ORGANIC CHEMISTRY
SYLLABUS

CHEMISTRY HONS.

DEPARTMENT OF CHEMISTRY
ST. XAVIER'S COLLEGE (AUTONOMOUS)
KOLKATA-700 016

Semester-I

(36-38 Lectures)

A) General Introduction and Bonding Features in Organic Molecules (12 lectures)

IUPAC and trivial names, DBE, Hybridization, formation of σ and π-bonds, pπ-d π bonds, bond distance, bond angles, shapes of molecules, strain due to valence shell electron pair repulsion, bond stretching, angular distortion, steric effects, inductive effects, bond energy, bond polarity & bond polarizability.

Resonance, Steric inhibition of resonance, hyperconjugation, bond moment, dipole moment, orbital pictures of ethylene, acetylene, allene, formaldehyde and carbene. π -orbital pictures of dienes, enynes, enones, vinylcyanide; π- MO diagrams of butadiene, 1,3,5-hexatriene, benzene: HOMO & LUMO in the g.s & e.s; Aromaticity, Huckel's (4n+2) rule, anti-aromaticity, application of Huckel's rule to benzenoid and non-benzenoid compounds.

B) Stereochemistry of Acyclic Compounds (12-13 lectures)

Representation of molecules in Fischer, flying wedge, Saw-horse and Newman formulae and their inter-translations.

Chirality, elements of Symmetry, simple axis,plane of symmetry, centre of symmetry, alternating axis of symmetry. Asymmetry & disymmetry, optical activity, specific rotation, molar rotation.

Enantiomerism & Diastereoisomerism, Stereogenic centres, systems with chiral centres, Stereogenic centres involving C=C, C=N; D/L, R/S, E/Z, syn/ anti, cis/trans, meso/dl, threo/erythro nomenclature. Isomerism involving two like/unlike stereogenic centres (ABA and ABA types), pseudo-asymmetric centres, stereogenicity, chirotopicity, achirotopicity;

C) Reaction Mechanism, Tautomerism, Organic Acid-Base Reaction & Kinetics of Organic Reactions (12-13 lectures)

Bond Cleavage & Bond Formation- heterolytic & homolytic Bond Cleavage at stereogenic (single) and non-stereogenic centres, racemization, formation of racemic

products.Structure, stability, formation and fates of electrophiles, nucleophiles, radicals. Concept of onium and enium ions, carbocations (onium and enium ions) carbanions, carbenes, benzynes. Classification of reactions- Substitution, elimination, addition, rearrangement.

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Tautomerism

Prototrotropic shifts, Ring-chain tautomerism, valence tautomerism, relative stability of tautomers with reference to bond energy, resonance energy, H-bonding and solvent effects.

Organic Acid-Base Reaction & Kinetics of Organic Reactions,

i) Acid- Base Reactions-Bronsted & Lewis concept of organic acids & bases, acid base catalysis; effects of structure, substituents and medium on relative acid-base strength of substituted alkanes, alkenes, alkynes, alcohols, phenols, enols, carbonyls, carboxylic acids, amines, HSAB principle.

ii) Reaction Kinetics- Rate equation, T.S. Theory, rate constant and Gibb's free energy; free energy profile for one-step & two-step reaction. Hammond postulate, Kinetically Controlled Vs Thermodynamically Controlled reactions, catalyzed reactions.

Semester-II

(36 - 38 Lectures)

A) Stereoisomerism & Conformation (12-13 lectures)

Axial chirality, systems with odd and even number of cumulated double bonds, atropisomerism in biphenyl systems, R/S nomenclature of axially chiral systems. Resolution of recemic acids, bases and alcohols; Optical purity/enantiometric excess. Topicity of ligands and faces (elementary idea). Homotopic, Enantiotopic & Diastereotopic ligands and faces; pro-chirality, pro-R, Pro-S, and re/si descriptors.

Conformational Nomenclature- eclipsed, staggered, gauche, anti; dihedral angle, energy barrier of rotation, relative stability of conformers on the basis of steric effects; dipole-dipole interaction, H-bonding; conformational analysis of ethane, propane, n-butane, 1,2-dchloroethane, 2-methylbutane, 1,2-glycols, invertomerism of trialkylamines.

B*) *Elucidation of Reaction Mechanism, Nucleophilic substitution and elimination reactions and Aromatic substitution reactions (24- 25 lectures)

(i) Kinetic studies, study of intermediates, cross over experiments, stereochemical proof, isotope labelling- kinetic & non-kinetic, primary kinetic isotopic effect (kH/kD only).

(ii) **Nucleophilic substitution and elimination reactions** of alkyl halides; S_N1, S_N2, S_Ni, NGP, E1, E2, E1cB mechanisms; elimination vs substitution; Saytzeff and Hoffmann rules; reactivity of aryl, vinyl, allyl and benzyl halides.

(iii) **Aromatic substitution reactions**

π-complex, σ-complex, activating and deactivating groups, orienting influence of groups. Aryl halides: activated aromatic nucleophilic substitution, cine substitution. ipso substitution.

(iv) **Mechanism of free-radical substitution** of alkane H, allyl/benzyl H; reactivity and selectivity of substitution by chlorine and bromine;

Semester III

(36 - 38 Lectures)

A) Corey-House syntheis of alkanes; synthesis of alkenes, alkynes and alkadienes; alkyl and alkenyl benzenes. Interconversion of constitutional isomers of alkene and alkynes; Interconversion of E and Z isomers of alkenes. ***(12 - 13 lectures)***

Electrophilic addition to carbon-carbon multiple bonds; reactivity, regioselectivity (Markownikoff's rule), stereoselectivity, chemoselectivity; halogenation, hydrogenation, hydration, oxymercuration-demercuration, hydroboration-oxidation, epoxidation, hydroxylation, ozonolysis, carbene addition to alkynes, allenes,; free radical addition to C=C bond, peroxide effect; electrophilic and free radical addition to conjugated dienes; 1,2- vs 1,4-addition; Birch reduction of alkadienes and alkynes; reactions involving alkynic C-H cleavage; Diels-Alder reaction (simple treatment).

Polynuclear hydrocarbons ***(3 lectures)***

nomenclature, synthesis and important reactions of naphthalene, anthracene and phenanthrene.

B*) *Alcohols & Ethers (3 lectures)

Relative reactivity of 1°, 2°, and 3° alcohols in reactions via H-O and C-O cleavages; reactions of alcohols as nucleophiles, nucleophilic substitution reactions at carbinol C, S_Ni, dehydration, dehydrogenation, oxidation of alcohols. Reactions of epoxides and ethers via C-O cleavage, reactions of α-glycols: cyclic ketal/acetal formation, complex formation with H_3BO_3, oxidative cleavage of glycolic bond.

C) Phenols (3 lectures)

Ambident nucleophile, ring substitution Vs O-Substitution. Reactions of phenols: Reimer-Tiemann reaction, alkylation, acylation, Fries rearrangement, Claisen rearrangement, nitration, sulphonation, halogenation, oxidation (aerial), oxidative coupling by Fe^{3+}.

D) Spectral Methods in Organic Chemistry- UV & IR and NMR Spectra (15 -16 lectures)

UV-Spectra: Electronic Transitions ($\sigma\rightarrow \sigma$, $n\rightarrow\sigma$, $\pi \rightarrow\pi$, $n \rightarrow\pi$), Relative position of λ_{max} considering conjugative effect, steric effect, solvent effect, effect of pH, relative intensity of absorption of allowed transitions, bathochromic shift, hypochrromic shift, hyperchromic shift, hypsochromic shift with typical examples.

IR-Spectra: Modes of molecular vibrations, application of Hooke's law, Characteristics of diagnostic stretching freqeuncies of O-H, N-H, C-H, C-D, C=C, C=N, C=O; factors affecting stretching frequencies.

NMR Spectra

Nuclear spin, NMR-active nuclei, principle of PMR, equivalent & non-equivalent protons, chemical shifts, shielding/deshielding protons, upfield & downfield shifts.

NMR peak area, relative peak positions of Toluene, nitro-benzene, o, m, p- dichloro- and dinitro-benzenes & chloronitobenzenes; spin-spin coupling in ethanol (ordinary grade), ethyl bromide; 1,1-dibromoethane; 1,2-dibromoethane; 1,1,2-tribromoethane.

Semester IV

(36 -38 Lectures)

Aldehydes & Ketones (16- 18 Lectures)

Nucleophilic addition to C=O bond: reactivity of carbonyl compounds, relative stability of adducts, formation of acetal, ketal, thioacetal, thioketal, and cyanohydrin, Grignard reaction, $LiAlH_4$ and $NaBH_4$ reductions, electrolytic reductions, reductive coupling, M.P.V reduction, Cannizzaro reaction, Internal Cannizzaro reaction, benzil-benzilic acid rearrangement; nucleophilic addition to α, β- unsaturated carbonyl compounds, reactions of benzoquinones, reactions with derivatives of NH_3, Wolff-Kishner reduction, Aldol condensation, Claisen condensation, Directed Aldol condensation, Wittig reaction, Mannich reaction, Enamine reaction, Reformatsky reaction, Darzen's reaction, Perkin reaction, Benzoin condensation, Tischenko reaction. Electrophilic substitution at α–position of carbonyl compounds, D-exchange, Nitrosation, halogenation., Haloform reaction, SeO_2 oxidation.

Carboxylic Acids & Derivatives

Nucleophilic substitution reaction at the acyl carbon of acyl halide, anhydride, ester, amide; tetrahedral mechanism, esterification of carboxylic acid and hydrolysis of esters: AAc2, AAc1, AAl1, BAc2, BAl1, BAl2 mechanisms. Reactions via cleavage of α-C-H (use of trimethyl silyl chloride): HVZ reaction, Claisen ester condensation, Bouveault Blanc reduction, decarboxylation, Hunsdiecker reaction, action of heat on hydroxy acids.

Organometallic compounds and Organonitogen Compounds (8 lectures)

A) Grignard reagents: Preparation and synthetic applications of Grignard reagents and organolithium compounds.

B) Organonitogen Compounds: Acidity of α-H of nitroalkanes, reduction of aromatic nitro compounds, alkyl cyanides and isocyanides and their hydrolysis, Von Richter reaction. Distinction among 1°, 2°, and 3° amines and their separation, Hofmann's

exhaustive methylation, carbylamine reaction, partial reduction of aromatic nitro compounds.

Amines: Ring substitution vs N-substitution in aromatic amines, diazotisation and coupling reactions, synthetic applications of aromatic diazonium compounds. Preparation and synthetic uses of diazomethane and diazoacetic ester.

Rearrangement Reactions (8 lectures)

Rearrangements involving electron deficient C, N and O: Allylic rearrangement, Wagner rearrangement, Wolff rearrangement, Arndt-Eistert synthesis, Baeyer-Villiger oxidation, Cumene peroxide-phenol rearrangement, Dakin reaction, Beckmann rearrangement, Schmidt rearrangement, Hofmann rearrangement, Lossen rearrangement, Curtius rearrangement, Orton rearrangement, rearrangements of N-azo to C-azo compounds, Hofmann-Martius rearrangement, benzidine rearrangement.

Polymers (4 lectures)

Mechanism of polymerization reaction (acid induced and radical induced), production and uses of Polythene, Polystyrene, PVC, Teflon, Nylon and Terylene.

Semester V

(40 Lectures)

Organic Synthesis (14 lectures)

Disconnection approach towards synthesis of bifunctional molecules (both cyclic and acyclic): concepts of synthons, synthetic equivalents (ethyl acetoacetate, ethyl cyano acetate and diethyl malonate as examples). Functional group interconversion (FGI). Protection and deprotection of common functional groups (-OH, carbonyl, $-NH_2$, $-CO_2H$) in synthetic route, activation of synthetic equivalents. Umpolung: Illogical electrophiles and nucleophiles. Disconnection and synthesis of 1,3; 1,4 and 1,5-dioxygenated compounds. Robinson ring annulation, applications of Claisen rearrangement, Favorskii rearrangement and Demjanov rearrangements involving electron deficient C, O, N. Large ring synthesis: High dilution techniques, Acyloin condensation (use of trimethyl silyl chloride).

Pericyclic reactions (8 lectures)

Definition and classification.Electrocyclic reactions: FMO approach, examples of electrocyclic reactions (thermal and photochemical) involving 4 and 6 π-electrons and corresponding cycloreversion reactions. Cycloaddition reactions: FMO approach, Diels-Alder reaction, photochemical [2 + 2] reactions. Sigmatropic shifts and their order. [1,3] and [1,5] H-shifts. [3,3]-shifts with reference to Claisen and Cope rearrangements.

Stereochemistry of alicyclic compounds and Dynamic stereochemistry (12 lectures)

Stereoisomerism of di-substituted ring compounds, ring size strain and Baeyer strain theory, concept of I-strain. Conformational analysis of cyclohexanes: energy profile of ring inversion of cyclohexane, symmetry properties of chair,boat and skew-boat conformations, conformational analysis of mono- and di-substituted cyclohexanes.

E2, S_N2 and NGP, lactonisation reactions of cyclohexane systems, oxidation of cyclohexanols with chromic acid, pinacol-pinacolone rearrangements,esterification, saponification of esters, steric assistance and steric hindrance.

Photochemistry (6 lectures)

Reactivity of electronically excited ketones, α-cleavage, γ-hydrogen transfer, Photoreduction, Paterno-Buchi reaction, Reactivity of π,π* excited ketones, Photochemistry of α,β-unsaturated ketones, Photochemistry of conjugated olefins and aromatic systems.

Semester VI

(40 Lectures)

Heterocyclic compounds (12 lectures)

Synthesis (including retrosynthetic approach), reactivity, orientation and important reactions of furan, pyrrole, thiophene, pyridine, indole, quinoline, and isoquinoline. Knorr pyrrole synthesis, Hantzsch pyridine synthesis, Fisher indole synthesis and Bischler-Napieralski synthesis.

Carbohydrates (10 lectures)

Monosaccharides- classification, osazone formation, stepping up and stepping down of aldoses, interconversion of aldoses to ketoses and vice versa, epimerisation. Constitution and configuration of D-glucose and D-fructose, ring structure and conformational aspects of D-glucose and its derivatives, anomeric effect, mutarotation of D-glucose.

Disaccharides: structure of sucrose.

Amino acids (10 lectures)

Synthesis of α-amino acids (Gabriel, Strecker, azlactone, acetamido, malonic ester methodologies). Isoelectric popint, ninhydrin reaction, resolution of amino acids.

Peptides: geometry of peptide linkage, peptide synthesis including Merrifield synthesis, structure determination of peptides, C-terminal and N-terminal unit determination, determination of amino acid sequence.

Mass spectrometry (8 lectures)

Basic principles, Isotope abundances, The molecular ion, metastable ions, Fragmentation processes, factors influencing fragmentations, fragmentations associated with functional groups, McLafferty rearrangement.

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Semester I
(16 lectures)

Unit I

Introductory Concept & Isomerism (6 -7 lectures)

Inductive effect, electrometric effect, conjugation, resonance and resonance energy, hyper conjugation. Homolytic and heterolytic bond breaking, electrophiles and nucleophiles; carbocations, carbanions and radicals (stability and reactivity).

Constitution and nomenclature of carbon compounds (IUPAC and trivial systems). Stereochemistry of carbon compounds: different types of isomerism, geometrical and optical isomerism, optical activity, asymmetric carbon atom, elements of symmetry, chirality, enatiomers and diastereoisomers; E and Z nomenclature, D and L nomenclature (for carbohydrates and aminoacids only). R and S nomenclature. Fischer and Newman Projection formulae of simple molecules containing one and two asymmetric carbon atom (s).

Unit II

Aliphatic & Aromatic Hydrocarbons (4 -5 lectures)

Isomerism, synthesis and chemical reactivity of alkanes, mechanism of free-redical halogenation of alkanes. Sulphonation of alkenes, detergents. General methods of synthesis of alkenes, heat of hydrogenation and stability of alkenes. Electrophonic addition reactions, mechanism of bromination and hydrohalogenation; Markownikoff's addition, peroxide effect. Hydration, hydroboration, ozonide formation, epoxidation, hydroxylation, polymerization reactions of alkenes (definition and examples only). General methods of synthesis, acidity, hydration and substitution reactions of alkynes.

Isomerism of aromatic compounds and their nomenclature, resonance structure of benzene. General mechanism of electrophilic substitution reactions of benzene. Synthesis of aromatic compounds using nitration, suplhonation. Halogenation, Friedel-craft alkylations and acylation reactions. Nuclear and side-chain halogenation of toluene.

Unit III

Alkyl and Aryl halides (4 lectures):

Methods of synthesis, S_N1, S_N2, E1, E2 reactions (elementary mechanistic aspects). Saytzeff and Hofmann elimination reactions, reactivity of aromatic halides, nucleophilic aromatic substitution reactions. Synthesis of DDT.

Semester II

(16 lectures)

Unit I

Organometallic Compounds , Alcohols & Ethers (6-7 lectures)

Grignard Reagents – Preparation and reactions. Application of Grignard reagents in organic synthesis.

Methods of synthesis, physical properties, distinction of primary, secondary and tertiary alcohols and their chemical reactions. Ethers: Williamson's ether synthesis, physical properties chemical reactions and uses of ethers.

Unit II

Cabonyl compounds, Carboxylic acids & derivatives (6 – 7 lectures)

The nature of carbonyl group, methods of synthesis, physical properties derivatives of carbonyl compounds, nucleophilic addition cannizzaro reaction, reformatsky's reaction. Relative reactivities and distinction aldehydes and ketones, formation and reactions of enolates aldol condensation (with mechanism), Perkin reaction, Knoevenagel reaction, Benzoin Condensation, Claisen Condensation, Oxidation and Reduction, reactions. Aliphatic and aromatic aldehydes.

Carboxylic acid and their derivatives (2 lectures)

Acidity of carboxylic acids and effects of substituents on acidity, chemical reactivity, mechanism of esterification of carboxylic acids and hydrolysis of ester (BAc2 and AAc2 only); methods of synthesis and reacuons of acyl halides, amides, esters and acid anhydrides.

Semester III

(16 lectures)

Organic Compounds Containing Nitrogen (8 lectures)

Aromatic nitro – compounds – their synthesis and reduction under different condition. Methods of synthesis of aliphatic amines, Hinsberg, method of amine separation. Hofmann degradation, Gabriel's phthalimide synthesis; distinction of primary, secondary and tertiary amines. Methods of synthesis of aromatic amines, basicity of aliphatic and aromatic amines. Diazotisation and coupling reactions and their mechanisms. Synthetic applications of diazonium salts.

Phenols (8 lectures):

Synthesis. Acidic character and chemical reactions of phenols, Kolbe's reactions, Reimer- Tiemann reaction, Fries rearrangement, Claisen rearrangement, Houben- Hoesch reaction. Mannich reaction, Cresols, nitro phenols and amino phenols.

Semester IV

(16 lectures)

Carbohydrates (5 -6 lectures)

Introduction, occurrence and classification of carbohydrates, constitution of glucose. Osazone formation. Reactions of glucose and fructose mutarotation. Cyclic structures–pyranose and furanose forms (determination of ring size excluded), epimerization, chain lengthening chain-shortening in aldoses.

Amino Acids and Proteins (5- 6 lectures)

Methods of synthesis of α–amino acids (glycine and alanine using Gabriel's phthalamide synthesis and Strecker synthesis). Physical properties.

Nucleic Acids (4 lectures)

Zwitterion structures, isoelectric point; peptide synthesis (elementary idea). Nucleic acids: components, nucleosides and nucleotides, structures and functions (basic idea).