National Academy of Sciences of Ukraine
V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry

PROGRAM

in organic chemistry

for passing additional entrance exams to postgraduate studies

for studying at the third (educational and scientific) level of higher education

Doctor of Philosophy (PhD)

in the specialty E3 Chemistry

Kyiv - 2025

Approved by the Academic Council
Institute of Bioorganic Chemistry and
Naftochemistry V.P. Kukhar
NAS of Ukraine
from 08 May 2025,
Protocol No. 6

Explanatory note

The program "Organic Chemistry" is designed for applicants who are applying for postgraduate studies in the specialty E3 Chemistry from another field of knowledge (specialty) indicated in their master's (specialist's) degree.

The purpose of the additional entrance examination for postgraduate studies in the specialty E3 Chemistry is to find out the level of theoretical knowledge and practical skills of applicants acquired during their studies at the educational degree / specialist / master's level in order to form a rating list and competitive selection of applicants for the degree of Doctor of Philosophy in the specialty E3 Chemistry within the license volume of the Institute.

Form of additional entrance exam

The additional entrance exam is held in writing. Applicants write answers to the questions on the exam paper with the Institute's seal. The exam lasts 60 minutes.

Structure of the exam ticket

The ticket of the additional entrance exam contains 3 theoretical questions. The questions in the tickets are formed on the basis of this program.

Requirements for the applicant's answer

The questions assess the applicant's knowledge of organic chemistry necessary for the correct expression of certain concepts, as well as for understanding a wide range of theoretical and practical tasks, and possession of skills required for professional activities within the program. The correctness of the tasks is assessed in accordance with the criteria for assessing knowledge.

criteria

The evaluation of the applicant's response to the postgraduate program is based on the level of his/her preparedness for research and experimental activities in the field of organic chemistry.

Each question is scored on a 100-point scale. The total score is determined as the arithmetic mean of the sum of the scores for all questions.

Scale of evaluation: national and ECTS

Sum of points for all types of learning activities	ECTS evaluation	Score on the national scale
		for the exam, practice, differentiated test
90 - 100	**A**	excellent

82-89	**B**	well
74-81	**C**	
64-73	**D**	satisfactorily
60-63	**E**	
35-59	**FX**	unsatisfactory with the possibility of reassembly
0-34	**F**	unsatisfactory with mandatory re-study of the discipline

90-100 - "excellent". The applicant presents the program material in a reasoned and complete manner. In his answers, he relies on the research of scientists, uses the methods of comparative analysis, generalization, gives examples, proofs. Consciously, accurately, and fully presents the program material in writing; highlights the main points. Shows a creative approach to revealing the essence of phenomena. Skillfully combines the acquired knowledge, skills, abilities with practice. Excellent performance of the task with only a small number of errors

74-89 - "good". The entrant shows knowledge of the course content. Gives examples when reproducing the program material, but lacks a creative approach to solving the problem. Shows knowledge of the course content, but does not fully reveal the essence of the phenomena. Correctly uses knowledge, skills, abilities only in standard situations.

60-73 - "satisfactory". The applicant makes mistakes in the answers and has difficulties in eliminating them. The answers to the questions are not complete. Has difficulties in applying the acquired knowledge, skills and abilities in practice. In general, the program material is partially mastered.

0-59 - "unsatisfactory". Has difficulty in explaining the content of basic concepts. Makes a significant number of mistakes in the reproduction of program material. Has a poor command of basic concepts, reveals the essence of phenomena, concepts at the level of reproduction. Cannot combine the acquired knowledge with practice. Answers to questions are fragmentary, do not reflect the essence of the problem.

PROGRAM CONTENT

INTRODUCTION

The program "Organic Chemistry" is designed for applicants entering postgraduate studies in the specialty 102 "Chemistry" from another field of knowledge (specialty) indicated in their master's (specialist's) diploma.

The subject of organic chemistry. Carbon compounds, their features. The role of organic substances in living nature and human activity. Organic chemistry in the system of other chemical disciplines and natural sciences. The origin and main stages of development of organic chemistry. Natural raw materials for industrial organic synthesis.

Composition and structure of organic compounds. Historical development of theoretical concepts in organic chemistry. Radical theory and type theory. Theory of chemical structure, its main provisions and methodological aspects. Structural formulas. Homology. Isomerism. Hydrocarbon radicals and functional groups. Classification of organic compounds.

Types of chemical bonds in organic compounds. The octet model of chemical bonding. Covalent and electrovalent bonds. Donor-acceptor bonding. Semipolar bonding. Quantum mechanical theory of covalent bonding. $Sp^{(3)}$ -, sp^2- and sp-hybridization of carbon atom orbitals and location of hybrid orbitals in space. The concept of bond polarity and partial charges. Induction effect in the system of σ-bonds. Positive and negative induction effects. Conjugation (mesomerism, resonance) in a system of π-bonds. Mesomeric effect and methods of its representation. Resonance energy. The effect of overconjugation (hyperconjugation).

Principles of classification and nomenclature of organic compounds. Trivial, radical functional, substituent nomenclature. Principles of nomenclature of IUPAC and refereed journals RZHim and Chemical Abstracts.

Features and classification of reactions of organic compounds. Classification of reactions by their consequences (substitution, addition, cleavage, rearrangement). Classification by the type of bond breaking and the nature of the reacting particles. Homolytic and heterolytic bond breaking. Radical, electrophilic and nucleophilic reagents. Transition state (active complex), intermediate product. The order of reactions. Kinetic and thermodynamic control of reactions. Static and dynamic approaches to the study of electronic structure and reactivity of a molecule. Static approach: reactivity indices, molecular diagrams. Dynamic approach: the nature of the reagent, substrate, medium, their mutual influence, energy profile of the reaction, energy barrier of the reaction, activation energy, transition state energy, thermal effect of the reaction. Reaction mechanism.

ACYCLIC COMPOUNDS. HYDROCARBONS

Alkanes. Isomerism. Nomenclature. Homologous series of alkanes. The nature of C-C and C-H bonds (sp^3- hybrid state of the carbon atom). Conformations, Newman projections.

Methods for the synthesis of alkanes: hydrogenation of unsaturated hydrocarbons, reduction of halogenalkanes and carbonyl compounds, Wurz and Corey-House synthesis, Kolbe reaction, industrial methods of production. Physical properties of alkanes.

Chemical properties of alkanes: causes of resistance to ionic reagents, free radical reactions of alkanes (halogenation, sulfochlorination, nitration, oxidation, sulfoxidation). Chain reactions. Factors that determine the selectivity of these reactions. Reactivity and selectivity of primary, secondary and tertiary carbon atoms. Oil, its composition and processing. Thermal and catalytic cracking. Industrial importance of alkanes.

Alkenes. Isomerism and nomenclature. Nature of the double bond (sp^2- hybridized state of the carbon atom). Conformation, methods of its determination. Structural and spatial structure, relative stability of isomers.

Methods for the synthesis of alkenes: cleavage (elimination) reactions - dehydration of alkanes, dehydration of alcohols, dehydrohalogenation of dihalogenated derivatives, hydrogenation of acetylenes, Wittig reaction, thermolysis of quaternary ammonium bases. Mechanism and stereochemistry of elimination reactions. Zaitsev's rule. Industrial sources of alkenes. Ethylene, propylene, butylene.

Reactions of electrophilic addition to alkenes, their mechanism, concepts of π- and σ-complexes. Markovnikov's rule. Attachment of halogens, halides, mercury acetate, water. Conjugated addition. Reverse addition of hydrogen bromide against Markovnikov's rule. Oxidation of alkenes by Wagner, Prilezhaev, oxidation to carboxylic acids (its industrial importance), ozonolysis. Hydrogenation and relative stability of alkenes. Hydroboration. The concept of telomerization. Radical and ionic

polymerization. Reactions catalyzed by transition metal complexes (metathesis, hydroformylation, polymerization). Alkene reactions involving the allyl position. Electron delocalization in allyl free radical and carbonium ion.

The use of alkenes in industrial organic synthesis. Methods of synthesis of acrylonitrile, acrolein and vinyl chloride.

Alkadiens. Types of dienes. Methods for the preparation of dienes (alkenes, conjugated dienes, dienes with isolated bonds). Conjugated dienes, structure and stereochemistry. Methods for the preparation of butadiene, chloroprene and isoprene. Specific properties and structure of alkene and conjugated dienes. π,π-Conjugation and its detection by UV spectra. Conjugation energy. Heat of hydrogenation of dienes. 1,2- and 1,4-Attachments to conjugated dienes. Interaction of conjugated dienes with bromine, chlorine and bromine hydrogen. Kinetic and thermodynamic control. Hydrogenation. Diene synthesis and rules of orbital symmetry. Cycloaddition. Cyclization of dienes (thermal and photochemical). Woodward-Hoffman rule. Di- and oligomerization of divinyl.

Polymerization of dienes, methods of its initiation. Butadiene, isoprene and chloroprene rubbers. Vulcanization. Rubber.

Alkynes. Isomerism, nomenclature. Physical properties. Nature of the triple bond (sp-hybridized state of the carbon atom). Methods of synthesis of alkynes: elimination reactions, synthesis of acetylene homologues via organometallic compounds, industrial synthesis of acetylene (from calcium carbide and methane cracking).

Chemical properties. C-H acidity of acetylene: Acetylenides and organometallic acetylene derivatives. Addition of halogens and hydrogen chloride, water (Kucherov) to alkynes, hydrogenation, stereochemistry of these reactions. Addition of alcohols, carboxylic acids, hydrogen cyanide. Condensation of acetylene with ketones and aldehydes (Favorsky, Reppe). Di-, tri-, and tetramerization of acetylene. Syntheses based on acetylene. Chloroprene. Enines.

MONO- AND POLYFUNCTIONAL HYDROCARBON DERIVATIVES

Halogen derivatives. Classification. Isomerism. Nomenclature. Methods of preparation: halogenation of alkanes, addition of halogen hydrogens to unsaturated compounds, synthesis by substitution of a hydroxyl group with a halogen. Physical and chemical properties. General laws of nucleophilic substitution reactions of halogens. Nucleophilicity and basicity. Carbonium ions, their stability. S_N1 and $S_{(N)\ 2}$reactions, the influence of electronic and structural factors, halogenalkyl molecules, the nature of the leaving group, reagent, solvent. Ambivalent ions (nitrile and cyanide anions). Understanding of the principle of hard and soft acids and bases.

Use of nucleophilic substitution reactions. Preparation of fluorides, iodides, nitriles, nitro compounds, amines, mercaptans, esters, and ethers.

Stereochemistry of compounds with one asymmetric atom. Optical antidotes, racemates. R,S nomenclature. Dependence of the stereochemical result of halogen substitution on the reaction mechanism. The idea of solvent participation in SN1-type reactions. Competition of substitution and elimination reactions, E1 and E2 mechanisms, their stereochemistry.

Halogenalkenes. Chlorides and bromides of allylic and vinyl types, their preparation from alkenes, conjugated dienes, and diacetylene. Reasons for different halogen mobility in allylic and vinyl positions. Examples of their use in organic synthesis.

Interaction of halogenated hydrocarbon derivatives with metals. Wurz synthesis. Preparation of organometallic compounds from alkyl, allyl and vinyl halides, their properties. Syntheses based on organometallic compounds.

Polyhalogenated alkanes. Tetrachloromethane, chloroform, dichloroethane, trichloroethylene. Preparation and special properties of perfluoroalkanes and perfluoroalkenes. Organochlorine products in industry. Dichlorocarbene.

Alcohols. Classification. Isomerism. Nomenclature. Methods of synthesis of alcohols: hydrolysis of halogen derivatives, hydration and hydroboration of alkenes, reduction of carbonyl compounds and acid derivatives using organometallic compounds, hydrocarbon fermentation.

Physical properties of alcohols. Acidity. Formation of associates, hydrogen bonding. Chemical properties. Alcohols and alcohols as bases. Nucleophilic substitution of a hydroxy group with a halogen; influence of the nature of the reacting substances and solvents on the reaction and its mechanism. Effect of thionyl chloride and phosphorus halides on alcohols. Dehydration of alcohols. Retropinacolinic rearrangement. Substitution of hydroxy group with amino and alkoxy groups. Oxidation with lead tetraacetate and iodic acid, interaction with carboxylic acids.

Esters of inorganic acids: preparation and properties of alkyl sulfates, alkyl nitrates, and alkyl nitrites. Their properties.

Methanol, ethanol, propanols, butanols - modern methods of production and industrial application.

Unsaturated alcohols. Eltekow-Erlenmeyer rule. Derivatives of vinyl alcohol. Allyl alcohol.

Polyhydric alcohols. Features of 1,2-alkanediols: formation of complexes with copper hydroxide, oxidation with lead tetraacetate and iodic acid, interaction with boric acid, conversion to α-oxides. Ethylene glycol and glycerin, their industrial synthesis and application. Nitroglycerin. Diethylene glycol.

Ethers. Isomerism. Nomenclature. Synthesis by Williamson and dehydration of alcohols. Properties of esters: formation of oxonium compounds, splitting, halogenation, formation of hydroperoxides. Crown ethers and their application in synthetic practice. Diethyl ether, ethylene glycol, diethylene glycol and cellulose esters. Tetrahydrofuran and dioxane. Vinyl esters.

Alpha-oxides, methods of their synthesis (halogen hydride, epoxidation with oxygen and superacids, Darzan synthesis) and properties: reactions with electrophilic reagents and triphenylphosphine. Ethylene oxide as a raw material for the industrial synthesis of solvents and ethanolamines. Polyoxyethylene.

Aldehydes and ketones. Oxo compounds. Isomerism. Nomenclature. Methods for the preparation of aldehydes and ketones: dehydration of alcohols, oxidation of alcohols, ethylene hydrocarbons, glycols, reduction of acyl chlorides, nitriles, amides, hydrolysis of heminal dihalogen derivatives, hydration of acetylenes, via organometallic compounds, using acetoacetic ester, oxosynthesis. The structure of the carbonyl group, its polarity and polarizability.

Physical and chemical properties. Interaction with nucleophilic reagents, formation of bisulfite compounds, cyanhydrins, hydrazones. Preparation of oximes and their transformation. Preparation of enamines, their alkylation and acylation. Reactions with organomagnesium compounds: synthesis of alcohols, side reactions in these syntheses.

Carbonyl compounds in the Wittig reaction. Condensation of carbonyl compounds, interaction with phosphorus pentachloride. Preparation of acetals and ketals. The Prince reaction.

Reduction of aldehydes and ketones to alcohols and hydrocarbons, Tyshchenko reaction, Meierwein-Pondorff-Oppenauer equilibrium. Pinacolin reduction and pinacolin rearrangement. Reduction by complex hydrides. Reductive amination of ketones. Synthesis of pentaerythritol. Oxidation of aldehydes and ketones.

Enolization of aldehydes and ketones by acid and basic agents. Ambidextrous nature of enolate anions. Reactions of enolic forms: halogenation, nitrosation, ketone oxidation, aldol-croton condensation. Carbonyl and methylene components. Condensing agents. Choice of agent depending on the acidity of the methylene component. Condensation of aldehydes with ketones. Self-condensation of unsaturated ketones. Mannich reaction. Oxidation of aldehydes and ketones, dependence on the nature of the oxidizing agent and oxidation conditions.

Formaldehyde, acetaldehyde, acetone, their industrial production and application. Synthesis of divinyl by Lebedev and Reppe, isoprene by Favorsky.

α,β-Unsaturated aldehydes and ketones, their syntheses. Carbonyl and alkene double bonds: 1,2- and 1,4 bonds. Vinology. Participation in diene synthesis reactions. Selective oxidation and reduction. Polymerization and oxidation of acrolein. Dicarbonyl compounds: glyoxal, diacetyl and its dioxide, acetylacetone (tautomerism, chelated metal derivatives).

Carboxylic acids. Classification. Isomerism and nomenclature (mono-, di-, and polycarboxylic acids, unsaturated acids). Methods of preparation: oxidation of alkanes, alkenes, alcohols, aldehydes, ketones, carboxylation of organometallic compounds, nitrile synthesis, Conrad syntheses (via acetoacetic and malonic esters), oxosynthesis, hydrolysis of derivatives. Structure of carboxyl. Association of acids. Inductive effect and its influence on acidity. Reaction centers of carboxylic acids: hydrogen, hydroxyl group, carbonyl group and alkyl radical.

Reactions of carboxylic acids: preparation of salts, chlorohydrides, esters, and superacids. Properties of functional acid derivatives, the relation of various functional derivatives to hydride reducing agents, to ammonia and amines, to organometallic compounds. Halogenation of carboxylic acids.

Salts: pyrolysis and electrolysis, reactions with pentachloride phosphorus, alkyl and acyl halides.

Ester. Mechanism of the esterification reaction. Hydrolysis, ammonolysis and transesterification of esters. Ester condensation. Vinyl acetate, its polymerization.

The use of anhydrides and chloranhydrides as acylating agents. Comparison of the activity of the carbonyl group of carboxylic acids and their functional derivatives.

Ketones as internal anhydrides: their structure, methods of preparation, and properties.

Nitriles and amides, their mutual transformations. Alcoholysis and amonolysis of nitriles. Rearrangement of amides (Hoffmann) and azides (Curtius). The concept of sextet (nucleophilic) rearrangements.

α,β-Unsaturated acids: acrylic, methacrylic, crotonic. Synthesis, reactions of addition to the C-C bond. Acrylonitrile, cyanoylation reaction. Polymers based on derivatives of acrylic and methacrylic acids, industrial synthesis of the corresponding monomers. Higher fatty acids and their derivatives. Fats. Hydrogenation and saponification of fats. Soaps.

Dibasic acids, methods of their synthesis and main representatives. Oxalic acid, its features, diethyl oxalate in ester condensation. Malonic acid: syntheses based on malonic ester, Michael reaction, condensation with aldehydes. Succinic acid: its anhydride and imide. Bromosuccinimide as a

halogenating agent. Condensation of succinic acid esters with ketones and aldehydes (Stobbe). Acyloid condensation.

Two-basic unsaturated acids: fumaric and maleic, their geometric isomerism, mutual transitions, methods of determining the configuration, C-C bond reactions. Maleic anhydride in diene synthesis.

Acetylene dicarboxylic acid: preparation, use of its ester as a dienophile.

Nitro compounds. Classification, isomerism, nomenclature. Synthesis of nitro compounds (from alkanes and halogen alkanes). Structure of the nitro group (semipolar bond, mesomerism). Tautomerism of nitro compounds. Interaction with alkalis and nitric acid, condensation with carbonyl compounds. Acidolysis of primary nitro compounds. Preparation of carboxylic acids and hydroxylamine.

Amines. Classification. Isomerism. Nomenclature. Stereochemistry of tertiary amines and quaternary ammonium bases. Methods for the preparation of primary, secondary and tertiary amines: alkylation of ammonia and amines, Gabriel's reaction, reduction of nitro compounds, amides, nitriles, oximes, rearrangement of nitrogen-containing compounds (Hoffmann, Curzius, Beckmann).

Basicity of amines. Dependence of the basicity on the number and nature of substituents bound to the nitrogen atom. Reactions of amines as nucleophilic reagents (formation of quaternary ammonium bases and their Hoffmann splitting), interaction with carbonyl compounds, acylating agents, nucleophilic addition to C=C bonds activated by conjugation with electroacceptor groups. Nitric acid action and primary, secondary and tertiary aliphatic amines. Detection of primary, secondary and tertiary amines by the Ginsberg test. Application of amines in industry. Diamines, their nomenclature, methods of preparation, properties. Ethylenediamine, putrescine, cadaverine, hexamethylenediamine: their preparation and properties. Use in the polycondensation reaction. Nylon.

Diazo compounds of the aliphatic series. Classification. Diazomethane. Methods of preparation, structure, properties: interaction with unsaturated compounds, phenols and other aromatic compounds, aldehydes and ketones, carboxylic acid chlorohydrides. Diazomethane as a methylating agent. Aliphatic diazo compounds as sources of carbenes. Other ways of generating carbenes. Structure and reactivity of carbenes. Isonitriles. Preparation and properties. Diazirin.

HYDROCARBONS

Monosaccharides (monoses) are polyoxyaldehydes and polyoxyketones. Classification of monosaccharides: according to the number of carbon atoms - pentoses, hexoses with the presence of aldehyde or ketone groups - aldoses and ketoses. Stereochemistry of monoses. Absolute and relative configurations. D- and L- series, their stereochemical relationship with glycerol aldehyde. Stereochemical series of monoses, the most important representatives. Ring-chain tautomerism. Pyranose and furanose forms of Howors. Conformations of hexoses.

Mutual transformations of cyclic and open forms. The phenomenon of mutation, a- and ß-stereoisomers (anomers). Special properties of glucoside hydroxyl (formation of glucosides and their hydrolysis). Determination of the size of the monosaccharide cycle by exhaustive methylation and sequential oxidation. Chemical properties of monosaccharides: acylation, alkylation, formation of sugars, oxidation, reduction, interaction with hydrocyanic acid, hydroxylamine, phenylhydrazine (ozones and ozones). Epimerization under the influence of alkalis. Methods of shortening and extending the carbon chain of monosaccharides. Proof of stereochemical affinity of monosaccharides on the example of arabinose, glucose and fructose, as well as glucose, mannose and fructose.

Conversion of pentoses and hexoses into furfural derivatives. Specific properties of monoses that are incompatible with the notion of the Fischer chain formula for these compounds.

Disaccharides (bioses). Classification. Nomenclature. Structure. Reducing and non-reducing disaccharides. Maltose, cellobiose, lactose, sucrose. Methods for determining the structure of disaccharides. Inversion of the optical activity of sucrose during hydrolysis. Chemical properties of disaccharides. Amino sugars. Chitin. Structure. Biological significance.

Polysaccharides. Starch, glycogen, fiber (cellulose), their distribution in nature, importance. Structure of polysaccharides. Cellulose ethers and esters: methyl, ethyl, acetyl cellulose nitrocellulose, celluloid, cellophane. Artificial fibers based on cellulose. Acetate silk. Fiber xanthonate. Viscose.

AMINO ACIDS

Classification. Isomerism. Nomenclature. Natural amino acids. Their stereochemistry. Methods of preparation: by substitution of halogen in halogen-substituted carboxylic acids, by the action of ammonium cyanide on oxo compounds (Strecker, Zelinsky), by addition of ammonia to unsaturated acids, by the action of malonic acid and ammonia on aldehydes, from nitroacetic acid ester.

Physical and chemical properties of amino acids, their betaine-like structure. The concept of an isoelectric point. Amphotericity. Reactions of amino acids involving the carboxyl group (formation of salts, esters, halides) and the amino group (formation of salts with acids, acylation, alkylation, interaction with nitric acid). Specific properties of amino acids: formation of diketopiperazines of a^-unsaturated acids, lactams, peptides, and complexes with metal salts. The most important representatives of aliphatic, aromatic and heterocyclic amino acids, their preparation and use: a-amino acids - components of proteins (feed additives), aminocaproic acid (nylon), ethylenediaminetetraacetic acid (complexes).

Peptides and polypeptides. Proteins. Methods for the preparation of peptides and polypeptides from various amino acids. Protection of the amino group, activation of the carboxyl group. Methods for determining the composition and structure of polypeptides. Hydrolysis. Determination of N-C-terminal groups of amino acids. Natural amino acids (aliphatic, aromatic and heterocyclic).

Proteins: general characteristics and composition. Proteins and proteids. Properties of proteins. their qualitative reactions. Natural proteins and proteids. Primary, secondary and tertiary structure of proteins. Role in living nature, their importance as a component of food and industrial raw materials.

ORGANOMETALLIC COMPOUNDS

Organic sulfur compounds, comparison of their properties with those of corresponding oxygen-containing compounds. Thiols, thioesters, thiocarbon compounds. Sulfonic acids and their functional derivatives. Synthetic detergents. Organic derivatives of silicon, their use in the synthesis of polymers. Types of organic phosphorus compounds, their mutual transitions. Arbuzov's reaction. Organophosphorus insecticides and chemical warfare agents.

Metal-organic compounds. Preparation of organometallic compounds. Grignard's reagents. Conditions of formation, influence of the structure of halogen derivatives (nature of the halogen and the structure of the radical bound to it). Solvents for the preparation of organometallic compounds, their influence on the course of reactions, side processes, activating effect of iodine in the reactions of magnesium with halogens. Modern ideas about the structure of organometallic compounds.

Organometallic compounds as bases: reactions with compounds containing a mobile hydrogen atom. Nucleophilic properties of organomagnesium compounds - interaction with halogens, oxygen,

carbon dioxide and sulfur. The use of organometallic compounds for the synthesis of hydrocarbons, halogen derivatives, alcohols, aldehydes, ketones, carboxylic and sulfonic acids.

Organo-zinc compounds. Comparative characteristics of their synthesis and reactivity with organometallic compounds. Application of organo-zinc compounds for the synthesis of esters of α-oxy acids and unsaturated acids (Reformatsky reaction).

Methods for the synthesis of organolithium compounds and their use in the production of alcohols and carboxylic acids. Comparison with organomagnesium compounds.

Organosodium compounds. Sodium alkanes. Application in organic synthesis.

Organic aluminum compounds, their preparation by Ziegler, their use in synthesis and as polymerization catalysts.

AROMATIC HYDROCARBONS (ARENES)

Arenas, their classification. **Benzene** and its homologues. Nomenclature and isomerism. Sources of aromatic hydrocarbons: coal (coking), oil (distillation, aromatization, reforming), acetylene and essential oils, Kekulé's formula for benzene. Electronic structure, Quantum chemical description of the benzene molecule: valence bond method (resonance).

Scheme of molecular orbitals and their construction for aromatic and non-aromatic systems. Aromaticity and antiaromaticity, Hückel's rule.

The empirical energy of resonance. Conjugation and delocalization energy of the benzene molecule. Features of benzene: relative stability to oxidation, susceptibility to substitution reactions, thermochemistry of hydrogenation and combustion of benzene, its formation in the reactions of cyclohexadienes disproportionation, preparation of aromatic systems by pyrolysis of various classes of organic substances. Physical properties and main spectral characteristics of benzene and its homologues (UV-, IR- and PMR-spectra).

Chemical properties of arenes. Reactions of addition to benzene: catalytic hydrogenation, reduction with sodium in liquid ammonia to hydrobenzene (Birch), halogenation. Benzene oxidation reactions: catalytic oxidation to maleic anhydride, biochemical oxidation to muconic acid, ozonation. Expansion of the benzene nucleus: interaction with carbenes (cycloheptatrienes), aryl- and alkylazides (azepines). Isomerization of benzene by UV radiation. Benzene Duarte, synthesis and isomerization.

Alkyl benzene. Nomenclature and isomerism. Industrial and preparative methods of preparation. Wurz-Fittig reaction. Alkylation by Friedel-Krafts. Alkylation by halogenalkyls. Influence of the nature of the halogen and the structure of the halogen alkyl. Catalysts - metal halides, their role and activity. Isomerization of alkyl radical in the process of alkylation. Influence of spatial obstacles and basicity of the aromatic substrate on the ratio of the formed isomers. Alkylation by alkenes. The role of the nature of the alkene, catalysis by metal halides and mineral acids. Alkylation with oxiranes. Alkylation with alcohols. Influence of alcohol structure (alkylating agents). Oxidation of alkyl benzene.

Individual representatives of the arenas: benzene, -toluene, cumene. Unsaturated fatty aromatic compounds: styrene, divinylbenzene, phenylacetylene, toluene, styrene and its substitutes, diarylpolymers.

Halogen derivatives of aromatic hydrocarbons. Preparative and industrial methods of preparation. Chlorination, bromination, fluorination and oxidative halogenation. Catalysts for halogenation - Lewis acids. The mechanism of halogenation. A range of activity of Lewis acids catalysts. Iodine as an activator of chlorination, and bromination of arenas. Solvents as catalysts for

halogenation (dioxane, water, acetic acid). Dependence of halogenation conditions (nature of the catalyst, temperature, etc.) on the structure of the aromatic system. Production of arene halides by decomposition of aromatic diazonium salts. Conditions for halogenation of benzene into an aromatic nucleus and side chain. Chloromethylation of arenes

Sulfonic acids and their derivatives. Structure and nomenclature of sulfonic acids. Sulfonation of benzene and its homologues. Reversibility of the reaction (causes), side processes. Sulfurizing agents. Features of the isolation and identification of arenesulfonic acids. Nucleophilic and electrophilic substitution of the sulfonic group, its elimination (preparation of picric acid by sulfonation of phenol), other ways of synthetic use of sulfonic acids, desulfurization. Sulfochlorides. Sulfonic acid amides. Esters of sulfonic acids. Reactions of sulfonic acids with the participation of a benzene nucleus. The value of sulfonic acids. Chloramines. Saccharin and other sulfonic acid derivatives.

Nitro compounds. Nitration of benzene, alkyl benzene, halogen benzene, phenol, aniline and other derivatives. The mechanism of the reaction, evidence of the participation of the nitronium cation. Nitrating agents. Orientation, side reactions. Synthesis of di- and trinitrobenzene. Nitrotoluenes. TNT. Nucleophilic hydrogen substitution reactions in nitrobenzene and halogenonitrobenzene. Meisenheimer complexes. Formation of charge transfer complexes by polynitro compounds. Nitration of benzene homologs in the side chain. Tautomerism of phenylnitromethane. Transformation of phenylnitromethane.

Amines. Nomenclature, isomerism. Preparation of aromatic amines in industry and in laboratories. Electronic structure of the aniline molecule. Comparative characteristics of fatty and fatty-aromatic amines. Oxidation of primary, secondary and tertiary aromatic amines. Mono- and dialkylanilines and their properties. Influence of the amino group on the properties of the benzene nucleus. Aromatic amines with an amino group in the side chain. Drugs based on them (levomycetin, ephedrine). Sulfanilic acid. Benzene sulfamides. Streptocide and other sulfonylamides as medicinal products.

Aromatic diazo compounds. Reactions of diazotation of primary amines with nitric acid. Reaction conditions. The mechanism. Direct and reverse diazotation. Diazotation of alkyl nitrites. Other methods of diazotation. Solid salts of diazonium (chlorides and tetrafluoroborates, complexes with metal chlorides, sulfonic acids - diazoles). Structure and tautomerism of aromatic diazonium salts: diazonium salts as Lewis bases, diazonium hydroxides.

Phenols. Classification. Single-atom phenols: methods of preparation - industrial (from coumol, arylsulfonic acids, halogenated aryls) and laboratory (oxidation of arenes, decomposition of arenadiazonium salts, from aromatic carboxylic acids). Acid-base properties of phenols: mutual influence of hydroxyl and nucleus and nature of substituents in the nucleus. Properties of phenolic hydroxide: comparison of the structure of phenols and alcohols, qualitative reaction with iron (III) chloride, preparation of esters and esters. Substitution reactions in the phenol nucleus. Conditions and mechanism, nitration. Effect of nitro group on the acidity of phenol. Effect of alkalis on nitrophenols. Picric acid. Sulfonation. Halogenation. Phenols and their derivatives as pesticides. Dioxins. Tetrabromophenol. Action of electrophilic reagents on 2,4-disubstituted phenols. O-alkyl and o-allyl phenols. Stability. Isomerization. Kleisen rearrangement.

Two- and three-atom phenols. Keto-enol tautomerism of multinuclear phenols. Pyrocatechin, methods of its synthesis. Synthesis of resorcinol, its reduction with hydrogen at the time of isolation,

carboxylation of phenolate, nitrogen coupling. Preparation of hydroquinone, pyrogallol and fluroglucin. Oxidation of pyrogallol, use in gas analysis. Photographic Developers.

Aromatic aldehydes and ketones. Their classification. Industrial and laboratory methods of synthesis of aromatic aldehydes. Special properties of aromatic aldehydes: auto-oxidation, reaction with chlorine, Cannizzaro reaction, Perkin synthesis, condensation with phenols, ammonia, benzoin condensation. Condensation of aromatic aldehydes with acetone, acetophenone. Cinnamic aldehyde, chalcones. Synthesis of fatty aromatic and aromatic ketones by acylation according to the Friedel-Krafts reaction, from nitriles, etc. Properties of fatty aromatic ketones. Their behavior in the conditions of aldol-croton condensation, Mannich reaction, halogenation into the side chain.

Reduction of acetophenone to ethylbenzene, pinacone and secondary alcohol. Oximes of aromatic ketones and their stereochemistry. Beckmann rearrangement.

Properties of aromatic ketones: alkali cleavage, photoexcitation. Benzophenone as a promoter of oxidation reactions. Diketones. Benzoin rearrangement. Electrophilic substitution reactions in the aromatic nucleus of aldehydes and ketones.

Benzoquinones. Preparation of benzoquinones. Properties of p-benzoquinone: preparation of mono- and dioxides, addition of hydrogen chloride, bromine, aniline, hydrogen, acetic anhydride, hydrocyanic acid. Reactions of quinones with arendiazonium salts. Quinones as oxidizing agents (chloranil). Quinhydrone. Semiquinone as a free radical.

Carboxylic acids. Classification. Methods of synthesis of aromatic carboxylic acids. Influence of the nature and position of substituents on the dissociation constants of benzoic acids. Hammett's equation. Examples of its application and limitations. Properties of benzoic acid. Industrial method of obtaining benzoyl chloride. Preparation and use of benzoyl peroxide to initiate radical reactions. Superbenzoic acid, its use for the synthesis of a-oxides (oxiranes) from alkenes according to the Prilezhaev method. Electrophilic substitution reactions in the aromatic core. Unsaturated fatty aromatic acids. Cinnamic acid and synthesis. Properties, application. Synthesis of p-aminobenzoic acid and its biological activity. Anthranilic acid, synthesis, its reactions involving only the amino group or only the carboxylic group. Diazotation. Formation of dehydrobenzene and its identification as trypticene.

Phthalic acids and their preparation. Properties. Phthalic anhydride, interaction with alcohols and, in particular, with glycerol (glyphthalic acid). Phthalides. Preparation of phthalimide. Synthesis of amines by Gabriel. Condensation of phthalic anhydride with phenol, resorcinol. Phenolphthalein, fluorescein, eosin, their indicator properties. Polyester fibers.

Aromatic carboxylic acids with a carboxyl in the side chain.

MULTINUCLEAR AROMATIC COMPOUNDS AND THEIR DERIVATIVES

Multinuclear aromatic hydrocarbons with uncondensed nuclei. Diphenyl, di- and triphenylmethane compounds. Isomerism of biphenyl derivatives (atropoisomerism). Methods of preparation, properties. Reactions involving a benzene nucleus and a methane carbon atom. Salts of triphenylmethane (halochromia). Triphenylmethyl radical, cation and anion. Reasons that determine their stability. Dyes of the triphenylmethane series: basic (parafuchsin, malachite green, crystal violet) and acidic (phenolphthalein, fluorescin). Relationship of structure to color.

Multinuclear aromatic hydrocarbons with **condensed nuclei.** Isomerism and nomenclature of derivatives. Industrial sources of their production. Hydrocarbons of linear and annular structure. Comparative assessment of the aromatic character of benzene, naphthalene, anthracene, phenanthrene

and their delocalization energies. Naphthalene. Proof of structure. Synthesis from benzene compounds. Electrophilic substitution and addition reactions in the naphthalene series. Sulfation, nitration, halogenation and acylation of naphthalene. Orientation rules for electrophilic substitution in naphthalene and its derivatives. Oxidation and hydrogenation of naphthalene. Synthesis of naphthols and naphthylamines. The importance of naphthalene derivatives in industry. Anthracene and phenanthrene. Structure, isomerism, nomenclature of derivatives. Methods of preparation. Features of addition, oxidation and reduction reactions. Anthraquinone and phenanthrenequinone. Diphenic acid. Alizarin. Mordant staining.

Varnishes. Natural compounds with phenanthrene backbone (steroids, abietic acid, terpenes). Higher condensed systems. The concept of carcinogenic substances.

HETEROCYCLIC COMPOUNDS

General characteristics of heterocycles. Classification. Nomenclature. Aromatic heterocycles. The nature of p-electron delocalization in five- and six-membered heterocycles, the influence of the heteroatom. Delocalization energy as a quantitative characteristic of the aromaticity of heterocycles. Comparative characterization of the aromaticity of benzene and heterocyclic aromatic compounds. The role of heterocycles in nature and various branches of industrial organic synthesis.

Five-membered heterocycles with one heteroatom. Comparative characterization. Influence of heteroatom on aromaticity, unsaturation and acidophobicity. Acid-base transformations, hydrogenation and halogenation, oxidation with oxygen. Ozonation of pyrrole and furan and their methyl substituted compounds. Substitution reactions, heteroatoms as substituents of the first kind. General and specific methods of synthesis of furan, pyrrole and thiophene. Reactions of heteroatom substitution (mutual transformation by Yuriev). Cycle extension reactions. Mechanism.

Furan. Preparation. Electrophilic substitution reactions: nitration, sulfation, halogenation, acylation, mercurization. Reagents and orientation of substitution. Hydrogenation of furan. Participation in the Diels-Alder reaction, pH value of the medium. Reactions of furan cycle opening. Furfural: preparation and reactivity. Syntheses based on furfural. Pyrosilicic acid. Lack of acidophobicity of substituted furans (furfural, nitrofurfural, halogenated furans, pyrosilicic acid, etc.). Syntheses based on furfural. Condensation of furfural with acetone and synthesis of high molecular weight compounds. Aryl furfural. Synthesis. Properties.

Pyroleum. Preparation. Electrophilic substitution reactions. Acidic properties of pyrrole: potassium pyrrole and pyrrole-magnesium halides, comparison of their properties with phenolates. Condensation of pyrrole with formaldehyde and formic acid. Dipyrimethane and pyromethane. Hydrogenated pyrroles: pyrrolidine and pyrrolines. Properties of pyrrolidine. Vinyl pyrrolidine, polyvinyl pyrrolidine, nylon-4. Synthesis and aromaticity of porphyrin. Structure and biochemical role of hemoglobin, chlorophyll and vitamin B_{12}.

Thiophene. Preparation of thiophene and its derivatives. Special methods. Properties as an aromatic system. Affinity for benzene. Separation of thiophene from coke oven benzene. Interaction of thiophene with isatin. Hydrogenation, mercurization of thiophene. Thiophene nucleus in natural compounds. Bromination of a-methylthiophene in light and under heterolytic conditions. Other thiophene reactions.

Five-membered heterocycles condensed with an aromatic nucleus. Indole, thionaphthene, coumarin, carbazole. Synthesis of indole and its derivatives by the Fischer reaction and cyclization of o-amino benzene derivatives. Electrophilic substitution reactions in the indole molecule, substitution

orientation (comparison with pyrrole). Proton mobility (acidity) of the hydrogen of the NH-group (indolylmagnesium halides, indolylsodium, indolylkali and their reactions). Oxygen-containing indole derivatives: oxyindole, indoxyl, isatin. Their keto-enolic and lactic-lactic tautomerism. Indoleacetic acid (heteroauxin). Indigo. Indecanes. Occurrence in nature. Industrial methods of indigo synthesis. Modern data on the structure of indigo. Cube dyeing with indigo dyes. Indigo carmine, dibromindigo - ancient purple. Thioindigo. Chromophore and auxochrome groups of indigo dyes.

Five-membered heterocycles with several heteroatoms. Classification. Methods of synthesis and properties. Acid-base properties. Electrophilic substitution reactions. Phenylmethylpyrazolone and its use in the synthesis of drugs and dyes. Antipyrine, amidopyrine, analgin. Imidazole derivatives: histidine, histamine. The concept of triazoles and tetrazoles.

Six-membered heterocycles with one heteroatom. Pyridine. Pyridine bases from coal tar. Synthetic methods for the preparation of pyridine and its simplest derivatives. The structure of pyridine and the influence of its heteroatom on the distribution of electron density in the nucleus. Basicity and nucleophilicity of pyridine. Electrophilic substitution reactions: nitration, sulfation and bromination. Comparison with nitrobenzene. Nucleophilic substitution in the interaction of pyridine with sodium amide, potassium cyanide, and phenyllithium. Reactions with mineral acids, alkyl halides. Six-membered heterocycles with one heteroatom condensed with a benzene nucleus.

Quinoline and its derivatives. Synthesis by Skraup and Debner-Miller. Properties: electrophilic and nucleophilic substitution reactions, formation of quaternary salts. The relationship of quinoline to oxidizing agents and reducing agents. Synthesis of substituted derivatives in the benzene and pyridine nuclei of quinoline. Condensation of quinaldine and lepidine with carbonyl compounds. 8-Oxyquinoline, preparation and use in analytical chemistry. Quinoline nucleus in drugs and alkaloids. Isoquinoline, acridine. Preparation, properties, application.

Six-membered heterocycles with several heteroatoms.

Diazines. Pyrazine, pyrimidine and pyridazine. Methods of preparation, structure and properties. Reactions of electrophilic and nucleophilic substitution, formation of salts. Properties of derivatives. Tautomerism of oxy- and amino derivatives. The role of pyrimidine bases in nature. Uracil, thymine, cytosine - components of nucleic acids. Synthesis of uracil from malic acid, transition from uracil to cytosine. Tautomerism of cytosine. Sulfodimesine. Vitamin B_1.

Purine. Structure, nomenclature of derivatives. Purine acids and their role in nature. Uric acid, its synthesis, obtaining adenine, guanine, xanthine, hypoxanthine from it.

NUCLEIC ACIDS

The concept of nucleosides and nucleotides. Ribo- and deoxyribonucleic acids (RNA, DNA). Components of nucleic acids. The concept of the secondary structure of DNA and the mechanism of heredity transmission.

IMPORTANT NATURAL COMPOUNDS

The concept of alkaloids, vitamins, antibiotics. General concepts of chemical structure, isolation from natural objects and synthesis. Biological action and ways of use.

RECOMMENDED READING LIST

Main

1. Berezan, O. V. Organic chemistry: theory, problems, tests, answers: a textbook. Edition 3, with changes and additions. Ternopil: Textbooks and manuals, 2019. 208 c.

2. Chirva V.Y., Yarmolyuk S.M., Tolkacheva N.V., Zemlyakov O.E. Organic chemistry. Kyiv: Otova, 2009. - 996 c.

3. Krotenko V.V., Bukhtiarov V.K., Boyko R.S. Kovshun L.O. Organic chemistry: NUBiP of Ukraine, 2016. - 398 c.

4. Shved OM, Sinelnikova MA, Bespalko YM. Mechanisms of organic reactions: a textbook. Vinnytsia: DonNU, 2016. 60 c. URL: https://r.donnu.edu.ua/bitstream/123456789/1079/1/%D0%9C%D0%B5%D1%85%D0%B0%D0%BD%
D1%96%D0%B7%D0%BC%D0%B8%20%D0%BE%D1%80%D0%B3%D0%B0%D0%BD%D1%96%
D1%87%D0%BD%D0%B8%D1%85%20%D1%80%D0%B5%D0%B0%D0%BA%D1%86%D1%96% D0%B9.pdf

5. Kurta S.A. Mechanisms of organic reactions: a textbook for higher educational institutions of chemical profile. Ivano-Frankivsk: Precarpathian National University named after V. Stefanyk, 2020. 146 c. URL: https://moodle.znu.edu.ua/pluginfile.php?file=/966034/mod_resource/content/2/11111%20Mechanisms% 20of%20organic%20reactions.pdf 6. General and organic chemistry. Topic 6. Mechanisms of organic reactions. Lecture notes. URL: https://elearning.sumdu.edu.ua/free_content/lectured:5df7011dd2ba3fd1467ffc0f892ff9da2731ded5/latest /259458/index.html

6. Kovtunenko V.O. General Stereochemistry (2nd edition, revised). Textbook for students of higher educational institutions. K., Condor, 2005.

7. Lozynskyi M.O., Kovtunenko V.O. Carbanions. Synthesis and alkylation. - K.: Treo-Plus, 2008. - 626 p

8. Dombrovsky A.V. Organic chemistry. Kyiv: Vysha Shkola, 1991. 504 c.

9. Chernykh V.P., Zimenkovsky B.S., Gritsenko I.S. Organic chemistry: Textbook for pharmaceutical universities and faculties. In 3 books: - Kharkiv: Osnova, 1993 - 1997.

Additional

1. Boichuk I.D. Organic chemistry: a textbook for students of higher medical (pharmaceutical) educational institutions. I - III levels of accreditation. Kyiv: Medicine, 2012. 240 c.

2. Kotlyar, Z.V. Organic chemistry: a manual for teachers and students. Ч.1. Kharkiv: Osnova, 2012. 80 p. (Library of the journal "Chemistry"; Issue 2 (110).

3. Ransky, A.P. Organic chemistry and ecology: a textbook: in 2 parts. Part 1: Theoretical foundations of organic chemistry. Aliphatic hydrocarbons. Vinnytsia: VNTU, 2012. 120 c.

4. Maitland J. Jr. OrganiChemistry. W.W. Norton & Company. 1997. 1394 p.

The recommended list of references is indicative and does not exclude the applicants' own initiatives in their selection and use.