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Должность: Ректор PECOPLES' FRIENDSHIP UNIVERSITY OF RUSSIA named after P. Lumumba (RUDN University)

**Science Faculty** 

educational division (faculty/institute/academy) as higher education programme developer

## **COURSE SYLLABUS**

### **METHODS OF ORGANIC CHEMISTRY**

course title

### **Recommended by the Didactic Council for the Education Field of:**

**04.04.01 CHEMISTRY** 

field of studies / speciality code and title

The course instruction is implemented within the professional education programme of higher education:

«Fundamental and applied chemistry»

higher education programme profile/specialisation title

## 1. COURSE GOAL(s)

The main goal of the course of "Methods of Organic Chemistry" is to study the methods of introducing functional groups into the molecules of organic compounds and the reactions of transformation of functional groups, which make it possible to obtain almost all classes of organic compounds.

## 2. REQUIREMENTS FOR LEARNING OUTCOMES

Mastering the course "Methods of Organic Chemistry" is aimed at developing the following competencies /competences in part:

Table 2.1. List of competences that students acquire through the course study

Competenc e code	Competence descriptor	Competence formation indicators (within this course)
	To be able to plan work and choose adequate methods for solving research problems in the	PC-1.1. Draw up a general plan of research and detailed plans for individual stages.
PC-1	chosen field of chemistry, chemical technology or sciences related to chemistry	PC-1.2. Select experimental and computational- theoretical methods for solving the problem based on the available material and time resources.

## **3. COURSE IN HIGHER EDUCATION PROGRAMME STRUCTURE**

The course refers to the elective component of (B1) block of the higher educational programme curriculum.

Within the higher education programme students also master other (modules) and / or internships that contribute to the achievement of the expected learning outcomes as results of the course study.

Table 3.1. The list of the higher education programme components/disciplines that contribute to the achievement of the expected learning outcomes as the course study results

Competence	Competence	Previous	Subsequent
code	descriptor	courses/modules*	courses/modules*
PC-1	To be able to plan work and choose adequate methods for solving research problems in the chosen field of chemistry, chemical technology or sciences related to chemistry		Domino reactions in the synthesis of heterocycles NMR of organic compounds Molecular spectral analysis Chemistry of natural compounds Chemistry of heterocyclic compounds Mass spectrometry of organic compounds Stereochemistry Fundamentals of drug design

Competence code	Competence descriptor	Previous courses/modules*	Subsequent courses/modules*
			Experimental research
			methods in chemistry
			Research work
			Undergraduate practice

\* To be filled in according to the competence matrix of the higher education programme.

## 4. COURSE WORKLOAD AND ACADEMIC ACTIVITIES

The total workload of the course is 3 credits.

*Table 4.1. Types of academic activities during the periods of higher education programme mastering (full-time training)* 

F • • 8 • • • • • • • • • • • • • • • •		Total	Semesters			
Type of academic activities		academic hours	1	2	3	4
Contact academic hours		72	72			
including:						
Lectures (LC)		36	36			
Lab Works (LW)		36	36			
Seminars (workshops/tutorials) (S)						
Self-studies		18	18			
Evaluation and assessment (exam/passing/fagrade)	uiling	18	18			
Course workload	academic hours	108	108			
	credits	3	3			

# **5. COURSE CONTENTS**

Table 5.1. Course contents and academic activities types

Course module title	Course module contents (topics)	Academic activities types
Section 1. Introduction	Theme 1. Methods of organic chemistry as the basis of theoretical and experimental organic chemistry. Classification of reagents: electrophilic, nucleophilic and radical reagents. Classification of reactions in organic chemistry: heterolytic and homolytic reactions. Order of reactions. Types of reactions.	LC
Section 2. Nitration	Theme 2.1. Direct and indirect nitration. Nitrating agents. Nitration of aromatic compounds. The concept of the reaction mechanism. Nitronium cation. Effect of substituents on the nitration of aromatic compounds. Nitration of benzene, toluene,	

Course module title	Course module contents (topics)	Academic activities types
	phenol, aniline, naphthalene, benzoic acid, chlorobenzene. Protection of the amino group and aldehyde group during nitration. Side reactions during nitration of aromatic	
	compounds. Nitration of furan, pyrrole, thiophene, pyridine. Nitrocompounds of the aliphatic series. Konovalov's reaction.	
	Parophase. The concept of the mechanism of nitration of aliphatic compounds. Indirect nitration. The reaction of the replacement of a halogen and a sulfo group by a nitro group.	
	Theme 2.2. Synthesis of 5-nitrofuran-2- carbaldehyde (5-nitrofurfural)	LW
	Theme 3. Sulphonating agents. Sulfonation of aromatic compounds. reversibility of reactions. Influence of sulfuric acid concentration and temperature on the course of sulfonation. Sulfonation of benzene, toluene, phenol, anthraquinone. Influence of catalysts. Obtaining sulfanilic acid. Side reactions during	
Section 3. Sulfonation	sulfanilic acid. Side reactions during sulfanilic acid. Side reactions during sulfonation. Preparation of sulfonic acid chlorides. Features of isolation and identification of sulfonic acids. Exchange of the sulfo group for H, OH and CN groups. Sulfonation of paraffins and olefins. Sulfochlorination reactions. Sulfonation of heterocyclic compounds.	
Section 4. Halogenation	<ul> <li>Theme 4.1. Halogenation agents: free halides, hydrohalic acids, phosphorus halides, thionyl chloride, dioxane dibromide, N-bromosuccinimide, dichloromonoxide.</li> <li>Halogenation of aromatic compounds as an electrophilic substitution reaction. The reaction mechanism, the role of the catalyst. Conditions for the introduction of a halogen into the aromatic nucleus and into the side chain. Dichloromonoxide as a selective reagent with respect to benzyl chlorination. The difference in the mechanisms of both reactions and in the properties of the resulting halogen derivatives. Halogenation of heterocyclic compounds. Halomethylation reaction.</li> <li>Radical substitution of hydrogen by halogen. Methods for introducing a halogen into olefins in the allyl position. Thermal chlorination of propylene.</li> <li>Addition of hydrogen bromide to C=C bond in the presence of peroxides (Harash effect). Polyhalogen derivatives. Telomerization</li> </ul>	

Electrophilic addition of a halogen and hydrogen halides via a multiple bond. Addition of halogens to olefins. Conditions for this reaction and its mechanism. Stereospecificity of the reaction of halogenation of cycloolefins. Addition of halogens to acetylenes and diene hydrocarbons. Hydrohalogenation of olefins. The dependence of the course of this reaction on the nature of the olefin, hydrogen halide, reaction conditions. Markovnikov's rule. Mechanism of the hydrohalogenation reaction. Halogenation of carbonyl compounds. Obtaining $\alpha$ - and $\beta$ - halogen-substituted carbonyl compounds. haloform reaction. The method of introducing halogens into $\alpha$ - the position of carboxylic acids (Gel-Volhard- Zelinsky reaction). Substitution of halogens in alkyl halides. Mobility of halogens. Hydrolysis of alkyl halides as a nucleophilic substitution reaction. Mechanisms of S <sub>N</sub> I and S <sub>N</sub> 2. Influence on the rate and type of nucleophilic substitution by various factors: the structure of the starting substance (electronic and spatial factors), the nucleophilic activity of the substituting group and the solvent. Theme 4.2. Synthesis of 1,5-bis(2- hydroxyphenoxy)-3-(oxopentane). Synthesis of crown ether (reaction of catechol with 1,5-
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crown ether (reaction of catechol with 1,5-
dichloro-3-pentane)
Theme 5. Reduction of the nitro group in the
aromatic series. Reduction agents. Reduction in
alkaline, neutral and acidic media. The products
of incomplete reduction are nitroso compounds, arylhydroxylamines, azoxy-, azo- and hydrazo
Section 5. Reduction of the compounds. Rearrangement of incomplete LC
nitro group reduction products. Benzidine and semidine
rearrangements. Reduction in an acidic
environment. Technical production of aniline.
Partial recovery. Obtaining nitroamines,
diamines, aminophenols.
Section 6. Amination Theme 6.1. Introduction of an amino group by LC
replacing a hydrogen atom in an aromatic or
heterocyclic ring. Chichibabin reaction.
Replacing a halogen with an amino group
(Hoffmann reaction). Synthesis of primary
amines from potassium halides and phthalimide,
Tamines from potassium nations and phinalimide.

Course module title	Course module contents (topics)	Academic activities types
	amines by interaction of halides with metal cyanamides. Replacing a hydroxyl group with an amino group. Reaction conditions. Joint catalytic dehydration of butanediol and ammonia (amines). Replacement of a hydroxyl group with an amino group in the aromatic series (Bucherer reaction). Reactions of ethers and oxides with ammonia and amines. Preparation of ethanolamines. Synthesis of amines from aldehydes and ketones. Reductive amination. Recovery of oximes and Schiff bases. Leuckart reaction. Beckmann rearrangement, its mechanism. Aminomethylation of ketones, phenols, heterocyclic compounds (Mannich reaction). Preparation of amines from acid derivatives. Hoffmann, Curtius, Schmidt rearrangements.	
	Recovery of nitriles. Theme 6.2. Synthesis of furfurylideneaniline	LW
oxygen-containing compounds	Theme 7. General ideas about redox processes in organic chemistry. reductive agents; metals: sodium, sodium amalgam, magnesium, zinc, aluminum; complex metal hydrides: lithium aluminum hydride, alkali metal borohydrides; aluminum alcoholates; hydroiodic acid. Organic reductive agents. Reduction of acids and their derivatives to aldehydes, alcohols and hydrocarbons. Reduction of acid chlorides according to Rosenmund-Zaitsev. Preparation of aldehydes from nitriles and acid hydrazides. Preparation of alcohols from acids and esters by the action of lithium aluminum hydride. Reduction of aldehydes and ketones. Preparation of alcohols by the action of aluminum isopropoxide (Meerwein-Pondorff- Werley). Reduction by the action of sodium, sodium amalgam and amalgamated magnesium. Pinacon formation, reaction mechanism. Cannizzaro reaction, Cannizzaro "cross" reaction. Tishchenko's reaction. Reduction of carbonyl compounds by the action of lithium aluminum hydride and metal borohydrides. Preparation of hydrocarbons from carbonyl compounds by the action of lithium aluminum hydride and metal borohydrides. Preparation of hydrocarbons from carbonyl compounds by the action of amalgamated zinc (Clemmensen) and hydrazine hydrate (Kizhner). Modifications of the Kizhner reaction. Recovery of $\alpha$ -, $\beta$ -unsaturated carbonyl compounds. Reduction of quinones.	LC
Section 8. Oxidation	Theme 8. Oxidizing agents: oxygen, ozone; metal oxides - chromic anhydride, manganese	

Course module title	Course module contents (topics)	Academic activities types
	dioxide, lead dioxide, osmium tetroxide, silver	•
	oxide, selenium dioxide; peroxide compounds:	
	hydrogen peroxide, peracetic and	
	monoperphthalic acid, Caro's acid; salts:	
	potassium permanganate, dichromates, sodium	
	hypochlorite, lead tetraacetate; acids; nitrogen,	
	sulfuric, hypochlorous, iodine.	
	Oxidation of the double carbon-carbon bond.	
	Catalytic production of ethylene oxide. Effect of	
	peracids on olefins (Prilezhaev's reaction).	
	Trans opening of the epoxy ring as an $S_N 2$	
	reaction. The formation of cis-glycols by the	
	Wagner reaction. Double bond ozonation.	
	Determination of the structure of olefins by	
	ozonolysis. Oxidation of hydrocarbons to	
	alcohols, aldehydes and ketones, acids.	
	Selenium dioxide as a specific reagent for	
	oxidation in the allyl position and for the	
	production of aldehydes.	
	Special cases of hydrocarbon oxidation. cumene	
	process. Formation of cumene hydroperoxide	
	and its decomposition to phenol and acetone.	
	Oxidation of aromatic hydrocarbons to	
	quinones. Obtaining maleic anhydride from	
	benzene and phthalic anhydride from	
	naphthalene.	
	Oxidation of alcohols and diols. Oxidation with	
	a Beckmann mixture; possible side reactions.	
	Oppenauer oxidation. Catalytic dehydrogenation	
	of alcohols. Oxidation of glycols with cleavage	
	of the carbon-carbon bond (lead tetraacetate and	
	iodic acid). Obtaining acids from alcohols.	
	Oxidation of aldehydes and ketones.	
	Autooxidation of benzoic aldehyde. Oxidation	
	of the aldehyde group in carbohydrates. Popov's	
	rule for the oxidation of ketones. Oxidation of	
	ketones by the action of peracids (Bayer-	
<u> </u>	Villiger). The concept of biochemical oxidation.	
Section 9. Diazotization	Theme 9. Importance of diazo compounds in	LC
	organic synthesis and azo dye industry.	
	Diazotization reaction, its mechanism. The role	
	of mineral acid in the diazotization reaction.	
	Diazotization of weakly basic amines and	
	diamines. Various forms of diazo compounds.	
	Reactions of diazo compounds with nitrogen	
	release. Replacing diazo groups with hydrogen,	
	hydroxyl, halides, cyano and nitro groups.	
	Homolytic arylation reactions (Gomberg-	
	Bachmann). Decomposition of double	
	diazonium salts (A.N. Nesmeyanov). Reactions	

Course module title	Course module contents (topics)	Academic activities types
	of diazo compounds without nitrogen release.	
	Reduction to arylhydrazines. Azo coupling as an	
	electrophilic substitution reaction. The choice of	
	pH of the medium in azo coupling with amines	
	and phenols. Influence of substituents in the	
	benzene ring on the activity of diazo and azo	
	components in the azo coupling reaction.	
	Theme 10.1. Alkylating agents: alkyl halides,	
	unsaturated hydrocarbons, alcohols. Friedel-	
	Crafts alkylation reaction mechanism.	
	Alkylation catalysts and their activity. Isolation	
	of $\sigma$ -complexes. Influence of substituents in the	
	aromatic nucleus on the ease of alkylation. Side	
	reactions during alkylation: alkyl radical	
	isomerization, polyalkylation,	
	disproportionation reaction. Reactions of di- and	
	polyhalogen derivatives with aromatic	
Section 10. Alkylation	hydrocarbons.	
	Carbenes, their formation, structure. Singlet and	
	triplet methylene. Reactions of insertion of	
	carbenes into CH bonds and addition to olefins.	
	Reactions of carbenes with aromatic compounds	
	(Simmons-Smith reagent).	
	Theme 10.2 Synthesis of 1.5-bis(2-	
	hydroxyphenoxy)-3-(oxapentane). Synthesis of	T 337
	crown ether (reaction of catechol with 1,5-	LW
	dichloro-3-pentane)	
	Theme 11.1. Acylating agents. Obtaining	
	ketones by Friedel-Crafts reaction; reaction	
	mechanism. Intramolecular acylation.	
	Preparation of heterocyclic ketones.	
	Synthesis of aromatic aldehydes using carbon	
	monoxide and hydrogen chloride (Gattermann-	LO
	Koch), hydrocyanic acid and hydrogen chloride	LC
Section 11. Acylation	(Gattermann), formylation using	
	dimethylformamide and phosphorus	
	oxychloride (Vilsmeier reaction). Obtaining	
	aromatic acids. Synthesis of salicylic acid	
	(Kolbe-Schmitt).	
	Theme 11.2. Synthesis of 1-(2-thienyl)ethanone	I W
	(2-acetylthiophene).	
Section 12. Condensation c		LC
aldehydes and ketones	Reaction mechanism, role of catalysts (bases	
•	and acids). Comparative activity of aldehydes	
	and ketones.	
	Condensations of aldehydes with malonic acid,	
	esters of halogenated acids, nitro compounds,	
	acetylene, cyclopentadiene, hydrocyanic acid.	
	Condensation of aromatic aldehydes with acid	
	anhydrides (Perkin reaction), with aromatic	

Course module title	Course module contents (topics)	Academic activities types
	amines and phenols. Benzoin condensation, its mechanism. Effect of substituents on benzoin condensation.	
	Theme 12.2. Synthesis of furfurylideneaniline	LW
	Theme 12.3. Synthesis of 1-phenyl-2- nitropropene	LW
Section 13 Ester Condensation	Theme 13. Synthesis of esters of $\beta$ -keto acids (Claisen condensation). Reaction mechanism for the synthesis of acetoacetic ester. Condensing agents. Reversibility of the reaction. The use of esters of formic and ovalic acids in the Claisen	
Section 14. Diene synthesis (Diels-Alder reaction)	Theme 14.1. Diene components of the Diels- Alder reaction. Aliphatic, cyclic and heterocyclic dienes (divinyl and its homologues, cyclopentadiene, cyclohexadiene, furan, vinylcyclohexene). Dienophiles: acrolein, acrylic acid and its derivatives, unsaturated nitro compounds, maleic anhydride, fumaric acid, quinones, acetylenedicarboxylic acid. Influence of electron-donating and electron-withdrawing groups on the activity of diene and dienophile in the Diels-Alder reaction. Reversibility of the Diels-Alder reaction. Structural orientation of diene synthesis. Stereospecificity of the reaction (endo- and exoforms). Reaction conditions, formation of mono- and diadducts (quinones, acetylenedicarboxylic acid). Synthesis of bridge structures (endoxo- and endomethylenecyclohexane systems). Substitutional addition reaction.	LC
	Theme 14.2. Azadiene synthesis: condensation of furfurylideneaniline and dihydrofuran	LW

\* - to be filled in only for **<u>full</u>**-time training: *LC* - *lectures; LW* - *lab work; S* - *seminars.* 

# 6. CLASSROOM EQUIPMENT AND TECHNOLOGY SUPPORT REQUIREMENTS

Table 6.1. Classroom equipment and technology support requirements

Type of academic activities	Classroom equipment	Specialised educational / laboratory equipment, software, and materials for course study (if necessary)
Lecture	A lecture hall for lecture-type classes, equipped with a set of specialised furniture; board (screen) and technical means of multimedia presentations.	Software: Microsoft Windows, MS Office / Office 365, MS Teams, Chrome (latest stable release), Skype
Lab work	A classroom for laboratory work, individual consultations, current and mid-term assessment; equipped with a set of specialised furniture and machinery.	Room is equipped with a set of specialized furniture; specialized equipment of the chemical laboratory: ventilation hood cabinet SHVP-4 (4 pcs.), rotary evaporator Hei-value digital G3B, rotary evaporator IKA, digital devices for determining the melting point SMP10; electronic laboratory scales AND EK- 610, MK-M mantles of different sizes, drying cabinet PE-4610, magnetic stirrer MRHei-Mix S, magnetic stirrer with heating MRHei-Standart, refractometer, combined laboratory bath BKL, vacuum chemical station PC3001 VARIO-pro, circulating cooler Rotacool Mini, rotary vane vacuum pump RZ2.5, chemical membrane vacuum pump MZ2CNT, Steinel thermal blower, Spectroline EB- 280C UV lamp, electronic vacuum controller with CVC3000 detect Vacuumbrand valve, chemical ware, refrigerator; there is wi-fi
Self-studies	A classroom for independent work of students (can be used for seminars and consultations), equipped with a set of specialised furniture and computers with access to the electronic information and educational environment. es for students' self-studies are subject to <b>MANDATORY</b>	Room is equipped with a set of specialized furniture there is wi-fi

#### 7. RESOURCES RECOMMENDED FOR COURSE STUDY

Main reading:

1. C.W. Wood, A.K. Holliday. Organic chemistry. An introductory text: For students. London : Butterworths, 1963.

2. A.N. Nesmejanov, N.A. Nesmejanov. Fundamentals of organic chemistry. V. 1-4. Moscow : Mir, 1981.

3. M.F. Grundon, H.B. Henbest. Organic chemistry: An introduction: For students. London : MacDonald and Jane's, 1976.

4. О.А. Реутов, А.Л. Курц, К.П. Бутин. Органическая химия. Учебник для вузов. В 4-х ч. М.: Лаборатория знаний, 2017.

5. В.А. Смит, А.Д. Дильман. Основы современного органического синтеза. Учебное пособие. М. : БИНОМ. Лаборатория знаний, 2015.

6. Д. Джоуль, К. Миллс. Химия гетероциклических соединений. Пер. с англ. М.: Мир, 2004.

Additional reading:

1. Advances in Organic Chemistry. Methods and Results. New York; London : Interscience Publishers, 1960.

2. А.Л. Терней. Современная органическая химия. В 2-х томах. Под ред. Н.Н.Суворова. М.: Мир, 1981.

3. М. Физер, Л.Ф. Физер. Реагенты для органического синтеза. В 7-ми томах. Пер. с англ. М.: Мир, 1978.

Internet sources

1. Electronic libraries (EL) of RUDN University and other institutions, to which university students have access on the basis of concluded agreements:

- RUDN Electronic Library System (RUDN ELS) <u>http://lib.rudn.ru/MegaPro/Web</u>

- EL "University Library Online" <u>http://www.biblioclub.ru</u>

- EL "Yurayt" http://www.biblio-online.ru

- EL "Student Consultant" <u>www.studentlibrary.ru</u>

- EL "Lan" http://e.lanbook.com/

- EL "Trinity Bridge"

- Library of the Faculty of Chemistry, Moscow State University <u>http://www.chem.msu.su/rus/library/welcome.html</u>

2. Databases and search engines:

- electronic fund of legal and normative-technical documentation http://docs.cntd.ru/

- Yandex search engine https://www.yandex.ru/

- Google search engine <u>https://www.google.ru/</u>

- abstract database SCOPUS http://www.elsevierscience.ru/products/scopus/

- abstract database WoS https://www.webofscience.com/

- web-based tool (database) REAXYS https://www.reaxys.com/

- web-based tool (database) SciFinder https://scifinder-n.cas.org/

- education portal https://www.organic-chemistry.org/

- education portal http://www.ch.ic.ac.uk/local/organic/

Training toolkit for self- studies to master the course \*:

1. The course of lectures on «Methods of Organic Chemistry».

2. Guidelines for laboratory works on the discipline «Methods of Organic Chemistry».

\* The training toolkit for self- studies to master the course is placed on the course page in the university telecommunication training and information system under the set procedure.

#### 8. ASSESSMENT TOOLKIT AND GRADING SYSTEM\* FOR EVALUATION OF STUDENTS' COMPETENCES LEVEL UPON COURSE COMPLETION

The assessment toolkit and the grading system\* to evaluate the competences formation level (competences in part) upon the course study completion are specified in the Appendix to the course syllabus.

\* The assessment toolkit and the grading system are formed on the basis of the requirements of the relevant local normative act of RUDN University (regulations / order).

#### **DEVELOPERS:**

#### **Associate Prof.**, Organic V.P. Zaytsev **Chemistry Department** Position, Department Signature name and surname **HEAD OF DEPARTMENT: Organic Chemistry Department** L.G. Voskressensky Name of Department Signature name and surname **HEAD OF GP HE:** Dean of Science faculty, Chief of the Department of organic L.G. Voskressensky chemistry name and surname Position, Department Signature