pericyclic Reactions

Main features of pericyclic reactions; Woodward-Hoffman rules, correlation diagram and FMO approaches; Electrocyclic reactions . conrotatory and disrotatory motions for 4n and 4n+2 systems;. Cycloadditions . antarafacial and suprafacial additions, [2+2] and [4+2] reactions (h and ), 1,3-dipolar cycloadditions and chelotropic reactions; Sigmatropic [i,j] shifts of C-H and C-C bonds; Sommelet-Hauser, Claisen, thio-Claisen, Cope and aza-Cope rearrangements.

# 6. Stereochemistry of Organic Compounds

Center of chirality: molecules with C, N, S based chiral centers. Axial, planar and helical chirality with examples, stereochemistry and absolute configuration of allenes, biphenyls and binaphthyls, , spiranes, exo-cyclic. Topicity and prostereoisomerism, topicity of ligands and faces as well as their nomenclature.

### Unit IV

# 7. Conformational Analysis

a. Conformational Analysis of cyclohexane and its derivatives, decalins, adamantane, congressane, sucrose and lactose. Fused and bridged bicyclic systems. Conformation and reactivity of elimination (dehalogenation, dehydrohalogenation, semipinacolic deamination and pyrolytic elimination-Saytzeff and Hofmann eliminations), substitution and oxidation of 2<sup>0</sup> alcohols. Chemical consequence of conformational equilibrium - Curtin Hammett principle.

# 8. Chiral drug synthesis

a. Chiral drug synthesis Introduction to Chiral drugs, importance of stereochemistry in drug action, concepts of eutomer, distomer and eudesmic ratio, stereospecific and stereoselective synthesis, Synthesis of Chiral drugs like Ibuprofen, Propranolol, ramipril, levofloxacin.