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ORGANIC CHEMISTRY SYLLABUS

Academic 2021/2022

Mechanism of organic reactions. Radical and ionic processes, electrophiles and nucleophiles. Types of ionic reactions – substitution, addition, elimination, condensations, rearrangements (examples). Energy diagrams, endothermic and exothermic processes.

Electronic effects in organic molecules. Polar and non-polar bonds. Induction effect. Localized and delocalized chemical bonds – examples of systems with delocalized bonds. Mesomeric (resonance) effect. Resonance theory – canonical structures, hybrid structure, resonance energy.

Alkanes and cycloalkanes. Basic principles of the IUPAC nomenclature. Preparation of alkanes, *Würtz* reaction. Halogenation of alkanes – mechanism of radical substitution reactions (S_R); reactivity and selectivity. Stability and specific reactions of cycloalkanes. Cracking and combustion of alkanes, petroleum products.

Stereochemistry part I. Conformational isomerism. Perspective and *Newman* projections. Conformation analysis of ethane and butane. Cyclohexane – "chair" and "boat" conformations, equatorial and axial substituents. Conformation analysis of substituted cyclohexanes. Conformations of polycyclic compounds. Conformation and biological activity.

Stereochemistry part II. Enantiomers. Optical activity and molecular chirality – examples of asymmetry in organic molecules. Absolute and relative configuration. *Fischer* projection formulas, D, L-configuration. *Kang-Ingold-Prelog* system (R, S-notational system). Enantiomers and biological activity. Sigma-diastereomers.

Alkenes and cycloalkenes. π-stereoisomerism in alkenes (E-, Z-notational system). Preparation of alkenes – mechanism and stereochemistry of β-elimination reactions (E2 and E1). *Zaytsev*'s rule, *Hoffman*'s rule. Addition reactions of alkenes – hydrogenation, halogenation, hydration, addition of hydrogen halides. Mechanism and stereochemistry of electrophilic (A_E) reactions. Oxidation of alkenes. Examples of alkene polymerization.

Alkynes. Preparation and properties of alkynes. *Kucherov*'s reaction, tautomerism. Acidity of alkynes; alkynides as nucleophiles and bases.

Arenes. Classification and nomenclature. Criteria for aromaticity, *Hükkel*'s rule. Benzene and benzene homologues, styrene, biphenyl, condensed arenes. Chemical properties of benzene and its derivatives – mechanism of electrophilic substitution reactions (S_E), energy diagram. Nitration, sulfonation, halogenation, *Friedel-Crafts*' alkylation and acylation. Radical substitution, oxidation and reduction of arenes.

Theory of directing effect of substituents. Activating and deactivating substituents, o-, m- and p-directors. Stability of the corresponding arenium ions (σ-complexes) in o-, m- and p-substitution. Influence of two or more substitutes. Naphthalene sulfonation.

Alcohols, diols and thioalcohols. Industrial and laboratory methods for preparation. Chemical properties of alcohols – mechanism and stereochemistry (*Walden* inversion, racemization) of nucleophilic substitution (S_N2 and S_N1) reactions, dehydration, etherification, esterification. Laboratory and biological oxidation of alcohols. Specific properties of thioalcohols.

Phenols. Acidity of phenols, effect of substituents in aromatic ring. Natural sources of phenols, industrial production of phenols. Electrophilic substitution in benzene ring. Competitive acylation and alkylation reactions in benzene ring and phenol group. Laboratory and biological oxidation of phenols. Concept of polyphenols.

Aldehydes and ketones. Classification and nomenclature. Keto-enol tautomerism. Industrial and laboratory methods for preparation – ozonolysis of alkenes, hydration of alkynes, oxidation of alcohols. *Gattermann–Koch* reaction, *Friedel-Crafts* acylation of aromatic compounds. Chemical properties – mechanism of nucleophilic addition (A_N) and addition – elimination ($A_N + E$) reactions. Synthesis with *Grignard* reagents. Condensation reactions – aldol condensation (mechanism). Oxidation and reduction of carbonyl compounds; *Cannizzaro* reaction. Quinones.

Carboxylic acids. Classification and nomenclature; common names of biologically important carboxylic acids. Methods for synthesis of carboxylic acid, *Perkin* reaction (mechanism). Acidity of mono-, di- and substituted carboxylic acids. Carboxylic acid salts. Preparation of halogenated acids – *Hell-Volhard-Zelinsky* reaction.

Carboxylic acid derivatives. Esters, acyl halides, anhydrides, amides, hydroxamic acids, nitriles – structure, more important methods of preparation, reactivity and specific properties.

Oxy- and oxoacids. Biological important oxy- and oxoacids; stereoisomerism of lactic, malic, and tartaric acid. Synthesis of salicylic acid. Decarbonylation and decarboxylation, lactides, lactones and polyesters.

Aliphatic and aromatic amines. Classification and structure. Methods for preparation (from ammonia and amines, by reduction, etc.). Basicity (pK_b) of amines. Salt formation, N-alkylation and N-acylation. Diazonium salts – production and chemical properties (*Zandmeyer* reaction and coupling). Biogenic amines; drugs derived from 3-amino-1,2-propanediol (β-blockers).

Amino acids. Classification and properties – isoelectric point, formation of 2,5-dioxopiperazines, specific properties of some amino acids. Strategies of protein synthesis.

Lipids. Classification. Fatty acids. Fats, oils, waxes, and phospholipids – composition, properties and biological role. Terpenes – classification, isoprene rule. Mono, di- and tetraterpenes (carotenoids). Steroids (triterpenes) – cholesterol, vitamin D, bile acids, corticosteroids and sex hormones.

Five-membered aromatic heterocyclic compounds. Pyrrole, furan and thiophene. *Knorr* pyrrole synthesis. Structure and reactivity – comparison of chemical properties. Indole – *Fischer* synthesis, biologically important pyrrole and indole derivatives.

Six-membered heterocyclic compounds. *Hantzsch* pyridine synthesis. Chemical properties – basicity, electrophilic and nucleophilic substitution reactions (*Chichibabin* reaction). Pyridine derivatives of biological significance – nicotinamide, nicotine, vitamin B_6, piperidine alkaloids. Fused with benzene heterocyclic compounds – *Skraup* synthesis of quinoline and the *Bischler-Napieralski* synthesis of isoquinoline. Quinoline and isoquinoline alkaloids – examples. Acridine.

Five-membered heterocyclic compounds with two heteroatoms. Oxazoles, thiazoles and diazols – nomenclature and general characterization. Histidine and its derivatives with biological activity. Pyrazolone derivatives, synthesis of antipyrine.

Six-membered heterocyclic compounds with two heteroatoms. Oxazines, thiazines and diazines – nomenclature and general characteristics. Lactam-lactim tautomerism in pyrimidine hydroxyl derivatives. Barbiturates, pyrimidine bases, nucleosides and nucleotides.

Fused Heterocyclic Compounds. Purines – nomenclature and general characteristics. Purine nucleic acid bases, uric acid, purine alkaloids.