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**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:

Competenc e code	Competence descriptor	<b>Competence formation indicators</b> (within this course)
M-PC-1-s	To be able to plan work and choose adequate methods for solving research problems in the	M-PC-1-s-1. Draw up a general plan of research and detailed plans for individual stages.
M-PC-1-8	chosen field of chemistry, chemical technology or sciences related to chemistry	M-PC-1-s-2. Select experimental and computational- theoretical methods for solving the problem based on the available material and time resources.
M-PC-2-s	C-2-s To be able to conduct patent information research in the chosen field of chemistry and/or related sciences	M-PC-2-s-1. Search for specialized information in patent information databases.
M-PC-2-8		M-PC-2-s-2. Analyse and summarize the results of a patent search on the subject of the project in the selected field of chemistry (chemical technology).

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

### **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*
M-PC-1-s	To be able to plan work		Domino reactions in the
	and choose adequate		synthesis of heterocycles
	methods for solving		NMR of organic compounds
	research problems in the		Molecular spectral analysis
	chosen field of		Chemistry of natural

Competence	Competence	Previous	Subsequent
code	descriptor	courses/modules*	courses/modules*
			compounds
			Chemistry of heterocyclic
			compounds
			Mass spectrometry of organic
	chemistry, chemical		compounds
	technology or sciences		Stereochemistry
	related to chemistry		Fundamentals of drug design
			Experimental research
			methods in chemistry
			Research work
			Undergraduate practice
			Domino reactions in the
			synthesis of heterocycles
			NMR of organic compounds
			Molecular spectral analysis
			Chemistry of natural
	To be able to conduct		compounds
	not on the formation		Chemistry of heterocyclic
M DC 2 s	research in the chosen		compounds
IVI-F C-2-5	field of chamistry and/or		Mass spectrometry of organic
	related sciences		compounds
	related sciences		Stereochemistry
			Fundamentals of drug design
			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)* 

Type of academic activities		Total		Sem	esters	
		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			
<i>Evaluation and assessment (exam/passing/failing grade)</i>		18	18			
Course workload academic hours_		108	108			
	credits	3	3			

# **5. COURSE CONTENTS**

Table 5.1.	Course contents	s and academic	e activities types
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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, 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.	LC
	carbaldehyde (5-nitrofurfural)	LW
Section 3. Sulfonation	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 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.	LC
Section 4. Halogenation	Theme 4.1. Halogenation agents: free halides, hydrohalic acids, phosphorus halides, thionyl	LC

Course module title	Course module contents (topics)	Academic activities types
	chloride, dioxane dibromide, N-	v 1
	bromosuccinimide, dichloromonoxide.	
	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.	
	Radical substitution of hydrogen by halogen.	
	Methods for introducing a halogen into olefins	
	in the allyl position. Thermal chlorination of	
	propylene.	
	Addition of hydrogen bromide to C=C bond in	
	the presence of peroxides (Harash effect).	
	Polyhalogen derivatives. Telomerization	
	reaction and its mechanism.	
	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 $S_N$ l and $S_N$ 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 substituent group,	
	the nature of the substituting group and the	
	solvent.	
	Theme 4.2. Synthesis of 1,5-bis(2-	LW

Course module title	Course module contents (topics)	Academic activities types
	hydroxyphenoxy)-3-(oxopentane). Synthesis of crown ether (reaction of catechol with 1,5- dichloro-3-pentane)	
Section 5. Reduction of the nitro group	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 compounds. Rearrangement of incomplete reduction products. Benzidine and semidine rearrangements. Reduction in an acidic environment. Technical production of aniline. Partial recovery. Obtaining nitroamines, diamines, aminophenols.	LC
Section 6. Amination	Theme 6.1. Introduction of an amino group by 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, halides and urotropine. Synthesis of secondary 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.	LC
	Theme 6.2. Synthesis of furfurylideneaniline	LW
Section 7. Reduction of 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;	LC
	auminum alconolates; hydrolodic 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	

Course module title	Course module contents (topics)	Academic activities types
	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 amalgamated zinc (Clemmensen) and hydrazine hydrate (Kizhner). Modifications of the Kizhner reaction. Recovery of $\alpha$ -, $\beta$ -unsaturated carbonyl compounds.	
Section 8. Oxidation	Reduction of quinones. Theme 8. Oxidizing agents: oxygen, ozone; metal oxides - chromic anhydride, manganese 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 <sub>N</sub> 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 henzene and phthalic anhydride from benzene oxidation. Catalytic dehydrogenation	LC

Course module title Course module contents (topics)		Academic activities types
	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- Villiger). The concept of biochemical oxidation.	
Section 9. Diazotization	Theme 9. Importance of diazo compounds in 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 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.	LC
Section 10. Alkylation	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 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 crown ether (reaction of catechol with 1,5- dicklame 2 mentane).	LC LW
Section 11. Acylation	Theme 11.1. Acylating agents. Obtaining ketones by Friedel-Crafts reaction; reaction	LC

Course module title	Course module contents (topics)	Academic activities types
	mechanism. Intramolecular acylation. Preparation of heterocyclic ketones. Synthesis of aromatic aldehydes using carbon monoxide and hydrogen chloride (Gattermann- Koch), hydrocyanic acid and hydrogen chloride (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 (2-acetylthiophene).	LW
Section 12. Condensation of aldehydes and ketones	Theme 12.1. Aldol and croton condensations. 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 amines and phenols. Benzoin condensation, its mechanism. Effect of substituents on benzoin condensation.	LC
	Theme 12.2. Synthesis of furfurylideneaniline Theme 12.3. Synthesis of 1-phenyl-2-	LW
Section 13 Ester Condensation	nitropropene Theme 13. Synthesis of esters of β-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 oxalic acids in the Claisen reaction. Condensation of dicarboxylic acid esters (Dickmann cyclization). Condensation of esters with ketones and nitriles. Acyloin condensation. Ziegler cyclization of dinitriles. The use of acetoacetic ester for the synthesis of ketones and acids. Theme 14.1 Diene components of the Diels	
(Diels-Alder reaction)	Ineme 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	LC

Course module title	Course module contents (topics)	Academic activities types
	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.	
	Theme 14.2. Azadiene synthesis: condensation	
	of furfurylideneaniline and dihydrofuran	

\* - 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

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

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)
		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.	Room is equipped with a set of specialized furniture there is wi-fi

\* The premises for students' self-studies are subject to **MANDATORY** mention

#### 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" www.studentlibrary.ru

- 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 https://www.google.ru/
- 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<sup>\*</sup> 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

**Chemistry Department** 

Position, Department

$\leq$		
	Signature	

V.P. Zaytsev

name and surname

#### HEAD OF DEPARTMENT: Organic Chemistry Department

Name of Department

Signature

L.G. Voskressensky

name and surname

HEAD OF GP HE: Dean of Science faculty, Chief

L.G. Voskressensky

of the Department of organic

# chemistry

Position, Department



name and surname