

MANGALORE UNIVERSITY
Department of Industrial Chemistry

ICH 402: ORGANIC CHEMISTRY-I

Course Outcomes:

- Nature of reaction intermediates and the factors affecting reaction conditions such as nature of solvent, isotope effects and salt effects.
- Reaction types and their kinetics, thermodynamic and effect of thermodynamic parameters on reaction with kinetic aspects.
- Application of fundamentals on aliphatic nucleophilic and electrophilic substitution by studying their mechanism with named reactions.
- Aromatic nucleophilic substitution, addition and elimination mechanisms with respect to stereochemistry.
- Student learns about the fundamental and applications of chirotechnology.

UNIT I:

14 hrs

Acids and Bases: Introduction to acids and bases, Bronsted-lowry and acid-bases concept, organic acids and bases, pK_a and pH, effect of solvent on acid and base strength, effect of structure of organic compound on acid and base strength. Running scale of acidity, general and specific acid base catalysis.

Reactivity in relation to molecular structure and conformation. Steric effects. F strain. Ortho effect. Bond angle strain. The Hammett equation and its applications. Taft equation. Linear free energy relationships. Solvent polarity and parameters. Y, Z and E parameters and their applications. Primary and secondary kinetic isotope effects. Salt effects and special salt effects in S_N reactions. **Reaction intermediates:** Generation, structure, stability, reactivity & detection of classical & non-classical carbocations, carbanions, free radicals, carbenes, nitrenes & arynes. N, S & P ylides & enamines.

UNIT II: Organic Reactions and Mechanism (Part-I)

14 hrs Organic Reactions and Mechanism: Reaction mechanism & types, types of organic reactions, reaction profile diagrams, thermodynamic & kinetic control, leaving group and solvent. Methods of determining reaction mechanisms: Kinetic & non-kinetic methods-identification of products, detection of intermediates, isotopic labelling, stereochemical evidences, cross-over experiments, kinetic evidences & kinetic isotopic effects. The Hammond postulate. Principle of microscopic reversibility. Marcus theory. Phase transfer catalysis and its applications

Aliphatic Nucleophilic Substitution reactions: Mechanisms Nucleophilic substitution: Substitution reactions of ambident nucleophiles, neighbouring group participation of O, S, N, halogens, aryl groups, alkyl and cycloalkyl groups in nucleophilic substitution reactions.

Sigma, Pi bond participation in acyclic and bicyclic systems (Non- classic carbocations)
 Substitution at allylic, trigonal and Vinylic carbons, hydrolysis of esters, Meyer's aldehydes, ketones and carboxylic acids, alkylation with trialkyl boranes.

Aliphatic Electrophilic substitutions: SE1 SE2 and SEi mechanisms hydrogen exchange, migration of double bonds, halogenation of aldehydes, ketones, acids, acylhalides sulphoxides and sulphones, aliphatic diazonium coupling, nitrosation at Carbon and nitrogen diazo transfer reaction carbene and nitrene insertion, formation of sulphur yield, metalation with organometallic compounds and with metals. Decarboxylation of aliphatic acids. Haloform reaction and Haller-Baner reaction.

UNIT III: Organic Reactions and Mechanism(Part-II)

14 hrs Aromatic nucleophilic substitution: A general introduction to different mechanisms of aromatic substitution SN Ar, AN and aryne, Von Richter rearrangement, Sommelet, Hauser rearrangement Smiles rearrangement. Radical substitution Mechanism: Reaction at sp³ carbon: Reactivity in aliphatic substrates reactivity at bridged position, reactivity at sp² carbon. Reactivity in aromatic substrates neighbouring group assistance in free radical reactions, effect of reactivity in the attacking radical effect of solvent on reactivity halogenation at an alkyl carbon and allylic carbon, hydroxylation at aromatic carbon by means of Fenton's reagent, oxidation of aldehydes to carboxylic acids, formation of cyclic ethers with Pb(OAc)₄ Reed reaction, sandmeyer reaction, kolbe reaction and Hunsdiecker reaction.

Addition Elimination Mechanisms: (a) Addition to carbon multiple bonds- Addition reactions involving electrophiles, nucleophiles and free radicals, cyclic mechanisms, orientation and stereochemistry, hydrogenation of double and triple bonds, hydroboration, Birch reduction. Michael reaction, addition of oxygen and N₂; (b) Addition to carbon-hetero atom multiple bonds: Mannich reaction Aldol reductions of Carbonyl compounds acids, esters, nitrites, addition of Grignard reagents, Reformatsky reaction, Tollen's reaction, Wittig reaction, Prins reaction: (c) Elimination reactions: Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations - Saytzeff and Hoffman elimination propolitic elimination.

UNIT IV: Chirotechnology

14 hrs

Concept of chirality, optical isomerism, D,L-; R,S- designations, geometrical isomerism and E,Z designations, Stereoselective and stereospecific reactions, Racemisation, mechanism of racemisation, resolution of racemic mixtures, Asymmetric synthesis-definition, importance, mechanism, energy consideration, advantages and limitations, methods of determination of enantiomeric excess. Enantioselective reactions, The chiral pool, chiral auxiliaries and chiral reagents. Use of α -amino acids in the synthesis of benzodiazepines, carbohydrates in the synthesis of swainsonine (D-mannose) and tomolal (mannitol). Synthesis and applications of oxazaborolidines, IPC₂BH, (S)-BINAP-DIAMINE and (R)-BINAL-H. Use of (R,R)-DIPAMP, (S,S)-CHIRAPHOS, (R,R)-DIOP, SAMP, RAMP, , S-PBMgCl, (+) and (-)-DET.

References:

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