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Original Russian Text © I.S. Antipin, M.A. Kazymova, M.A. Kuznetsov, A.V. Vasilyev, M.A. Ishchenko, A.A. Kiryushkin, L.M. Kuznetsova, S.V. Makarenko, V.A. Ostrovskii, M.L. Petrov, O.V. Solod, Yu.G. Trishin, I.P. Yakovlev, V.G. Nenaidenko, E.K. Beloglazkina, I.P. Beletskaya, Yu.A. Ustynyuk, P.A. Solov'ev, I.V. Ivanov, E.V. Malina, N.V. Sivova, V.V. Negrebetskii, Yu.I. Baukov, N.A. Pozharskaya, V.F. Traven', A.E. Shchekotikhin, A.V. Varlamov, T.N. Borisova, Yu.A. Lesina, E.A. Krasnokutskaya, S.I. Rogozhnikov, S.N. Shurov, T.P. Kustova, M.V. Klyuev, O.G. Khelevina, P.A. Stuzhin, A.Yu. Fedorov, A.V. Gushchin, V.A. Dodonov, A.V. Kolobov, V.V. Plakhtinskii, V.Yu. Orlov, A.P. Kriven'ko, O.V. Fedotova, N.V. Pchelintseva, V.N. Charushin, O.N. Chupakhin, Yu.N. Klimochkin, A.Yu. Klimochkina, V.N. Kuryatnikov, Yu.A. Malinovskaya, A.S. Levina, O.E. Zhuravlev, L.I. Voronchikhina, A.S. Fisyuk, A.V. Aksenov, N.A. Aksenov, I.V. Aksenova, 2017, published in Zhurnal Organicheskoi Khimii, 2017, Vol. 53, No. 9, pp. 1257–1408.

#### = REVIEW =

"Looking back, it is impossible not to be surprised what a huge step made organic chemistry during its existence. However, much more lies ahead."

A.M. Butlerov

# Organic Chemistry. History and Mutual Relations of Universities of Russia

I. S. Antipin<sup>a</sup>,<sup>1</sup> M. A. Kazymova<sup>a</sup>,<sup>2</sup> M. A. Kuznetsov<sup>b</sup>,<sup>3</sup> A. V. Vasilyev<sup>b, c</sup>, M. A. Ishchenko<sup>d</sup>, A. A. Kiryushkin<sup>d</sup>, L. M. Kuznetsova<sup>b</sup>, S. V. Makarenko<sup>e</sup>, V. A. Ostrovskii<sup>d</sup>, M. L. Petrov<sup>d</sup>, O. V. Solod<sup>f</sup>, Yu. G. Trishin<sup>g</sup>, I. P. Yakovlev<sup>h</sup>, V. G. Nenaidenko<sup>i,4</sup> E. K. Beloglazkina<sup>i,4</sup>
I. P. Beletskaya<sup>i</sup>, Yu. A. Ustynyuk<sup>i</sup>, P. A. Solov'ev<sup>j</sup>, I. V. Ivanov<sup>j,5</sup> E. V. Malina<sup>j</sup>, N. V. Sivova<sup>j</sup>,
V. V. Negrebetskii<sup>k,6</sup> Yu. I. Baukov<sup>k</sup>, N. A. Pozharskaya<sup>l</sup>, V. F. Traven<sup>1</sup>, A. E. Shchekotikhin<sup>l, m,7</sup>
A. V. Varlamov<sup>n,8</sup> T. N. Borisova<sup>n</sup>, Yu. A. Lesina<sup>o,9</sup> E. A. Krasnokutskaya<sup>o</sup>, S. I. Rogozhnikov<sup>p,10</sup> S. N. Shurov<sup>p</sup>, T. P. Kustova<sup>q,11</sup> M. V. Klyuev<sup>q</sup>, O. G. Khelevina<sup>r</sup>, P. A. Stuzhin<sup>r,12</sup>
A. Yu. Fedorov<sup>s</sup>, A. V. Gushchin<sup>s,13</sup> V. A. Dodonov<sup>s</sup>, A. V. Kolobov<sup>t, u, 14</sup> V. V. Plakhtinskii<sup>u, 15</sup>
V. Yu. Orlov<sup>v,16</sup> A. P. Kriven'ko<sup>w,17</sup> O. V. Fedotova<sup>w</sup>, N. V. Pchelintseva<sup>w</sup>, V. N. Charushin<sup>x, 18</sup>
O. N. Chupakhin<sup>x</sup>, Yu. N. Klimochkin<sup>v, 19</sup> A. Yu. Klimochkina<sup>z</sup>, V. N. Kuryatnikov<sup>z</sup>, Yu. A. Malinovskaya<sup>y,20</sup> A. S. Levina<sup>aa</sup>, O. E. Zhuravlev<sup>aa,21</sup> L. I. Voronchikhina<sup>aa</sup>, A. S. Fisyuk<sup>ab, ac, 22</sup> A. V. Aksenov<sup>ad, 23</sup> N. A. Aksenov<sup>ad</sup>, and I. V. Aksenov<sup>ad</sup>

<sup>a</sup> Kazan (Volga Region) Federal University

<sup>b</sup> St. Petersburg State University

<sup>c</sup> St. Petersburg State Forest Technical University

<sup>d</sup> St. Petersburg State Institute of Technology (Technical University)

<sup>e</sup> Herzen State Pedagogical University of Russia

<sup>f</sup> St. Petersburg University of the Humanities and Social Sciences

<sup>g</sup> Higher School of Technology and Energy, St. Petersburg State University of Industrial Technologies and Design

<sup>h</sup> St. Petersburg State Chemical Pharmaceutical Academy

<sup>*i*</sup> Faculty of Chemistry, Moscow State University

<sup>j</sup> Moscow State University of Fine Chemical Technologies

<sup>k</sup> Pirogov Russian National Research Medical University

<sup>1</sup> Mendeleev University of Chemical Technology of Russia

<sup>m</sup> Gause Institute of New Antibiotics

<sup>n</sup> Peoples' Friendship University of Russia

<sup>o</sup> Tomsk Polytechnic University

<sup>p</sup> Perm State National Research University

<sup>*q*</sup> Ivanovo State University

<sup>r</sup> Ivanovo State University of Chemistry and Technology

<sup>s</sup> Lobachevskii State National Research University of Nizhny Novgorod

### ANTIPIN et al.

<sup>t</sup> Ushinskii Yaroslavl State Pedagogical University <sup>*u*</sup> Yaroslavl State Technical University <sup>v</sup> Demidov Yaroslavl State University <sup>w</sup> Institute of Chemistry, Chernyshevskii Saratov State National Research University <sup>x</sup> Yeltsin Ural Federal University <sup>y</sup> Samara State Technical University <sup>z</sup> Moscow Technological University <sup>*aa*</sup> Tver State University <sup>ab</sup> Dostoevskii Omsk State University <sup>ac</sup> Omsk State Technical University <sup>ad</sup> North Caucasus Federal University <sup>1</sup>*e-mail: iantipin54@yandex.ru* <sup>2</sup>e-mail: mkazymova@yandex.ru <sup>3</sup>e-mail: m.kuznetsov@spbu.ru <sup>4</sup>e-mail: bel@org.chem.msu.ru <sup>5</sup>e-mail: ivanov i@mirea.ru <sup>6</sup>e-mail: nmr rsmu@yahoo.com; negrebetsky1@rsmu.ru <sup>7</sup>e-mail: shchekotikhin@mail.ru <sup>8</sup>*e-mail: avarlamov@sci.pfu.edu.ru* <sup>9</sup>e-mail: lesina@tpu.ru <sup>10</sup>*e-mail: sir rog@mail.ru* <sup>11</sup>e-mail: kustova t@mail.ru <sup>12</sup>*e-mail: Stuzhin@isuct.ru* <sup>13</sup>*e-mail:* gushchin4@yandex.ru <sup>14</sup>*e-mail: kolobobav@ystu.ru* <sup>15</sup>*e-mail: plakhtinskiyvv@ystu.ru* <sup>16</sup>*e-mail: orl@bio.uniyar.ac.ru* <sup>17</sup>*e-mail: krivenko@info.sgu.ru* <sup>18</sup>e-mail: valery-charushin-562@yandex.ru <sup>19</sup>*e-mail: orgchem@samgtu.ru* <sup>20</sup>*e-mail: sandrrra@mail.ru* <sup>21</sup>*e-mail: Zhuravlev.OE@tversu.ru* <sup>22</sup>e-mail: fisyuk@chemomsu.ru <sup>23</sup>e-mail: aaksenov@ncfu.ru

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**Abstract**—The review describes the history of development of organic chemistry in higher schools of Russia over a period of 170 years, since the emergence of organic chemistry in our country till now.

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## ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS

1.	Introduction	1278
2.	Organic Chemistry in the Kazan University	1280
3.	St. Petersburg. Organic Chemistry in the Northern Capital	1301
4.	Organic Chemistry in Moscow Universities	1316
	4.1. History of Organic Chemistry in the Moscow University	
	4.2. History of Organic Chemistry in the Moscow Institute of Fine Chemical Technologies	1343
	4.3. Organic Chemistry at the Department of Chemistry in the Pirogov Russian National	
	Research Medical University	1348
	4.4. History and Scientific Achievements of the Department of Organic Chemistry	
	of the Mendeleev University of Chemical Technology of Russia	1351
	4.5. History of the Department of Organic Chemistry in the Peoples' Friendship	
	University of Russia	1361
5.	Department of Biotechnology and Organic Chemistry of the Tomsk National Research	
	Polytechnic University	
	Department of Organic Chemistry in the Perm State University	
7.	History of Organic Chemistry in Ivanovo	
	7.1. Organic Chemistry in Ivanovo until 1930	1370
	7.2. History of Organic Chemistry in the Ivanovo State University	
	of Chemistry and Technology	
	7.3. History of Organic Chemistry in the Ivanovo State University	1376
8.	Department of Organic Chemistry of the Faculty of Chemistry of the Lobachevskii State	
	University of Nizhny Novgorod	
	Organic Chemistry in Universities of Yaroslavl	
	Department of Organic and Bioorganic Chemistry in the Chernyshevskii Saratov State University	1392
11.	Department of Organic and Biomolecular Chemistry of the Ural Federal	
	University (Yekaterinburg)	
	11.1. Sulfonamides and Other Antibacterial Drugs	
	11.2. Participation in the Nuclear Project. Organofluorine Chemistry	
	11.3. Heterocyclic Chemistry	
	11.4. Nucleophilic Substitution of Hydrogen—A New Methodology for Organic Synthesis	1399
	11.5. Synthesis of Medicines	
	Department of Organic Chemistry of the Samara State Technical University	
	Organic Chemistry in Tver Oblast	
14.	Organic Chemistry Department of the Dostoevsky Omsk State University	1407
15.	Organic Chemistry in the Universities of Stavropol	1409

## 1. INTRODUCTION

This review article is devoted to the history of the emergence and development of organic chemistry at Russian universities and is a joint work of many scientific collectives (30 universities of Russia). None of the 58 authors of this review is a professional historian of science, so it is not surprising that the bulk of the factual material in it is known to a greater or lesser degree in the biographies of outstanding organic chemists and the publications of individual organizations, institutes and departments. However, as far as we know, there is still no single pattern covering the main educational and scientific centers of our country in which we were engaged in teaching and research in the field of organic chemistry, and this justifies the appearance of this article, although it does not claim to exhaustive coverage of all information. Unfortunately, for reasons beyond our control, the review does not include sections on the development of organic chemistry in several key scientific centers in Russia (Astrakhan, Vladivostok, Volgograd, Irkutsk, Novosibirsk, Rostov, etc.). We hope that the information on the history of organic chemistry in these cities will be included in the extended version of this review, which we plan to publish in the future in the form of a monograph. The authors of the review will gladly accept comments and suggestions about what was outside the scope of this article, and what should necessarily be noted in the planned book. Since the original components of the review were very diverse in style and content, it was not always possible to bring them "to a common denominator," for which the authors apologize to the reader. Each section of this review was written by colleagues representing one or another university in Russia.

The description of the history of any subject always puts before a choice, what is more important, the facts, events, or persons involved therein? Obviously, this is largely determined by the scale of both facts and personalities, so the style of presentation can vary greatly as it develops. Working on the review, we wanted to trace the internal genetic connections and mutual influence that the departments and outstanding organic scientists of Russian universities had on each other's development throughout their history.

There is one more important aspect that should be taken into account when analyzing the historical development of organic chemistry in Russia. After the brilliant beginning, which we owe to the great predecessors, wars and revolutions took place in Russia, each time taking millions of lives and plunging the country into hunger and devastation. Ideological obstacles and repression also made their significant contribution to the isolation of our science from the world. Let us recall the "Iron Curtain" and the defeat of the theory of resonance in the USSR. Therefore, one can only be amazed at how our science, including organic chemistry, continued to develop in these difficult times. All this is our history, and we tried to act as judges in the existing conflicts. However, we must remember that the wheel of history cruelly passed through the fate of such great chemists as Ipat'ev, Chichibabin, Balandin, Razuvaev, and many others. Nevertheless, the best traditions of Russian organic chemistry were preserved, and there were achievements of a truly world-class level in a number of directions.

The very concept of "organic chemistry" is a little more than two centuries old. According to the initial definition of Berzelius (1807), organic chemistry is a branch of chemistry that studies substances isolated from organisms and plants. It was believed that these substances can be obtained only in living systems due to "life force." However, in 1828 Friedrich Wöhler in Göttingen first received organic matter (urea) as a result of evaporation of an aqueous solution of ammonium cyanate, in an experiment where participation of the "life force" (except for experimenter's efforts) was clearly excluded. Thus, it was precisely in 1828 that the history of organic chemistry began as a science, now defined as the chemistry of hydrocarbons and their derivatives.

For a relatively short time of its existence as an independent scientific discipline, organic chemistry has passed several periods. Although the selection of individual stages in the history of science is always quite arbitrary, as a rule, the beginning of each new period is associated with the moments of fundamental changes in the conceptual apparatus of science, with a change in the paradigm. This is almost always accompanied by reorganization of the structure of science, change in the priorities of scientific research, and emergence of new areas of application of scientific knowledge. It seems that one can single out the following stages in the development of organic chemistry.

Analytical period and accumulation of knowledge (the end of the XVIIIth century–60th years of the XIXth century). During this period, most chemists engaged in a variety of chemical and physical problems. In essence, the whole scientific community of naturalists was still united. Therefore, it is difficult to talk about the interdisciplinary links of organic chemistry in the analytical period of its development.

Period of the formation and development of the classical structural theory (1861–1914). Methodical arsenal of organic chemistry during the formation and development of the structural theory has significantly expanded and improved. Methods for the isolation, purification, and identification of substances, as well as methods for quantitative analysis, have been improved. In accordance with the main idea of Butlerov, the main methods for structure determination were sequential decomposition of complex molecules to simpler ones and independent synthesis.

Organic synthesis has become the main direction of research. The main methods for constructing carbon skeletons and introduction and transformation of functional groups were developed, and general rules determining the course of chemical reactions were described and analyzed. During this period, thousands of substances belonging to all classes of mono- and polyfunctional compounds were obtained in laboratories, and the main types of complex biomolecules were isolated from natural sources and characterized.

It was during this period that noticeable changes were made in the structure of organic chemistry. Its large independent areas such as oil chemistry, carbohydrate chemistry, chemistry of heterocyclic compounds, dye chemistry, etc., began to develop. The knowledge obtained by organic chemists during this period formed the basis for the creation of a large number of chemical technologies and rapidly developing chemical industry.

Period of physical organic chemistry (1914-mid 70's of the XXth century). This period, encompassing two world wars, has become the key one in the development of modern organic chemistry and in the completion of its foundations. Hundreds of brilliant scientists have contributed to this gigantic work. In a short period from the beginning to the middle of the XXth century, quantum mechanics was created and developed, and it became the basis for the development of quantum chemistry. New data obtained during this period by physicochemical methods completely changed the meaning of the term "chemical structure" in organic chemistry. Static models proved to be unsuitable for describing the tautomerism phenomena and properties of many classes of so-called stereochemically nonrigid molecules. Therefore, dynamic

models of the molecular structure were developed. Photochemistry of organic molecules, which studies their electronically excited states, has been developed.

During that period, further specialization and division of organic chemistry into independent areas, up to their complete separation, have occurred. The chemistry of macromolecular compounds was spun off. At the border with biology, bioorganic chemistry, biochemistry, and molecular biology developed rapidly and then separated. At the border with inorganic chemistry, the chemistry of organoelement compounds has emerged and evolved.

There was a complete chemicalization of agriculture, food industry, production of synthetic detergents, plastics, and polymeric materials, and power industry. Heavy and fine organic syntheses have become the most important industrial branches of the economy of developed countries.

Modern period (from the mid 1970s). By the mid 70s of the XXth century, the methodological arsenal and theoretical basis of organic chemistry had reached the stage of development in which effective solution of problems at the molecular level of any conceivable degree of complexity often became a purely technical problem. A number of new methods of chemical research have appeared. Resolution and sensitivity of all spectral methods have been improved by an order of magnitude or more. It became possible to study mechanisms of chemical reactions by means of physical methods, including direct observation of shortlived highly reactive intermediates. A new convergent strategy for planning complex organic syntheses was developed on the basis of retrosynthetic analysis, which is often performed using computers. The use of chiral ligands and transition metal complexes has made it possible to carry out catalytic enantioselective syntheses to obtain pure optical isomers. Many "cascade" or "domino" reactions have been developed, where complex polycyclic and cage structures are constructed in a single stage under strict stereochemical control. Identification of sequences of monomeric units in complex biopolymers (proteins, nucleic acids) and synthesis of these biomacromolecules became fully automated.

Organic synthesis has become more focused on solving practical problems. In this case, by means of theoretical calculations or empirical structure–properties relationships a synthetic chemist often initially determines which substance should possess a required combination of properties, and only then proceeds to its synthesis. Computational methods of quantum chemistry became widespread. New research opportunities have opened the prospects of transition from studying individual molecules to sophisticated supramolecular structures.

These arbitrarily allocated periods are clearly traced on the research subjects, structure, and educational process in Russian universities. The review sections are arranged in chronological order, in accordance with the "age" of organic chemistry in this or that university. It starts from the history of organic chemistry in the cradle of Russian and world organic chemistry, Kazan, where Aleksandr Mikhailovich Butlerov in his works introduced the concept of organic chemistry and where the Periodic Table element ruthenium was discovered in 1844. The section devoted to the "youngest" (from the viewpoint of organic chemistry) higher schools, those of the Stavropol region, completes the review.

## 2. ORGANIC CHEMISTRY IN THE KAZAN UNIVERSITY

The history of the formation and development of organic chemistry in Russia is less than two hundred years. It actually began in the first half of the XIXth century. At this time, new universities were opened in various cities of Russia, and scientific societies were created. After the establishment of the Moscow University in 1755, universities were re-established in Dorpat (now Tartu) and Vilnius (1802-1803), universities were opened in Kazan (1804), Kharkov (1805), Petersburg (1819), and Kiev (1833). With the opening of universities, a new period in the development of chemistry and especially organic chemistry in Russia began, the period of university science, which was characterized by the emergence of Russian professors, Russian textbooks and journals in chemistry, and wellequipped at that time chemical laboratories.

In the second half of the XIXth century, scientific schools began to be formed at universities, which was not before that time. And here, of course, the role of the Kazan University and the Kazan School of Chemistry as the "cradle of organic chemistry" in Russia should be noted [1, 2]. The formation of scientific and pedagogical school at the Kazan University is associated with the activities of Karl Karlovich Klaus (1796–1864), Nikolai Nikolaevich Zinin (1812–1880), and their disciple Aleksandr Mikhailovich Butlerov (1828–1886). The importance of the activity of A.M. Butlerov follows from the remarkable words of Academician A.E. Favorsky who said in 1928 in Kazan at the Vth Mendeleev Congress dedicated to the centenary of Butlerov's birth: "Having educated Butlerov and giving the opportunity to develop its talents, the Kazan University thereby rendered Russian chemistry a service like none of the other universities, and it can rightly be called the cradle of Russian chemistry" [3].

The history of the development of chemistry at the Kazan University has been studied for many years and has been thoroughly documented in numerous reviews, articles, and monographs. A special place is occupied by monographs and collections of A.E. Arbuzov and B.A. Arbuzov [4-7]. The bibliography of A.E. Arbuzov's works on the history of chemistry includes more than 50 references. These are transcripts of public speeches, reviews in the books "People of Russian Science," and articles in scientific journals. The middle of the last century is associated with the names of G.V. Bykov [8, 9] and A.S. Klyuchevich [10–12] who published many interesting, previously unknown facts on the history of chemistry in Kazan. Interest in studying the history of chemistry at the Kazan University does not fade even today. A whole series of articles, books, and pamphlets dedicated to chemists of the XIXth and XXth centuries [13-16], including the article by Academician A.I. Konovalov [17], were published to the 200th anniversary of the Kazan University (2004). Unique books were those of the professor of the Kazan University A. Zakharov [18–21]. The author scrupulously worked with archival documents, and his books contain both previously unknown information about the development of the university and the chemical faculty, as well as interesting facts from the life of "personalities." Interest in the Kazan School of Chemists is also shown by foreign researchers. A wonderful series of works devoted to the history of Russian chemistry was published by the famous American historian of chemistry, Professor David Lewis of the University of Wisconsin–Eau Claire (USA); in 2016 it was translated into Russian and published as a separate book [22].<sup>24</sup>

The huge legacy of Kazan organic chemists can not be described in one review; therefore, the goal of this

<sup>&</sup>lt;sup>24</sup> Vast information on the development of organic chemistry at the Kazan University is available on the Internet. In particular, on the websites of the Museum of the Kazan chemical school, *http://kpfu.ru/museums/muzej-kazanskoj-himicheskoj-shkoly* and Kazan Federal University, *http://old.kpfu.ru/science/kch/page1.htm*, as well as at *http://pycmpaha.pdp/article.php?nid=11947*, *www.chem.msu.su/rus/elibrary/trifonov/kazan-school.html*, and others.

publication is only to attract attention of the scientific community and young organic chemists to the history and induce interest in the past and present Russian chemical science and in the understanding of the importance of modern science in the development of the society. The whole history of chemistry, as in principle of any other science, suggests that no country can successfully develop without the development of science.

"Science lives easily and freely where it is surrounded by the full sympathy of society. The science can hope for this sympathy, if the society is sufficiently close to it. Then the society does not consider its interests as strangers and realizes that science has the best source of its forces and that the path of knowledge and the path of development always coincide with each other in any direction. For rapprochement, one must acquaint society with the aims of science and with the means by which it achieves them; society needs confidence that the path chosen by science is indeed fruitful. To this end, I venture today to draw your enlightened attention to my science. It would seem unnecessary to speak about the benefits of the results achieved by chemistry. Apparently, her merits are recognized by all; everyone knows how indispensable are its successes to the industry, and everyone is ready to call chemistry extremely useful and extremely interesting science." This is a quote from the speech of A.M. Butlerov at a ceremonial meeting of the Academy of Sciences on December 29, 1870. How true are these words, written almost 150 years ago by the great Russian chemist, still sound!

The origin of the Kazan School of Chemistry is associated with the names of two scientists, Karl Karlovich Klaus and Nikolai Nikolaevich Zinin, who contributed to the emergence of a galaxy of young organic chemists in Russia. According to the historian of chemistry Prof. David Lewis, these scientists "carried out the Russian invasion ... into chemistry" [23]. Graduates of the Kazan University, who created their own scientific schools in the second half of the XIXth century and the first half of the XXth century, are listed in table.

Karl Karlovich Klaus (1796– 1864) in 1821 moved to Kazan from Saratov with the title of pharmacist received at the Petersburg Medical and Surgical Academy in 1817, opened his own pharmacy, and participated in expeditions as a botanist. Unexpectedly, in 1830, he dramatically changed the priority in his



scientific hobbies and became a laboratory assistant at the Chemistry Department of the Kazan University. However, because of the rampant epidemic of cholera, he was sent again to Saratov, where he worked in a pharmacy as a pharmacist. After that, he decided to continue studying chemistry, but not at the Kazan University where chemical education was at that time extremely poor, but at the University of Dorpat (now Tartu). In 1835, Klaus passed the exam for the degree of candidate of philosophy (the title of graduating from the university), and in 1837 sustained his thesis "Fundamentals of analytical phytochemistry." On August 1, 1837, he became an adjunct of pharmacy at the Kazan University. It is noteworthy that from this day Prof. I. Dunaev who taught chemistry was dismissed on the pretext of abolishing the department of

	Kazan	St. Petersburg	Moscow	Warsaw	Kiev	Kharkov
N.I. Zinin	1835–1847	1847–1880				
A.M. Butlerov	1850–1868	1868–1893				
V.V. Markovnikov	1860–1871		1873–1904			
A.M. Zaitsev	1865-1910					
A.N. Popov	1865–1869			1869–1881		
E.E. Wagner	1874–1875			1886-1903		
S.N. Reformatskii	1882–1891				1891–1934	
A.N. Reformatskii	1888–1989		1889–1937			
A.A. Al'bitskii	1882-1903					1903–1920
A.E. Arbuzov	1911–1968					

Graduates of the Kazan University and their scientific schools (second half of the XIXth century–first half of the XXth century) [3]



Old chemical laboratory building.

technology, but he had only three publications on water analysis which were not in scientific journals (at that time the number of publications was also significant!). In the same year, Klaus was appointed head of the chemical laboratory and instructed to read lectures on chemistry, both inorganic and organic.

At the same time, the construction of a whole complex of buildings in the courtyard of the university, including the chemical laboratory building, was completed. The new chemical laboratory which, according to Klaus, was not inferior to the best foreign laboratories contributed to the development of chemical science in Kazan. The lecture room arranged by an amphitheater adjoined the laboratory. This historical lecture room, later named *Butlerovskaya*, is still functioning; meetings of the academic council for the defense of dissertations, various conferences, and classes for students are held therein.

In 1839, Klaus was approved in the degree of Doctor of Philosophy and in the rank of extraordinary professor, and in 1843 he was elected an ordinary professor of chemistry. In 1850, due to poor health, Klaus gave a recommendation to young Aleksandr Butlerov to read lectures, and then he urged the university administration to leave A.M. Butlerov at the university. It is interesting to note that during these years Butlerov gave lectures on inorganic chemistry, and Klaus, on organic chemistry. In 1851, Klaus returned to Dorpat where, in his opinion, the conditions for work and the moral situation were better. But later Klaus wrote to Butlerov that Kazan is "the center of intellectual movement in Russia."

The total number of scientific works of Klaus is small, but they are very diverse in subject. Many monographs on botany and phytochemistry were pub-



Butlerov's auditorium. End of the XXth century.

lished. A large article by Klaus "On the behavior of camphor toward halogens" (1842) is considered the initial stage in the study of terpene hydrocarbons which were later studied by Kazan chemists (Butlerov, Flavitskii, Wagner, Arbuzovs). A half of the 16 known publications refer to the study of platinum group metals. It was the work in this field that brought Klaus and Kazan University world fame.

The problem of waste during the processing of platinum ore was urgent in Russia at the beginning of the XIXth century. In 1828 the Minister of Finance of Russia E.F. Kankrin sent samples of platinum ores to foreign and Russian chemists for a full study. The analysis was performed by Berzelius and professor of the University of Dorpat G.F. Ozanna. K.K. Klaus also joined to the research and scientific polemics with Berzelius. Unlike Berzelius, Klaus dealt with "platinum residues" that are the insoluble part of platinum ore remained after treatment with aqua regia. It was necessary to transfer these residues to solution and then separate platinum metals despite close proximity of their chemical properties and insufficient knowledge. Klaus persistently analyzed the residues, and in two years it succeeded in obtaining 6 g of ruthenium, preparing and studying its oxides, compounds with sulfur and chlorine, and several double salts, and determining its atomic weight with high accuracy. In 1884, Klaus published a long article "Chemical Investigation of the Remains of Ural Platinum Ore and Ruthenium Metal" in Academic Notes of Kazan University. An extract of this article by Klaus was published by the Swedish Academy of Sciences in 1845, and then Berzelius placed a detailed essay in his "Annual Report on Advances in Chemistry and Mineralogy." A new, 57th chemical element was thus recognized. Until now, the museum of the Kazan

Chemical School has original platinum metals and their compounds, including ruthenium preparations.

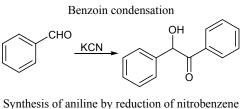


Nikolai Nikolaevich Zinin (1812–1880) worked within the walls of the chemical laboratory of the Kazan University simultaneously with K.K. Klaus after graduating in 1833 from the mathematical department of the Faculty of Physics and Mathematics of the Kazan Univer-

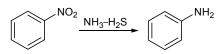
sity with the degree of candidate and the gold medal for the presented treatise "On perturbations of elliptical motion of planets." In 1835 the scientific destiny of N.N. Zinin abruptly changed. Rector of the University N.I. Lobachevskii instructed him to read a course of lectures on chemistry and recommended him to pursue a master's thesis in chemistry. Zinin wrote master's thesis on the proposed topic "On the chemical affinity phenomena" in a year and brilliantly defended it in October 1836.

In 1837, Zinin was approved as an adjunct of chemistry and was sent abroad to prepare for the professorship. Staying abroad, hearing lectures of famous scientists, and performing experimental studies in laboratories of Berlin and Giessen were very fruitful for the scientist. Zinin was mainly acquainted with laboratory research methods in the Giessen laboratory under the leadership of Justus von Liebig. After returning from abroad, in January 1841 in St. Petersburg N.N. Zinin brilliantly defended his doctoral thesis "On benzoyl compounds and discovered new substances of the benzoyl series" made in the laboratory of J. Liebig. It is believed that in his dissertation Zinin closely approached modern concepts of catalysis and described participation of a catalyst in intermediate reaction stages. In the spring of 1841 N.N. Zinin worked as an extraordinary professor, but in the chemical technology department rather than chemistry department headed at that time by Klaus. In fact, N.N. Zinin, from the very beginning, taught chemistry along with K.K. Klaus. N.N Zinin was not only an excellent experimenter but also a brilliant teacher. Lectures and practical exercises of N.N. Zinin attracted attention of a large number of students, including later A.M. Butlerov. Since 1845, Zinin became an ordinary professor in the chemical technology department.

Throughout the Kazan period, N.N. Zinin continued to engage in scientific research in the field of transformations of aromatic compounds. He developed a method for the preparation of benzoin from benzaldehyde in the presence of potassium cyanide and of benzil by oxidation of benzoin with nitric acid (1841). In 1841, by reduction of nitrobenzene with hydrogen sulfide he obtained aniline.



Synthesis of aniline by reduction of nitrobenzen with hydrogen sulfide



In 1842-1844 Zinin reported the syntheses of α-aminonaphthalene, naphthalenediamine and phenylenediamine from the corresponding nitro derivatives [24-26]. Thus, a general method for the preparation of amino derivatives from organic nitro compounds was discovered, which was later widely used to synthesize not only synthetic dyes, but also many pharmaceutical preparations, fragrances, explosives, etc. In 1880, in a speech dedicated to the memory of Zinin, the German chemist A. Hoffmann, one of the creators of the dye industry in Germany, recognized that "if Zinin had done nothing more than converting nitrobenzene to aniline, his name would have remained written down in gold letters in the history of chemistry" [27]. The brilliant completion of the Kazan period of Zinin's activity was the benzidine rearrangement which was discovered in 1845. Zinin remained in Kazan until 1847 when he received an invitation to the Department of Chemistry at the St. Petersburg Medical and Surgical Academy.

Modest Yakovlevich Kittary (1824–1880) graduated from Kazan University in 1844 and was left as a laboratory assistant in the technical and chemical laboratory. Helping Zinin in carrying out laboratory experiments, he proved himself to be a talented technologist (in particular, he proposed changes in the design of



chemical devices and tried to improve the efficiency of experiments). Zinin defined the further fate of Modest Yakovlevich, "You were born to be a technologist, and you have a flair and ability." Indeed, although he defended his master's thesis on zoology and in 1847 received a doctoral degree in natural sciences on zooanatomy, his whole life later was connected with the chemical technology. In 1848, he replaced Zinin, who left Kazan, as head of the Technology Department and headed it until 1857. In 1850, he received a professor's degree in technology for the essay "On soap production in the factories of the Kazan province" and became an extraordinary professor, and since 1853 he was an ordinary professor at the Kazan University.

Possessing high erudition and oratorical talent, Kittary earned a huge prestige among students. In addition, he popularized science by reading public lectures on technology and economics in the city. The great merit of Kittary is that he compiled a project according to which the Krestovnikov brothers built in Kazan in 1855 a stearin-candle plant, and the latter soon became one of the largest fat processing plants in Russia. In 1873. A.M. Butlerov noted that Krestovnikovs' factory was the first factory in Kazan "which arose on the basis of a completely rational principles of science." Later, under the influence of Kittary and his students, new and improved production methods were introduced in many factories and plants in the region. In addition, M.Ya. Kittary actively participated in the Kazan Economic Society and at the same time founded journal of the society and was its editor. He published therein over one hundred and fifty articles on candle, soap, leather, and other types of productions, as well as on beekeeping and horticulture. His fame penetrated the environment of Moscow merchants and manufacturers; at their request, in 1857 a department of technology was established at the Moscow University, to which Kittary was invited. This concluded the Kazan stage of M.Ya. Kittary's scientific research.



Aleksandr Mikhailovich Butlerov (1828–1886) entered the Kazan University in 1845 and at first paid more attention to botany and zoology; it is not surprising that his first thesis was written on the topic "Butterflies of the Volga–Urals fauna." Two outstanding representatives of the Kazan chemical school,

K.K. Klaus and N.N. Zinin, strongly influenced Butlerov's interest in chemistry. Under the guidance of Klaus in the laboratory and Zinin's advices, Butlerov successfully mastered the art of organic synthesis and was imbued with their love for chemical research. After Zinin's departure in 1847, Butlerov collaborated mainly with Klaus who recommended leaving him at the university to prepare for the professorship in the department of chemistry. In February 1851, Butlerov defended the master's thesis "On the oxidation of organic compounds." In 1852 K.K. Klaus returned to the Dorpat University, and the whole burden of teaching chemistry at the Kazan University fell on the shoulders of A.M. Butlerov. These were the most intense years of work, since he intensively engaged in scientific work in parallel with teaching and completed his doctoral thesis "On essential oils," which was successfully defended at the Moscow University in 1854. In 1858 Butlerov was confirmed as an ordinary professor at the Kazan University. He was 30 years old.

The results of scientific work in the subsequent period are significant: in 1859, polyoxymethylene (a polymer of formaldehyde) was discovered, and in the next year, hexamethylenetetramine. In 1861, Butlerov made a remarkable discovery in the history of chemistry: by the action of limewater on formaldehyde polymer, a sugar substance called *methylenitane* was obtained.

At that time, A.M. Butlerov, like his teacher N.N. Zinin, adhered to the views of Ch.F. Gerhardt and A. Laurent, but gradually came to the conclusion that the typical formulas are cramped for the actual state of chemistry of that time.

In 1857, A.M. Butlerov went on a one-year business trip abroad to Western Europe. He visited all the best laboratories in Germany, France, Switzerland, and Italy and met H. Kolbe, A. Kekulé, R. Bunsen, E. Erlenmeyer, and other Western European scientists. But most of the time he spent in Paris in the laboratory of A. Wurtz and, most importantly, became a member of the Paris Chemical Society, where at that time all pressing problems of chemistry were discussed. Butlerov was elected a member of the Society on December 22, 1857. Two weeks later, A. Couper became a member of the Paris Chemical Society.

A.M. Butlerov took an active part in the activities of the Society and on February 17, 1858, made a report "On the structure of bodies." A. Couper was present at the report of A.M. Butlerov, and after a while he submitted his report to the Society, which was held on June 23, 1858, but A.M. Butlerov had already left Paris by that time. The revised text of A. Couper's report in the form of an article "On a new chemical theory" [28] was published in French, German, and English in 1858. A. Couper was never published more. In April, 1858, A. Kekulé's article "On the constitution and transformations of chemical compounds and on the chemical nature of carbon" was published [29]. In both papers, two key ideas were presented: (1) carbon atom, the basis of organic compounds, is tetravalent; (2) the catenation concept, i.e., carbon atoms in organic molecules can be connected to each other, which gives rise to a diversity of organic compounds. A. Kekulé wrote a textbook on organic chemistry, the first issue of which was published in 1859 on the basis of Gerhardt's theory of types.

By the beginning of 1860 Butlerov has mainly established with his views, since, according to V.V. Markovnikov, he read the course on organic chemistry in the 1860–1861 academic year on the basis of the theory of chemical structure. On September 19, 1861, a young thirty three years old professor of the Kazan University A.M. Butlerov made a report "On the structure of substances" [30] in the German town of Speyer at the 36th congress of German doctors and naturalists. In this report he first laid out the initial assumptions of his concept of the chemical structure of substances. It is of fundamental importance that for the first time Butlerov proposed to introduce the term *chemical structure*.

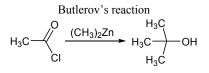
A.M. Butlerov formulated the fundamentals of his theory as follows:

(1) "Assuming that each chemical atom has only a certain and limited amount of chemical force (affinity) through which it participates in the formation of a body, I would call this chemical bond, or the way of interconnection of atoms in a complex body, a chemical structure";

(2) "... the chemical nature of a complex species is determined by the nature of elementary constituent parts, their number, and chemical structure."

Returning to Kazan, A.M. Butlerov proceeded to research where the theory of chemical structure served as a guiding star. These are works on explanation, proof, prediction of isomerism, and, what is extremely important, the synthesis of previously unknown isomers predicted by the theory. In 1863–1864 he published the articles "On different explanations of some cases of isomerism," "On tertiary pseudobutyl alcohol," and "On the systematic application of the atomic principle for the prediction of isomerism and metamerism."

Of fundamental importance was the work "On tertiary pseudobutyl alcohol" [31–33] where preparation of tertiary alcohols from acid chlorides and dialkylzinc derivatives (the Butlerov reaction) was described. Until the discovery of the Grignard reaction thirty years later, the Butlerov reaction remained the only reliable method of synthesis of these compounds.



The above articles were the landmark ones in the development of the theory of chemical structure. Simultaneously, during this period, A.M. Butlerov began to write a textbook "Introduction to the full study of organic chemistry." The first issue of the textbook in Russian was published in 1864. The entire edition was complete in 1866, and in 1867-1868 the textbook was published in German in Leipzig. Herein, A.M. Butlerov deduced the series of all alcohols on the basis of the theory of chemical structure. Methyl and ethyl alcohols have no isomers. But starting from propyl alcohols, isomers appear. A.M. Butlerov stopped on amyl alcohols since the number of isomers increased avalanche-like. He concluded that "the available data suggest the existence of a very large number of isomeric alcohols ... Therefore, the theory here goes farther than experiments ... ." And he was right: his disciples fully confirmed the validity of these words.

The publication of Butlerov's textbook was a historical event in chemistry. A textbook not only based on the theory of chemical structure but fully imbued with that theory has been published for the first time in the world. The principles of the theory of chemical structure were consistently carried through all classes of organic compounds. There was no such textbook before A.M. Butlerov.

In May 1868, when Butlerov was on the third overseas business trip, at the announcement by D.I. Mendeleev, he was elected an ordinary professor of the St. Petersburg University. The transition to capital's university was in accordance with Butlerov's wishes, and he handed over the chair and laboratory to his successor V.V. Markovnikov.

Vladimir Vasil'evich Markovnikov (1837–1904; see also Section 4.1) was the first and probably the most talented student of Butlerov. He was not only a student of Butlerov but also his ally possessing a sharp analytical mind and experimental skill and the main continuer of the development of Butlerov's theory of chemical struc-



ture. It is interesting to note that, like many chemists, he first entered the office department of the law faculty of the Kazan University, but in the third year he began to listen to Butlerov's lectures (A.M. Butlerov just returned from a business trip abroad) and at the same time to study in a chemical laboratory. After graduating from the University (1860), he was left as a laboratory assistant by Butlerov's suggestion, but already in 1862 he lectured on inorganic and later on analytical chemistry. In 1865 he brilliantly defended his master's thesis "On the isomerism of organic compounds," in which he was the first to show the existence of isomerism among saturated (fatty) acids. He succeeded in synthesizing isobutyric acid, predicted by the theory of structure.

Then followed two years of a business trip to Germany, for a while he worked in the laboratory of H. Kolbe in Leipzig. "Already in the first year after my arrival in Germany, I was convinced that the Kazan laboratory in theoretical terms far outstripped all laboratories in Germany, and the courses of lectures were elementary. There was no great need to follow practical instructions of professors, and if I staved in the German laboratories, it is only because all the life abroad is made up so that the time is spent more productive" [5] (as is true now!). Since January 1868, after the departure of Butlerov to St. Petersburg, Markovnikov was in charge of the Department of Chemistry and began to study orientation effects in the addition reactions. In the spring of 1869 he successfully defended the thesis "Data on the mutual influence of atoms in chemical compounds" and then published this work in the first volume of the Journal of the Russian Chemical Society [34].

V.V. Markovnikov formulated the main law of influence as follows: "As soon as any element is linked to another, it gets the ability to connect mainly with the same element or close to it in chemical character, if only in this case it is able in general to further connection ... The behavior of elements in compounds is determined not only by the elements directly linked thereto, but also by those that are held within the same chemical system only by means of some polyatomic element." Following Butlerov, Markovnikov believed that the affinity of atoms of the elements strongly affects the affinity of atoms of the elements linked thereto. For example, the oxygen atoms in carbon(IV) oxide saturate the entire affinity of the carbon atom, thereby preventing formation of its other compounds. On the contrary, hydrogen and chlorine, when combined with carbon, "give the rest of its affinity a strong desire for further connection," as a result of which a "compacted particle with a high carbon content" can form. In his doctoral dissertation, Markovnikov noted that this influence is transmitted "along the general chain of chemical action that holds all the elements in the particle."

On the basis of extensive experimental material, Markovnikov established a number of relations between the direction of substitution, cleavage, addition to double bond, and isomerization reactions and the chemical structure. In particular, these relations led to the formulation known as Markovnikov's rule [35, 36]: hydrogen halide adds to a double bond so that hydrogen goes to the carbon atom having more hydrogens.

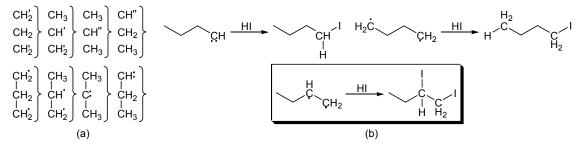
Markovnikov also showed peculiarities of double and triple bonds in unsaturated compounds, consisting of their greater strength in comparison with single bonds rather than their equivalence to two or three ordinary bonds. Markovnikov's arguments about a double bond are significant. Thus, he theoretically proposed four possible structures for propylene, differing in the distribution of "unsaturated hydrocarbon atoms" in the molecule. These structures correspond to cyclopropane, propene, and two isomeric carbenes.

The experimentally established fact of the predominant formation of 2-iodobutane in the addition of HI to but-1-ene unambiguously indicated that both "unsaturations" are located on neighboring carbon atoms rather than on one carbon atom or at the chain termini.

The contribution of Marknovnikov to the development of Russian science is also that he was an active popularizer of science and one of the founders of the Russian Chemical Society in 1868. By that time, chemical societies had already been founded in several European countries: the London Chemical Society (1841), the Paris Chemical Society (1857), and the German Chemical Society (1867). The American Chemical Society was founded in 1876.

The need to create the Society was announced at the First Congress of Russian Naturalists and Physicians, held in St. Petersburg in late December

Markovnikov's rule in the addition of HBr to propene  $H_3C-CH=CH_2 \xrightarrow{HBr} H_3C-CH-CH_3 + H_3C-CH_2-CH_2$ Br Br Br M (major product) aM (a) Possible distribution of "unsaturated" carbon atoms in propylene and (b) proof of their position at neighboring atoms



1867–early January 1868. The decision of participants of the Chemical Section was announced at the Congress: "The chemical section declared a unanimous desire to join the Chemical Society to communicate the already established forces of Russian chemists. The section believes that this society will have members in all cities of Russia and that its publication will include the works of all Russian chemists printed in Russian." Most of the works of Markovnikov, especially his theoretical works, were published only in Russian. He was a patriot of Russia and published his best works only in Russian journals, and he tried to increase the importance of Russian chemistry in the world.

However, a very successful scientific and pedagogical career in Kazan was soon interrupted. At the end of 1871, several professors of the Kazan University, including V.V. Markovnikov, resigned from the university in protest against the unfair dismissal of Prof. P.F Lesgaft, the student's favorite. In 1871–1872 Markovnikov was a professor at the Novorossiisk University in Odessa, where he lectured on organic chemistry and headed a chemical laboratory, and then received a proposal from the Council of the Novorossiisk University to head the department of chemistry. In 1872, after much reflection, V.V. Markovnikov accepted the offer to move to Moscow (see Section 4.1).

Aleksandr Nikiforovich Popov (1840–1881), according to contemporaries, was the closest disciple and follower of A.M. Butlerov. In 1861, A.N. Popov was enrolled in the cameral department of the Kazan University, but very quickly was carried away by chemistry. He graduated from the university in 1865 with the presentation of his Ph.D. thesis "On the affinity of the carbon atom." At the same time, it was published in German and French journals under the title "On the isomerism of ketones." This article refuted the opinion of the German chemist H. Kolbe on the unequality of the "affinity unit" (valence) of carbon and other elements. According to his ideas, a ketone obtained by different methods should represent two isomers. Popov refuted this claim by obtaining methyl ethyl ketone in various ways and proving that both ketones produce the same products during oxidation, i.e., all four units of affinity (valences of the carbon atom) are identical. This work was yet another brilliant confirmation of Butlerov's theory.

On Butlerov's recommendation, A.N. Popov was left at the university, where he continued working on the oxidation of organic compounds with mixture of potassium dichromate and concentrated sulfuric acid. In March 1869, Popov defended his master's thesis "On the oxidation of monoatomic ketones," where he formulated the known rule for the oxidation of ketones, which entered into science under the name of Popov's rule. According to this rule, oxidation of ketones involves cleavage of the bond between the carbonyl carbon atom and one of the neighboring carbons, and the site of cleavage and the composition of the oxidation products depend on the substituent nature.

Popov's rule  

$$\begin{array}{c} O \\ II \\ R-CH_2-C-CH_2-R' \xrightarrow{[O]} RCOOH \\ + RCH_2COOH + R'COOH + R'CH_2COOH \end{array}$$

However, A.N. Popov could not continue his work in Kazan because of the lack of vacancy. On Butlerov's recommendation in 1869, the year of the foundation of the University of Warsaw, he was transferred to this university as an extraordinary professor, where he continued to study oxidation reactions. His doctoral thesis "On the legality of oxidation of ketones" was defended in the St. Petersburg University in 1872.

Flavian Mikhailovich Flavitskii (1848–1917) belongs to the number of outstanding representatives of the Kazan school of chemists and Butlerov's students. After graduating from the Kharkov University, he worked for three years in St. Petersburg in Butlerov's laboratory. In



August 1873, while being in Kazan at a congress of natural scientists and doctors, he received, on Butlerov's recommendation, an offer to the Kazan University. His master's thesis "On the isomerism of amylenes from fermentation amyl alcohol" (1875) fully corresponded to the provisions of Butler's theory of chemical structure. In his studies he showed that the amylene hydrate obtained by W. Wurtz is not a secondary (as believed previously) but tertiary amyl alcohol dehydrated to isopropylethylene (Flavitskii's amylene). He then formulated a rule according to which the most stable form of isomeric hydrocarbons is the most methylated one; for example, tetramethylmethane is the most stable among isomeric pentanes (Flavitskii's rule).

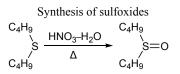
Scientific interest of F.M. Flavitskii was associated with the chemistry of terpenes and conifer resins. The doctoral thesis "On some properties of terpenes and their mutual relations" (1880) was carried out and successfully defended at the Kazan University. Flavitskii made important at that time conclusions about the genetic link between monocyclic and bicyclic terpenes and their mutual transformations. The transformation of pinene into optically active limonene is the reference point of the foundation of the Kazan School in the field of terpene chemistry. Who would then have thought that Kazan chemists would once again turn to the chemistry of terpenes in 1930s and that in the following many years the reactivity and stereochemistry of terpene hydrocarbons will be studied at the Kazan University.

Three years later, in 1884, Flavitskii headed the department of general and inorganic chemistry and worked fruitfully in the field of inorganic and physical chemistry on subjects close to D.I. Mendeleev. He wrote a magnificent textbook "General or inorganic chemistry," which survived three editions. F.M. Flavitskii served at the Kazan University for more than 40 years, in 1899 he was approved as a distinguished professor, and in 1901, after a service of 30 years, was left a supernumerary professor, with the instruction of teaching and managing the inorganic chemistry laboratory. In 1907 he was elected corresponding member of the Academy of Sciences.



Aleksandr Mikhailovich Zaitsev (1841–1910) was an outstanding Russian scientist, whose entire life was connected with the Kazan University. Like many of his predecessors, he first enrolled in the cameral department of the law faculty, but was later carried away by chemistry under the influence of Butlerov.

After graduating from the Kazan University in 1862, Zaitsev went abroad at his own expense. He worked at the University of Marburg in the laboratory of H. Kolbe, and later, at the Higher Medical School in Paris in the laboratory of A. Wurtz. In 1863 in Kazan he presented a candidate thesis based on Kolbe's structural theory. But the degree was not awarded. In Marburg he began to work on the oxidation of thioethers, which led to the discovery of sulfoxides [37, 38]. The University of Leipzig awarded him a Ph.D. for his work "On thioether oxides."



Having failed with his first Ph.D. thesis, Zaitsev sent the second one from Marburg on the topic "Diaminosalicylic acid and some its compounds with acids" and in 1865 obtained the desired degree. Upon his return to Kazan in 1865, Zaitsev worked "as a private person," that is, for free, under the guidance of A.M. Butlerov. When A.M. Zaitsev received his Ph.D. degree, Butlerov reserved a junior post for him at the faculty in the technological laboratory of agrochemistry. In 1867, Zaitsev defended his master's thesis "On the action of nitric acid on certain organic compounds of diatomic sulfur," and soon after Butlerov's transition to the Petersburg University (1869) was elected assistant professor in the department of chemistry. In 1870 Zaitsev defended his doctoral thesis "On a new method of converting fatty acids to their corresponding alcohols," in which a general method for the synthesis of alcohols by reduction of fatty acid chlorides with sodium amalgam was developed. In particular, he obtained unbranched primary butyl alcohol whose existence was predicted by Butlerov's theory, but it lacked among those isolated experimentally.

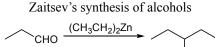
When Butlerov moved to the St. Petersburg University, the lecture course was given to Markovnikov, and after Zaitsev became an extraordinary professor, the teaching of chemistry was led by Markovnikov and Zaitsev. Zaitsev read lectures and conducted classes on the general course of inorganic and organic chemistry, and Markovnikov, a special course in organic chemistry. At the end of 1871, after the departure of Markovnikov, Zaitsev took charge of the department



A.M. Zaitsev reads a lecture for students in Butlerov's lecture room (late 1890s).

and laboratory of organic chemistry. He was in a difficult position, because it was necessary to conduct courses of organic, inorganic, and analytical chemistry, and only in 1874 another post of professor was introduced, and the teaching of general and analytical chemistry was entrusted to G.N. Glinskii.

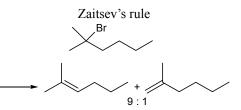
Since 1870, while studying alcohols, A.M. Zaitsev developed organozinc methods for obtaining alcohols of various classes, which received the names *Zaitsev's syntheses* and *Zaitsev's alcohols* in the history of chemistry. Thus, together with his student E.E. Wagner, in 1875 he discovered the synthesis of secondary and tertiary alcohols by the action of zinc and alkyl halides on carbonyl compounds [39–43]. This work initiated the research of French chemists P. Barbier and V. Grignard (Grignard reaction).



In 1875–1907 A.M. Zaitsev performed a series of studies on the synthesis of unsaturated alcohols by reaction of haloallyl organozinc compounds with carboxylic acid esters and anhydrides and ketones. The methods developed by Zaitsev and his students for the synthesis of saturated and unsaturated alcohols using

organozinc compounds made it possible to obtain a large number of these compounds and their derivatives. Together with the students he obtained polyhydric alcohols and studied their structure. The contribution of A.M. Zaitsev to the studies of chemical structure and isomerism of higher unsaturated fatty acids, hydroxy acids, and lactones (a class of organic compounds discovered by Zaitsev in 1873) [44], is also significant. Together with I.I. Kanonnikov he obtained acetic anhydride (1877–1878) by the action of acetyl chloride on glacial acetic acid. All the above listed constitutes only a small part of the synthetic works performed by A.M. Zaitsev with his disciples.

But probably the most significant achievement of A.M. Zaitsev, which was included in all textbooks on organic chemistry, was "Zaitsev's rule" [45, 46] (1875), according to which elimination of hydrogen halide from alkyl halides or of water from alcohols occurs in such a way that hydrogen is abstracted from the least hydrogenated neighboring carbon atom.



It is also necessary to note the contribution of Zaitsev to the development of industry in Russia. For a long time he was a scientific consultant at the famous soap-making and candle factory of the Krestovnikov brothers in Kazan. Zaitsev successfully solved the problem of isomerization of higher fatty carboxylic acids: oleic, elaidic, erucic, and brassidic. In his work "On the oxidation of oleic and elaidic acids with potassium permanganate in an alkaline solution," Zaitsev was the first to obtain dihydroxystearic acids.

In 1885, the St. Petersburg Academy of Sciences elected A.M. Zaitsev as its corresponding member for outstanding achievements in chemistry and in 1907 nominated him as a candidate for academics. However, he did not wish to part with the Kazan University, which was necessary in the case of election, and rejected this proposal. In 1905, Zaitsev was elected president of the Russian Physicochemical Society.

A.M. Zaitsev was an excellent teacher and scientific supervisor. He created a major scientific school, which included well-known chemists E.E. Wagner, A.N. Reformatskii, S.N. Reformatskii, and A.E. Arbuzov, and deservedly took one of the first places in the history of chemistry in terms of the number of outstanding students.



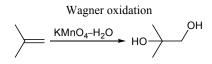
Egor Egorovich Wagner (1849– 1903) in 1867 entered the law faculty of the Kazan University, but under the influence of fascinating lectures of V.V. Markovnikov and A.M. Zaitsev moved to the natural department of the physical and mathematical faculty. At the same time he began to work in the labo-

ratory under the leadership of A.M. Zaitsev. Upon graduation from the university in 1874, on Zaitsev's recommendation, he stayed at the Kazan University as a professorship student. His first experimental work was done together with A.M. Zaitsev on the topic "New synthesis of alcohols (synthesis of diethylcarbinol, a new isomer of amyl alcohol)." A year later he was sent to St. Petersburg under the leadership of Butlerov, where he proved himself to be a talented synthetic organic chemist. The Kazan period was short, but meeting with such well-known chemists as Zaitsev, Butlerov, and later Menshutkin, had determined further scientific fate of E.E. Wagner.

In 1882–1886 he worked at the Institute of Agriculture and Forestry in New Alexandria (now Pulawy, Poland); since 1885, professor of chemistry, since 1886 professor of organic chemistry at the University of Warsaw, since 1898, simultaneously the dean of the chemical department of the Warsaw Polytechnic Institute.

In scientific terms, Wagner continued to develop the research started in Kazan. In particular, he refined (1885) the rule of oxidation of ketones, formulated by A.N. Popov who believed that oxidation always goes in one direction. Wagner showed that the oxidation direction considered by A.N. Popov the only one is the main direction and that it is necessary to take into account not only the structure and stability of initial and intermediate products but also the oxidant nature and oxidation conditions.

In 1888, he discovered the oxidation of organic compounds containing a double bond by the action of a 1% alkaline solution of potassium permanganate (Wagner oxidation) [47].



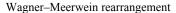
Using this method, Wagner proved the unsaturated nature of a number of terpenes and established the structure of limonene (1895) and  $\alpha$ -pinene (the major component of Russian pine turpentine). In 1899 he discovered camphene rearrangement of the first type (transformation of isoborneol to camphene and vice versa or Wagner–Meerwein rearrangement).

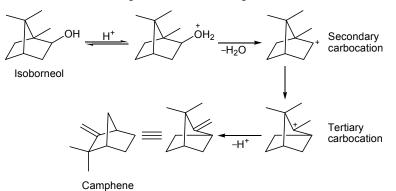
Sergei Nikolaevich Reformatskii (1860–1934)

enrolled in the Kazan University at the Natural Department of the Faculty of Physics and Mathematics in 1878. As with his predecessors, he very early took a great interest in Zaitsev's lectures and chose organic chemistry as his specialty. After graduation, he became curator of the chemical museum, and he then

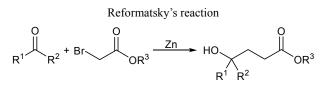


worked for 5 years as a laboratory assistant in the organic chemistry laboratory. In 1887, after passing the master's examination, he became a private docent. In 1889 he successfully defended his master's thesis "Saturated polyatomic alcohols" and was sent to Germany in the laboratory of W. Meier and





W. Ostwald. His work abroad was devoted mainly to the doctoral dissertation on his own topic in the field of Butlerov–Zaitsev's research on the synthesis of tertiary alcohols. There he wrote a treatise "The action of a mixture of zinc and monochloroacetic ester on ketones and aldehydes" which was presented as a doctoral dissertation. In 1890, he brilliantly defended his doctoral thesis at the University of Warsaw. The thesis was a logical development of Butlerov's synthesis of tertiary alcohols, and it gave rise to a whole series of syntheses of organic compounds, which received the name Reformatsky's reaction [48].



In 1891, Reformatskii left Kazan and became a professor at the Kiev University. S.N. Reformatskii is the founder of the Kiev school of organic chemists; his students were Ya.I. Mikhailenko, V. Yavorsky, E. Grishkevich–Trokhimovskii, and M.L. Zhdanovich; he is the author of the textbook "The initial course of organic chemistry" (since 1893 it has survived 17 editions).



Aleksandr Nikolaevich Reformatskii (1864–1937), the brother of Sergei Nikolaevich Reformatskii, graduated from the Kazan University in 1888 and was a student of Zaitsev as well. Although he was left at the Kazan University

to prepare for professorship, in 1889 he was invited by V.V. Markovnikov as an assistant to the organic chemistry laboratory at the Moscow University. All scientific work of A.N. Reformatskii was subsequently associated with the Moscow University and the Institute of Fine Chemical Technology (see Sections 4.1 and 4.2).



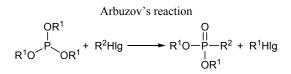
Aleksandr Erminingel'dovich Arbuzov (1877–1968) is the founder of organophosphorus chemistry in Russia and a student of A.M. Zaitsev. In 1896, A.E. Arbuzov became a student of the natural department of the Physics and Mathematics Faculty of the Kazan University. In his student years, he took a serious

interest in chemistry under the influence of Zaitsev and Flavitskii. In the laboratory of Prof. Zaitsev A.E. Arbuzov performed his first independent work called "From the chemical laboratory of Kazan University. About allylmethylphenylcarbinol of Aleksandr Arbuzov" which published in the Journal of the Russian Physicochemical Society. A.E. Arbuzov was the first Russian chemist who, independently of Grignard, carried out the reaction known today as organomagnesium synthesis (Grignard reaction).

It is worth noting excellent experimental capabilities of Arbuzov, including his mastery in glass blowing, which played a large role in the implementation of many interesting works of the scientist. Arbuzov made a great contribution to the development of laboratory techniques; in particular, he designed a vacuum distillation flask (Arbuzov's flask) which is still used throughout the world. A part of laboratory glassware for the separation of complex reaction mixtures was made according to Arbuzov's sketches or by himself. His experience in glass blowing was summarized in the "A brief guide to the independent study of glassmaking art." This brochure was published in 1912 and 1928 and for a long time was a unique tool for many generations of experimental chemists.

After graduating from the Kazan University in 1900, he worked in 1901-1910 at the Institute of Agriculture and Forestry in Novo-Alexandria (now Pulawy, Poland), where in 1906 he was elected the head of the Department of Organic Chemistry and Agricultural Chemical Analysis. Here, without a scientific leader, he independently chose and developed a topic in the field of chemistry of organophosphorus compounds. At that time, some chemists considered phosphorous acid to be a tribasic acid with a symmetrical arrangement of hydroxy groups at the trivalent phosphorus atom, while the others believed that it is a dibasic acid with two hydroxy groups at the pentavalent phosphorus atom. Arbuzov tried to solve this problem by studying properties of phosphorous acid ethers and began to search for compounds capable of giving characteristic crystalline trivalent phosphorus derivatives. In 1905 at the Kazan University A.E. Arbuzov sustained master's thesis "On the structure of phosphorous acid and its derivatives," where he developed Butlerov's theory of chemical structure mainly on organophosphorus compounds. Catalytic isomerization of neutral phosphorous acid esters into alkylphosphinic acid esters, discovered by A.E. Arbuzov (Arbuzov's rearrangement) [49, 50] has become a universal method for the synthesis of organophosphorus compounds. It is currently used not only for the synthesis of phosphonates from phosphites, but also

for the preparation of phosphoryl compounds with a C–P bond via alkylation or arylation of neutral trivalent phosphorus acid esters. According to the figurative expression of Academician A.N. Nesmeyanov, "it has become a high road to the synthesis of organophosphorus compounds." In the future, this area remained the main theme of his numerous works.



In 1910 A.E. Arbuzov became a professor at the Kazan University (with the condition that within three years he would write and defend his doctoral thesis). In 1914, Arbuzov submitted his doctoral thesis "On the catalysis phenomena in the transformations of some phosphorus compounds. Experimental study," in which he extended his views to esters of phenylphosphinous and other acids and showed the common nature of forces accelerating catalytic isomerization processes and those affecting the rate of ordinary chemical reactions. This conclusion refuted the energy interpretation of catalysis proposed by W. Ostwald.

Later, he was the first to first to synthesize phosphonoacetic,  $\beta$ -phosphonopropionic, and  $\gamma$ -phosphonobutyric acid esters. Phosphonocarboxylic acid esters, as well as phosphonocarboxylic acids themselves, were studied in more detail by A.E. Arbuzov together with his students (G.K. Kamai, A.I. Razumov, and others) during the Soviet period of activity. Like ethyl acetoacetate, phosphonoacetic acid esters and structurally related esters contain a hydrogen atom capable of being replaced by a metal such as sodium or potassium. It has been proposed and experimentally confirmed that their reactions with alkyl halides,



B.A. Arbuzov and A.E. Arbuzov in a laboratory.

analogous to those of ethyl acetoacetate and diethyl malonate, lead to the formation of the corresponding substituted phosphonoacetic esters.

Of exceptional interest are Arbuzov's studies of the structure of so-called Boyd's chloride (triphenylmethylphoshonic dichloride). These studies were logically connected with all previous works of A.E. Arbuzov, and they led not only to the correct determination of the Boyd's chloride structure but also to the discovery of a number of previously unknown classes of organophosphorus compounds. As concerns Boyd's chloride, A.E. and B.A. Arbuzovs have shown that it is a P(V) rather than P(III) derivative. In the course of these studies, they found quite unexpectedly (1929) that sodium diethyl phosphite reacts differently with chloro- and bromo(triphenyl)methanes (in the first case, triphenylmethylphosphinic acid ester is formed, and in the second case, triphenylmethyl radical). As a result, a new method for the preparation of triarylmethyl radicals has been discovered [51].

The contribution of Academician A.E. Arbuzov and his numerous disciples to the development of organophosphorus chemistry and chemistry of other organoelement compounds is exceptionally great. Many of his students later led studies in a number of fields. These students are Corresponding Member of the Academy of Sciences of Belarus P.S. Pischimuk, Academician of the Russian Academy of Sciences B.A. Arbuzov, Corresponding Members of the Russian Academy of Sciences A.N. Pudovik, S.R. Rafikov, B.M. Mikhailov, Prof. A.B. Razumov, Prof. G.Kh. Kamai, and others.

A.E. Arbuzov initiated foundation of the Institute of Organic and Physical Chemistry of the Academy of Sciences of the USSR (1965) in Kazan, which now bears his name. Almost 70 years of tireless work in science have earned deserved respect of many generations of scientists in our country and abroad for Academician A.E. Arbuzov who was an example of a prominent scientist and state and public figure serving his people.

Gilm Khairevich Kamai (1901– 1970), doctor of chemical sciences, professor, the first professor chemist among the Tatars, student and then the closest associate and follower of Academician A.E. Arbuzov. He is the founder of the Kazan chemical school of organoarsenic compounds,



which also made a significant contribution to the chemistry of organic phosphorus compounds. After the

October Revolution of 1917, Kamai was engaged in Komsomol and party work. In 1922 he entered the chemical department of the Physics and Mathematics Faculty of the Tomsk University. In 1926, he successfully defended his graduate thesis and in the same year he came to Kazan University for postgraduate studies under the guidance of Prof. A.E. Arbuzov. His postgraduate studies were concerned with organic derivatives of phosphorus thioacids.

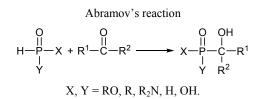
After graduating in 1929, he completed his training courses in Germany with Prof. Jakob Meisenheimer at the University of Tübingen. In Germany, Kamai worked for a year and a half on the synthesis of organoarsenic compounds. A vast experience acquired in the synthesis of organoarsenic compounds was used in his scientific activities in Kazan. In September 1931, after returning to Kazan, he was awarded the title of professor, and he began working at the Department of Organic Chemistry.

From February 1935 to August 1937, G.Kh. Kamai was rector of the Kazan University. However, Kamai fell under the repressions, and he was arrested, removed from the post of rector, and imprisoned until 1939. Although he was later released and reinstated as a professor at the Department of Organic Chemistry of the Kazan University, it was too difficult to work there, and he moved to the Kirov Kazan Institute of Chemical Technology. "I'm leaving the university with some pain, but the university will be forever in me. I ask you to release me from the office I hold on the basis of my personal request. July 9, 1939."

In the same year he was elected professor of the Department of Organic Chemistry of the Kirov Kazan Institute of Chemical Technology where he worked hard on his doctoral dissertation and brilliantly defended it on March 11, 1941. The theme of the thesis was "Studies in the field of asymmetric compounds of phosphorus and arsenic." His doctoral dissertation summed up many years of theoretical and experimental research performed by G.Kh. Kamai on organic compounds of the Vth Group elements.



Vasilii Semenovich Abramov (1904–1968) in 1930 graduated from the chemical department of the Physics and Mathematics Faculty of the Kazan University and was left in the graduate school of the Department of Organic Chemistry. At the end of the postgraduate studies (1933) he was sent to work at the Butlerov Research Institute of Chemistry, and in the same year he defended his candidate's dissertation "Action of halogen derivatives on dialkylphosphorous acid salts" concerned with the Michaelis–Becker reaction. In 1941 he became an assistant professor of the Department of Organic Chemistry of the Kazan University. He worked for a short time (1943–1948) in the laboratory of high-molecular compounds of the Institute of Organic Chemistry of the Academy of Sciences of USSR (Moscow). The condensation of dialkyl hydrogen phosphites with aldehydes and ketones entered the history of chemistry as the Abramov reaction and found wide practical application [52].



In 1949, V.S. Abramov moved to the Kirov Kazan Institute of Chemical Technology, where he defended his doctoral dissertation "Studies in the series of  $\alpha$ -hydroxyalkylphosphonic acid derivatives" (1959) and headed the Synthetic Rubber Department. His scientific interests were related to the chemistry of thiokols and polyurethanes. Since 1961, V.S. Abramov was head of a laboratory in the newly established trade Kazan Research Institute of Chemistry, where compositions and technologies for the preparation of various compounds for the manufactire of non-flammable and chemically resistant clothing were created under his leadership. Even during his lifetime, V.S. Abramov was considered a recognized authority on synthetic organic chemistry among Kazan chemists.

Boris Aleksandrovich Arbuzov (1903–1991) continued glorious traditions of the Kazan Chemical School and introduced much new into Butlerov's theory of the structure of organic compounds. All his scientific work was inseparably linked with the Department of



Organic Chemistry and the old chemical laboratory of the Kazan University, which, in accordance with the decision of the Vth Mendeleev Congress (1929), became the Butlerov Research Institute of Chemistry. Although initially he did not want to become a chemist, at the fifth year of the Kazan Institute of Agriculture and Forestry, his father, Arbuzov the elder, attracted him to studying the chemistry of natural compounds, thereby determining his future destiny.

In 1926, Boris Arbuzov entered postgraduate courses at the Department of Organic Chemistry of the Kazan University to Prof. A.E. Arbuzov. During these vears he carried out research on the liquid and solid fractions of oleoresin and its processing products, turpentine and rosin, using physical methods for this purpose. For this work, the Russian Physicochemical Society awarded the 25-year scientist with the A.M. Butlerov Prize. Since 1930, B.A. Arbuzov investigated chemical transformations of terpenes. The direction of oxidation of unsaturated terpenes has been established, the mechanism of isomerization of terpenes in the presence of zinc salts has been studied. and isomerization of bicyclic terpenes to aliphatic ones, in particular, of  $\alpha$ -pinene to alloocimene, has been discovered.

The results of studies on the isomerization of cyclic terpenes and their oxides were published in 1937 as the monograph "Studies in the field of isomeric transformations of bicyclic terpenes, hydrocarbons, and their oxides," which was presented as a doctoral dissertation and was brilliantly defended at the Moscow University. Academician N.D. Zelinskii, being the official opponent, noted that "the submitted material would be sufficient for two doctoral dissertations" [53]. In 1938, B.A. Arbuzov was approved in the scientific degree of Doctor of Chemical Sciences and became a professor of the Department of Organic Chemistry and then its head (1938–1967).

Continuing the studies related to the structure and chemical behavior of various terpenes, and especially resin acids, in 1944 B.A. Arbuzov finally established the structure of levopimaric acid. The problem over which the largest chemists of the world worked for more than 100 years was solved in an elegant way using the Diels–Alder reaction.

In 1929–1932, simultaneously with intensive work in the field of terpene chemistry, B.A. Arbuzov together with A.E. Arbuzov carried out interesting and important theoretical and practical studies on the chemistry of organophosphorus compounds; he proposed a new simple method for generation of triphenylmethyl radicals by the action of sodium diethyl phosphite on triarylmethyl bromides [54].

In the postwar years, scientific interests of B.A. Arbuzov at the university were focused on traditional directions, i.e., synthesis and structure of organophosphorus compounds and chemistry of terpenes and unsaturated compounds. Of great theoretical interest were reactions studied by B.A. Arbuzov and coworkers (N.A. Polezhaeva, E.N. Dianova), which deviated from the classical Arbuzov and Michaelis– Becker schemes and afforded a large series of new stable monocyclic phosphoranes containing nitrogen and sulfur atoms. By studying reactions of diazo compounds with diazophospholes, B.A. Arbuzov and E.N. Dianova pioneered a new direction in the chemistry of organophosphorus compounds, cycloadditions to P=C and As=C bonds in two-coordinate phosphorus and arsenic compounds. Factors determining the regioselectivity of reactions of trivalent phosphorus acid esters with unsaturated ketones were established by joint studies with A.V. Fuzhenkov.

Interesting and important results have been obtained in the field of chemistry of unsaturated compounds. Together with N.N. Zobova, a new convenient way of synthesis of cyclic compounds was discovered on the basis of the reaction of benzovl and trichloroacetyl isocyanates and isothiocyanates with unsaturated compounds. A new research line related to the structure and reactivity of sulfur and selenium compounds was created together with assistant professor E.G. Kataev (successor of B.A. Arbuzov in the Department of Organic Chemistry, head of the department from 1967 to 1974). This line was then successfully developed by Prof. G.A. Chmutova and her disciples. Electrochemical behavior of unsaturated compounds of sulfur and phosphorus was the subject of research by Prof. E.A. Berdnikov, a disciple of B.A. Arbuzov.

In 1957, together with the post-graduate student A.I. Konovalov, B.A. Arbuzov initiated studies of fine details of the Diels–Alder reaction mechanism at the level of the transition state nature and factors affecting the reactivity. This was a revolutionary breakthrough for the Kazan Chemical School.

Since the mid 1950s, B.A. Arbuzov has developed a new research line, application of physical methods to structure determination of organic compounds. At that time, problem laboratories equipped with modern instruments were created at the Faculty of Chemistry of the Kazan University. Thus, in 1957, at the Department of Organic Chemistry, a problem laboratory for studying the structure of organic compounds appeared where radiospectroscopic methods were planned to constitute the basis for studies. B.A. Arbuzov created a group of radio spectroscopy under the guidance of **Yu.Yu. Samitov**, assistant professor of the Faculty of Physics and Mathematics at the Kazan University. Studies of this group can be divided into four, to a certain extent independent, sections [55]: (1) design of equipment; (2) structural studies, including experimental spectral-structural correlations; (3) kinetics, dynamics, and intermolecular interactions; and (4) theoretical NMR calculations of spectral parameters and correlation of the latter with magnetic properties of bonds and groups of atoms.

The design of high-resolution NMR spectrometers has been started in Moscow, Leningrad, Kazan, and Tallinn. However, the first successful results were achieved by Yu.Yu. Samitov's group: it was a KGU-1 NMR spectrometer [56]. The logical conclusion of the series of studies of the structure of organic compounds on the basis of spectral-structural correlations, in combination with the instrumentation design, was the defense of doctoral dissertation by Yu.Yu. Samitov in 1967. This was one of the first doctoral dissertations in the USSR, entirely devoted to NMR spectroscopy. Later, other scientists of the laboratory became doctors of science, namely A.V. Aganov, V.V. Klochkov, and F. Kh. Karataeva.

One of the main topics of studies in the laboratory was the study of fine details of steric structure (conformational analysis) of organic and organoelement compounds using modern physical methods. These studies represent a logical continuation and development on the modern level of Butlerov's ideas on the relation between physical properties of organic compounds and steric structure of their molecules. Since 1960s, B.A. Arbuzov together with his disciples L.K. Yuldasheva, A.N. Vereshchagin, R.P. Arshinova, S.G. Vulfson, and later E.N. Klimovitskii, who subsequently became doctors of sciences, performed conformational analysis of a large series of heterocyclic derivatives of sulfur, selenium, phosphorus, arsenic, and antimony with a ring size of 4 to 8 atoms.

The high theoretical level of B.A. Arbuzov's research works was always successfully combined with their practical purposefulness. A number of works, carried out by him together with his colleagues, found practical applications in wood chemical industry, synthetic rubber industry, and manufacture of insecticides and medicines.

B.A. Arbuzov, as an outstanding scientist, was not limited to scientific activity only. He led a lot of pedagogical and organizational work. In 1931, he organized the synthetic rubber technology engineering department at the Kazan Institute of Chemical Technology, which he headed until 1938. From 1934 to Department of Organic Chemistry and Problem Laboratory "Investigation of the Structure of Organic Compounds" of the Faculty of Chemistry, Kazan State University (1973).

Yu.Yu. Samitov, A.I. Konovalov, and B.A. Arbuzov in the NMR laboratory (1983).

1990 he was director of the Butlerov Research Institute of Chemistry, and from 1958 to 1971 he headed first the Institute of Organic Chemistry and then the Arbuzov Institute of Organic and Physical Chemistry (Kazan Branch of the Academy of Science of the USSR). His high professional qualities had a huge impact on the formation of many chemists: among his disciples 23 Doctors of Science, Academician A.I. Konovalov, Corresponding Members of the Russian Academy of Sciences S.V. Rafikov, B.M. Mikhailov, N.V. Torgov, and A.N. Pudovik, and 75 candidates of science.

**Evgenii Gennad'evich Kataev (1917–1986)**, a disciple of B.A. Arbuzov, head of the Department of Organic Chemistry from 1967 to 1974. In 1946 he became a graduate student of Prof. B.A. Arbuzov at the







Butlerov Institute of Chemistry. At that time, scientific interests of B.A. Arbuzov were in the field of unsaturated compounds, both synthetic (piperylene, hexa-2,4-diene) and natural (resin acids). In 1949 E.G. Kataev became an assistant in the Organic Chemistry Department

and lectured "Organic chemistry and reaction mechanisms," In 1950 he defended his candidate's dissertation "Studies in the piperylene and hexa-2,4-diene series" and in 1952 was approved as associate professor of the Organic Chemistry Department.

After the defense, E.G. Kataev continued to study chemistry of unsaturated conjugate systems, but also included VIth Group elements, sulfur, selenium, and even tellurium. Together with his postgraduate students F.R. Tantasheva, T.G Mannafov, G.A. Chmutova, V.V. Plemenkov, and L.K. Konovalova, he carried out research in several fields: Diels–Alder reactions with divinyl sulfoxides and sulfones; synthesis and study of the electronic structure of a new class of compounds based on selenophenol and phenylselenium chloride, aryl alkenyl and aryl alkynyl selenides; synthesis of new unsaturated compounds of phosphorus, sulfur, and nitrogen.

This direction was developed in the works of G.A. Chmutova (professor of the Organic Chemistry Department) and her disciples (later associate professors) M.A. Kazymova and A.R. Kurbangalieva, in which the interest shifted to joint (experimental and theoretical) study of structural features and reactivity of heterocyclic compounds (mainly pyrazolones and their hetero analogs) and to search for chemo-, regio-, and stereoselective methods of thiylation (selenation) of five- and six-membered nitrogen-, oxygen-, sulfur-, and selenium-containing heterocycles with the goal of obtaining potentially biologically active compounds. In particular, the first selenium derivatives of mucochloric acid were synthesized; a variety of structures formed in reactions of mucochloric acid with sulfurcontaining binucleophiles under acidic and basic catalvsis was revealed.

Since the mid 1990s, G.A. Chmutova studied the structure and reactivity of organometallic compounds of the VIth Group elements (O, S, Se, Te) by highlevel quantum chemical methods. Together with the postgraduate student T.I Madzhidov, specific features of selenium atom as an electron donating center in reactions of organoselenium compounds with various Lewis acids were revealed and explained using modern methods of electron distribution analysis (QTAIM, IQA, IQF). Unlike associates involving classical donor centers (elements of the 2nd Period, oxygen, nitrogen, etc.), much more important contribution to the energy of intermolecular interactions of organoselenium compounds is made by electron density delocalization rather than by electrostatic effects. Moreover, depending on the structure of electron acceptor, the nature of the Se $\cdots$ A bond formed upon complexation can vary from van der Waals to weak covalent [57, 58].

Aleksandr Ivanovich Konovalov (born in 1934)

is one of the brightest students of B.A. Arbuzov. He entered the Kazan State University in 1951. Everything was determined in 1953, when the learning of organic chemistry began, and the lectures were read by B.A. Arbuzov. In 1957 problem laboratories were organized at depart-



ments of leading universities of the country, and A.I. Konovalov, at the invitation of B.A. Arbuzov, began to work in the problem laboratory "Investigation of the structure of organic compounds." Since that time, his life for sixty years is inextricably linked with the Kazan University. In 1964, A.I. Konovalov moved to the Organic Chemistry Department, and is now professor of the department. For 25 years, from 1974 to 1999, he was head of the Organic Chemistry Department, and he transferred the leadership to his disciple, now Corresponding Member of the Russian Academy of Sciences I.S. Antipin. A.I. Konovalov was rector of the university at a turning point in the modern history of Russia from 1979 to 1990.

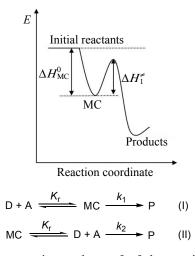
The 50–60th years of the XXth century were marked at the Kazan School of Chemistry by both development of traditional research in the field of chemistry of organophosphorus, unsaturated, and natural compounds and emergence of new scientific trends recognized by the scientific chemical community both in our country and abroad. First of all, this refers to research in the field of physical organic chemistry, i.e., study of the reactivity and mechanisms of organic reactions. And, rightly, one can call Academician A.I. Konovalov, a worthy disciple and successor to B.A. Arbuzov, the pioneer.

In the late 1950s, A.I. Konovalov, along with his teacher B.A. Arbuzov, began a kinetic study of the mechanism of the Diels–Alder reaction [59]. In his candidate's dissertation "Diels–Alder reaction and



A.I. Konovalov and B.A. Arbuzov

charge-transfer complexes" A.I. Konovalov was one of the first to establish the formation of molecular complexes in Diels–Alder reactions [60]. However, an important question arose: do these complexes lie on the reaction path or do they represent a dead-end equilibrium? The solution of this problem was of fundamental importance for predicting the reactivity of addends in cycloaddition reactions, and it determined for many years the direction of investigations of the Diels–Alder reaction mechanism. The problem is nontrivial since paths (I) and (II) cannot be distinguished on the basis of the kinetic data.



A direct experimental proof of the participation of molecular complexes as intermediates in the Diels– Alder reaction was obtained by Konovalov's student V.D. Kiselev while studying the kinetics of the reaction of a strong  $\pi$ -donor, 9,10-dimethylanthracene (IP 7.04 eV) with a strong  $\pi$ -acceptor, tetracyanoethylene (EA 2.88 eV) in a number of solvents. A unique phenomenon was discovered: the reaction rate constant decreased as the temperature rose; i.e., the reaction was characterized by a negative energy of activation. This is possible only when the enthalpy of formation of the complex  $(\Delta H_{\rm MC}^0)$  located on the reaction path is greater than the enthalpy of activation of the cycloaddition stage  $(\Delta H_1^{\sharp})$ .

A fundamentally important achievement in this research line was the discovery of so-called "neutral" Diels-Alder reaction, when both donors and acceptors in the addends accelerate the cycloaddition reaction [61]. Prior to this, in the most widespread version of interaction of the frontier orbitals (diene as donor and dienophile as acceptor), the interaction of the highest occupied molecular orbital (HOMO) of the diene and the lowest unoccupied molecular orbital (LUMO) of the dienophile was considered to be predominant. The opposite version implying diene as acceptor and dienophile as donor was experimentally observed in reactions with perchlorocyclopentadiene. The possibility of a "neutral" version was first experimentally confirmed by A.I. Konovalov and his students Ya.D. Samuilov and B.N. Solomonov in the Diels-Alder reactions of a number of cyclopentadienones with tetrachloro-oquinone. In the reaction of substituted phencyclones with styrenes, all three orbital control versions were detected.

The result of a large experimental and theoretical work was the creation of a single correlation describing the change in the reactivity (rate constant) of addends in the Diels–Alder reaction over enormous range (20 orders of magnitude) [62, 63]. It was proposed to consider three main parameters: (1) energies of the frontier orbitals of the diene and dienophile; (2) change in the coefficients of orbital overlap, determined mainly by the difference in the interatomic distance  $C^1-C^4$  in the diene ( $R_{1-4}$ ); and (3) balance of the energies of bond cleavage and bond formation, determined by the enthalpy of the reaction ( $\Delta H_r$ ).

In 1970–1980s, A.I. Konovalov with his disciples V.D. Kiselev, B.N. Solomonov, and I.S. Antipin began to study solvation effects in cycloaddition reactions, which gave impetus to the creation of a whole research line at the Kazan Chemical School, study of the thermodynamics of solvation and intermolecular interactions of organic compounds in nonaqueous solvents and their effect on the reactivity [64, 65].

A.I. Konovalov and B.N. Solomonov performed a detailed analysis of the influence of various intermolecular interactions on the enthalpy and free energy of solvation of organic nonelectrolytes, and original approaches were proposed to evaluate a number of important thermodynamic characteristics: enthalpies of evaporation, solvation, and specific interactions. The principal point was the use of molecular refraction as a descriptor for describing the energy of dispersion interactions in solution.

A correlation between the enthalpies of solvation in cyclohexane and molecular refraction of the dissolved substances was found for a wide range of organic compounds (more than 100 compounds of different classes) [66, 67]. Analogous linear relations between the enthalpies and free energies of solvation of organic compounds and molecular refraction were observed not only in saturated hydrocarbons but also in other solvents, from carbon tetrachloride ( $\varepsilon = 2.4$ ) to dimethyl sulfoxide ( $\varepsilon = 46.7$ ). An important conclusion drawn in the course of these studies was that there is no significant contribution of dipole–dipole interactions to the enthalpy of solvation of organic non-electrolytes.

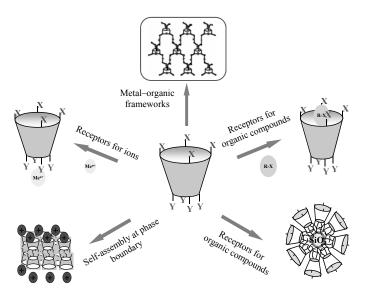
Estimation of the contribution of dipole-dipole interactions to the energy of solvation of organic nonelectrolytes was the main problem of solvation studies conducted in 1980–1990s at the Kazan Chemical School under the guidance of A.I. Konovalov. The auestion was not whether dipole-dipole interactions exist in solution (of course, exist), but are they manifested in the enthalpy of solvation? The point is that the energy of solvation of a substance can not be identified with the energy of its interaction with the solvent. Solvation is a more complicated process involving several stages, one of which may be the formation in a solvent of voids capable of accommodating the solute molecule. Obviously, this process requires partial rupture of solvent-solvent interactions and is endothermic, and, consequently, it can compensate for exothermic contribution of the solvent-solute dipoledipole interactions. This was confirmed by comparing the enthalpies of solvation of isomers having different dipole moments, as well as of highly polar model compounds, in a series of solvents with different polarities [62].

In 1980s, A.I. Konovalov together with I.S. Antipin's research group carried out fundamental studies of the influence of the medium on the acid–base properties of organic compounds. As a result, an original approach has been developed to the creation of a universal scale of ion-pair (cryptate) acidity of organic compounds in solvents with different solvating powers, which is free from the influence of solvation and association processes. This allowed determination of ion-pair acidities of organic compounds in low polar media with a fixed type of ion pairs in the  $pK_a$  range from 42 to 6 [68, 69].

It was actually the first acquaintance of Kazan scientists with the chemistry of inclusion compounds which in fact gave rise to supramolecular chemistry. It is not surprising that since the mid 1990s Academician A.I. Konovalov and his disciple I.S. Antipin (subsequently Corresponding Member of the Russian Academy of Sciences) initiated systematic research in the field of supramolecular chemistry at the Organic Chemistry Department of the Kazan University and in some laboratories at the Arbuzov Institute of Organic and Physical Chemistry (in 1990–2001 A.I. Konovalov was director of this academic institute). Supramolecular chemistry is the newest area of chemical science, located at the intersection of physics, chemistry, and biology. According to the definition of the



Department of Organic Chemistry of the Faculty of Chemistry of the Kazan State University (2003).



Nobel Prize winner J.-M. Lehn, supramolecular chemistry is "chemistry beyond the molecule," and supermolecules and supramolecular ensembles represent the next level of complexity of matter after elementary particles, nuclei, atoms, and molecules. A.I. Konovalov defined supramolecular systems as a "bridge between inanimate and living matter" [70].

For a very short historical period (just over 20 years), a school of supramolecular chemistry recognized in the world scientific community has been formed in Kazan. It now includes more than 100 researchers, 20 of which are doctors of science. The influence of the Kazan School on the development of supramolecular chemistry in Russia and in the world can be cited by the words of the creator of supramolecular chemistry, the Nobel Prize winner J.-M. Lehn: "Russia is a country of great traditions in chemistry, and Kazan plays a special historical role. This was again demonstrated by the successful entry of Russian chemists into supramolecular chemistry."

At present, the main scientific interests of the Kazan supramolecular school are focused on the use of calixarenes as a promising technological platform for the design of nanostructures by self-assembly.

Scientific foundations for the design of unique supramolecular systems and nanosized objects were created on the basis of a complex approach based on a combination of theoretical methods for the design of receptor and amphiphilic structures, new approaches to the directed synthesis of calixarene-based macrocyclic compounds, various experimental methods for establishing the structure of complex organic molecules, and studying their physicochemical properties under the guidance of A.I. Konovalov [71–73].



"Supramolecular squad"-2004: from left to right: sitting: A.I. Konovalov, S.E. Solov'eva, L.A. Kudryavtseva; standing: E.Kh. Kazakova, A.R. Burilov, M.A. Pudovik, V.V. Gorbachuk, I.S. Antipin, A.T. Gubaidullin, A.R. Mustafina, L.Ya. Zakharova, I.I. Stoikov.

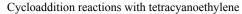
RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

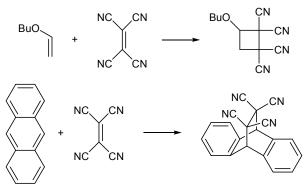


Igor' Sergeevich Antipin (born in 1954) is a student of A.I. Konovalov and his successor in the Organic Chemistry Department (1999). The scientific path of I.S. Antipin is interesting: from intermolecular interactions and solvation through inclusion complexes (cryptands) to

supramolecular chemistry of calixarenes.

In postgraduate school (1976–1979) under the leadership of A.I. Konovalov and B.N. Solomonov, he began studying solvation effects in cycloaddition reactions involving tetracyanoethylene and showed that the energy of the transition state in [2+2]- and [2+4]-cycloadditions with tetracyanoethylene changes insignificantly and that the observed differences in the activation energy are largely due to change in the energies of the reactants.

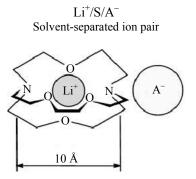




This was surprising, taking into account significant differences in the nature of transition states of these reactions, synchronous in the first case and zwitterionic in the second. The problem of quantitative evaluation of the effect of various intermolecular interactions, primarily dipole–dipole interactions, on the energy of solvation of organic compounds arose. It was studied in detail by B.N. Solomonov and A.I. Konovalov [74–77].

I.S. Antipin in his candidate's dissertation also proposed to use molecular refraction of a solute as a descriptor for the enthalpy of solvation of organic compounds in nonaqueous solvents [78]. Later, together with the scientific group of Academician N.S. Zefirov, he developed a topological model for describing dispersion interactions [79–81] on the basis of a new topological solvation index  ${}^{1}\chi^{S}$ , according to which a compound is represented as a single-edge graph where the atoms form vertices, and the bonds, edges. It is of fundamental importance that the calculation of  ${}^{1}\chi^{S}$  does not require any experimental characteristic of a substance, in contrast to molecular refraction, but it is necessary to know only its structure. In addition, the correlation quality was significantly improved.

In 1980s, I.S. Antipin drew attention to an interesting class of macrobicyclic ligands, cryptands, and their inclusion complexes, cryptates, which were synthesized in 1969 by two eminent scientists, J.-M. Lehn and J.-P. Sauvage (Nobel Prize winners in Chemistry in 1989 and 2016, respectively). The idea of creating a universal model of solvent-separated ion pair was to "dress" a small inorganic cation in a thick "organic coat" (cryptand) to prevent association and aggregation of counterions. In other words, the cryptand modeled the first solvation sphere of the ion, preventing the anion from coming close to the cation and forming a contact ion pair.



Cryptand-separated ion pair

A universal scale of ion-pair acidity of organic compounds in the  $pK_a$  range from 42 to 6 in solvents of different solvating powers, free from association, aggregation, and solvation effects, was created by using organolithium [2.1.1]cryptates in proton transfer reaction [82–84].

$$[Li^+ \subset 2.1.1]A_1^- + HA_2 \implies [Li^+ \subset 2.1.1]A_2^- + HA_1$$

Currently, the main scientific interests of I.S. Antipin are concentrated on supramolecular systems based on calixarenes. Over the past 10 years, two doctoral dissertations in the chemistry of calixarenes have been defended under his leadership by I.I. Stoikov (2008) and S.E. Solov'eva (2012).

The main results in the field of supramolecular chemistry of calixarenes obtained over the past two decades by A.I. Konovalov, I.S. Antipin and coworkers at the Organic Chemistry Department are the following:

(1) New preorganized receptors for *s*-, *p*-, *d*-, and *f*-metal cations, organic acids, and biologically important compounds (DNA, RNA) have been synthesized by directed functionalization of the lower rim of (thia) calix[4]arenes. These receptors were used to obtain host–guest complexes and supramolecular systems (both in solution and in the solid phase), which showed unique physicochemical properties, primarily extraction, catalytic, and photophysical [85–88];

(2) Novel calixarene-based amphiphilic compounds possessing receptor properties and capable of undergoing photopolymerization have been synthesized. Nanosized luminescent vesicles were obtained for the selective determination of a number of biosubstrates and pollutants in living and natural objects [89–91];

(3) Using the molecular tectonics principles, new 1D–3D metal–organic frameworks (MOFs) and clusters based on functionalized thiacalixarenes were obtained, and general patterns of their formation were revealed [92–94].

The Organic Chemistry Department currently employs 19 lecturers and 35 researchers, including 3 members of the Russian Academy of Sciences and 10 doctors of science; 65–70 students (specialists, bachelors, undergraduates) and 28 postgraduate students are specialized at the department.

The main research lines currently developed at the department are as follows:

(1) Supramolecular chemistry of macrocyclic compounds: from synthesis to functional devices and materials;

(2) Design and development of synthetic approaches to innovative glycoconjugates capable of selective recognition of target organs and tumors;

(3) Application of chemoinformatics methods and computer modeling for solving urgent problems of chemistry: QSAR, BIG DATA, databases;

(4) Chemical modification of natural products isolated from unconventional plant raw materials to obtain new biologically active compounds for veterinary and agriculture.

Currently, the department has six laboratories and scientific groups:

(1) Research laboratory "Studies of the structure of organic compounds" headed by Corresponding Member of the Russian Academy of Sciences I.S. Antipin; (2) Russian–Japanese research laboratory KFU– RIKEN "Laboratory of biofunctional chemistry" headed by Prof. K. Tanaka and Associate Prof. A.R. Kurbangalieva;

(3) Russian–French research laboratory "Chemoinformatics and molecular modeling" headed by Prof. A.A. Varnek and Associate Prof. T.I. Madzhidov;

(4) Supramolecular chemistry Group supervised by Prof. I.I. Stoikov;

(5) Smart nanosystems design group headed by Associate Prof. V.A. Burilov;

(6) Chemistry of renewable natural raw materials group headed by Corresponding Member of the Russian Academy of Sciences V.F. Mironov and Associate Prof. A.V. Nemtarev.

## 3. ST. PETERSBURG. ORGANIC CHEMISTRY IN THE NORTHERN CAPITAL

The section devoted to the history of the emergence and development of organic chemistry in St. Petersburg–Petrograd–Leningrad–St. Petersburg is a collective work of authors professionally engaged in organic chemistry. Some of the factual material available in it can be found in the biographies of outstanding organic chemists and in numerous publications on individual organizations, institutions, and departments [95–97]. However, as far as the authors know, there is still no single picture covering all universities of St. Petersburg where organic chemistry was lectured and studied.

The beginning of teaching and research in the field of organic chemistry in St. Petersburg is associated with the name of **Aleksandr Abramovich Voskresenskii** (1809– 1880), a disciple of the famous chemist Prof. G.H. Hess. In 1836, he graduated from the first category of the Main Pedagogical Institute,



received a gold medal, and was sent abroad, where in 1837–1838 he trained in Berlin under the guidance of at E. Mitscherlich, H. Rose, and G. Magnus and in Giessen under the guidance of an outstanding scientist Justus Liebig (since 1858, an honorary professor of St. Petersburg). In a well-equipped laboratory of Justus Liebig he studied natural compounds. First, he determined the composition of naphthalene, quinone, quinic acid, and theobromine and published his first articles in "Annalen der Pharmazie" (later "Liebigs Annalen

der Chemie"). In 1838, A.A. Voskresenskii returned to Russia and immediately began teaching at the St. Petersburg University, first as an adjunct and then as an ordinary professor. Since 1843, he lectured at the University of St. Petersburg on organic chemistry and, besides, taught at the Pedagogical Institute (where he replaced his teacher G.H. Hess after his death), at the Institute of Communications, at the Engineering Academy, at the Page Corps, and at the Guards Subkeepers School. The result of such intense pedagogical activity was a lot of students which gave Voskresenskii the nickname grandfather of Russian chemists. It is sufficient to say that his disciples were N.N. Beketov, N.A. Menshutkin, and D.I. Mendeleev. However, such pedagogical work almost completely excluded the possibility of experimental work, and Russian professors could work experimentally for a long time only abroad.



To get acquainted with the latest achievements of modern science at that time was also possible only abroad. The mecca of organic chemistry was the laboratory of J. Liebig at the small university of Giessen. It is not surprising that in 1838 the place of A.A. Voskresenskii in this

laboratory was immediately occupied by another Russian disciple, an adjunct from Kazan, Nikolai Nikolaevich Zinin (1812–1880). Based on the results of Liebig's studies of benzoyl derivatives, in 1841 he defended his doctoral dissertation in St. Petersburg and, after return to Kazan, he received a position first of extraordinary, and then, after the discovery of the conversion of nitrobenzene to aniline (Zinin's reaction), of an ordinary professor. In November 1847, he was elected ordinary professor of the Department of Chemistry and Physics of the Imperial Medical and Surgical Academy in St. Petersburg, and in late January 1848 was approved in this position, setting the stage for a brilliant galaxy of outstanding organic chemists who for a long time were in charge at this oldest in Russia department of chemistry. The "academic" period of Zinin's biography was marked by the creation of a fundamental system of teaching chemistry to doctors, which was the basis of medical education in Russia in the next 150 years. Another his merit was the design and construction in 1863 of the building of the Natural History Institute of the Moscow Art Academy, created on the basis of the best European scientific centers and intended not only for work but also for the residence of academic professors.

In 1857 **Dmitrii Ivanovich Mendeleev** returned to St. Petersburg from Odessa (1834–1907). At his

request, A.A. Voskresenskii gave him the course of lectures on organic chemistry at the St. Petersburg University, which D.I. Mendeleev first read in the autumn of 1858, and in 1861 he prepared the first Russian textbook on this subject, which withstood several editions and was marked by a full Demidov Prize.



Nevertheless, organic chemistry did not become any noticeable sphere of D.I Mendeleev's activity. Since 1865, he headed two departments of chemistry (general and inorganic chemistry and analytical and technical chemistry), which were at that time parts of the natural department of the Faculty of Physics and Mathematics of the St. Petersburg University, but they had no direct relationship to organic chemistry.

It is not surprising that in 1866– 1867 a question arose about invitation to the University from Kazan of **Aleksandr Mikhailovich Butlerov** (1828–1886), by that time already known as the creator of the theory of chemical structure of organic compounds. On May 11, 1868, the



Council of the Faculty of Physics and Mathematics of the Imperial St. Petersburg University, at the suggestion of D.I. Mendeleev, elected A.M. Butlerov an ordinary professor of chemistry, but without specifying the department, since D.I. Mendeleev did not concede to him any of the two! A.M. Butlerov read his first lecture on organic chemistry on January 23, 1869. In the same year the Department of Organic Chemistry was established for him (the Department of Analytical and Technical Chemistry was headed by N.A. Menshutkin). At the same time, A.M. Butlerov organized the laboratory of organic chemistry, in which his students, E.E. Wagner, G.G. Gustavson, M.D. L'vov, and V.E. Tishchenko, worked together with him. All chemical laboratories were located on the first floor of the "Twelve Colleges" building between the main entrance and the Neva embankment, occupying 25 windows along the facade between the apartments of D.I. Mendeleev and laboratory assistant D.P. Pavlov. In 1869, A.M. Butlerov was elected as an ordinary academician.

After retirement of N.N. Zinin in 1864, the Department of Chemistry at the Medical Surgical



Academy was headed by his disciple Aleksandr Porfir'evich Borodin (1833–1887) who taught not only in the academy, but also at Higher Female Courses and at the Agricultural Institute. The undoubted merit of Borodin was the creation (for the first time in Russia!) of a chemical practicum with elements

of organic synthesis for students of medical universities. However, Zinin did not stop his work in chemistry. In the same year he was appointed to the position of director of chemical works at the Medical Surgical Academy, which was specially created for him, and in 1865 he was elected an ordinary academician in technology and chemistry.

An important milestone in the life of Russian chemists was the foundation in 1868 of the Russian Chemical Society, the first president of which was N.N. Zinin. At that time, more and more "growth points" began to arise in St. Petersburg and across Russia, where teaching and research in the field of organic chemistry developed. It is enough to mention the Technological Institute, Agricultural Institute (now St. Petersburg State Forest Technical University), and Artillery Academy. Therefore, educational institutions are considered below separately, starting with the St. Petersburg University.

After the death of A.M. Butlerov in 1886, Nikolai Aleksandrovich Menshutkin (1842–1907) received a course of lectures on organic chemistry and manage-



ment of the department at the university. As early as 1883, N.A. Menshutkin published "Lectures on Organic Chemistry," which were then republished three times and were the main textbook on organic chemistry in Russian universities until the beginning of the XXth cen-

tury. At that time, the natural branch of the university was significantly expanded, and chemical laboratories were moved to a new building built according to the best European samples in the courtyard of the university. N.A. Menshutkin supervised this construction and in 1894 read the first lecture on organic chemistry in the new building. The kinetics of organic reactions (for example, esterification of acids, alkylation of amines) were studied in a new room of the Organic Chemistry Laboratory under the guidance of N.A. Menshutkin. These works formed the basis of classical chemical kinetics.



Large chemical lecture room in the St. Petersburg State University (end of the XIXth century).

However, in 1902 Menshutkin moved to the Polytechnic Institute, and **Aleksei Evgrafovich Favorskii** (1860–1945), a disciple of A.M. Butlerov and M.D. L'vov, became at the head of the department. The works of A.E. Favorskii created a new field of organic chemistry, the chemistry of acetylene. S.N. Danilov,



V.N. Ipat'ev, Zh.I. Iotsich, and S.V. Lebedev studied and worked in A.E. Favorskii's laboratory in the early XXth century. Here, the acetylene–allene rearrangement, keto–enol tautomerism, and isomerization of dimethylallene to isoprene were discovered, and dioxane was obtained for the first time.

In 1915, a chemical department was founded at the Faculty of Physics and Mathematics of the St. Petersburg University, but its activities practically ceased during the years of the revolution, civil war, and subsequent destruction. Only in 1925, its revival began, and the chemical department received a new building on the Middle Avenue; after a number of reorganizations, in June 1929 a chemical faculty was established within the Leningrad University. However, already in 1930, in accordance with the decision to create a single scientific and technical center on the basis of the Technological Institute, it was abolished, and students were transferred to the Technological Institute. In 1933 the chemical faculty of the university was restored as four departments, including the Organic Chemistry Department. Since September 1, 1933, it was headed by Konstantin Aleksandrovich Taipale (1882–1937), a disciple of V.E. Tishchenko.

Somewhat later, in 1934, the Chemical Institute was founded as a research department of the university. It included a special laboratory of organic chemistry, which was headed by A.E. Favorskii until 1941. In the pre-war time, A.E. Favorskii's laboratory became a real smithy of scientific personnel in organic chemistry. During this period he created the Institute of Organic Chemistry in Moscow and also organized new research directions at the Technological Institute. At that time, future academicians I.N. Nazarov and G.A. Razuvaev and professors N.A. Domnin, T.I. Temnikova, A.I. Zakharova, F.Ya. Perveev, I.A. D'yakonov, and K.A. Ogloblin worked with A.E. Favorskii.

After the death of K.A. Taipale in November 1937, **Boris Nikolaevich Dolgov** (1894–1959) became head of the department. He was one of the few surviving disciples of V.N. Ipat'ev, a major specialist in heterogeneous catalysis of organic reactions and application of high pressure in organic chemistry. In the 1940s, a laboratory of catalysis and later a laboratory of high pressures were created at the department on his initiative.

In 1959, the department was headed by **Ivan Aleksandrovich D'yakonov** (1911–1968) who was a student of A.E. Favorskii. I.A. D'yakonov was engaged in the chemistry of aliphatic diazo compounds



and small cycles, and he pioneered studies in the field of carbene chemistry. He dramatically changed and for many years forward determined the subject of scientific research and attracted a number of new teachers to work at the department. The fruitful activity of I.A. D'yakonov and his colleagues, B.V. Ioffe, K.A. Ogloblin,

I.A. Favorskaya, and I.K. Korobitsyna, resulted in modernization of the educational process and intensification of scientific research.

Two specializations were formed at the department, organic synthesis and organic analysis. In 1967, in addition to the organic analysis laboratory that existed at the department, a gas chromatography laboratory was set up, which for a long time was headed by **Boris Veniaminovich Ioffe** (1921–1997). B.V. Ioffe, of course, was one of the brightest professors of the department. He organized practicums on modern methods of organic synthesis (since 1962) and gas chromatography (since 1966), and a course of lectures on the application of physical methods in organic



V.P. Semenov, A.A. Potekhin, K.A. Ogloblin, and B.V. Ioffe (1989)

chemistry, which he brilliantly read for several decades, was created. B.V. Ioffe headed and developed a new scientific direction, gas phase analysis of complex mixtures and reaction systems, and the term *gas phase analysis* was proposed by B.V. Ioffe as a Russian equivalent of the English *headspace analysis*.

Since 1969 till 1989 the department was headed by **Konstantin Aleksandrovich Ogloblin** (1914–2005) who was the last postgraduate student of A.E. Favorskii. From 1989 until March 2007, the department was headed by his student **Anatolii Alekseevich Potekhin** (1938–2007) whose main interests lay in the field of chemistry of heterocyclic compounds. Since March 2007, the department is headed by the student of B.V. Ioffe **Mikhail Anatol'evich Kuznetsov**.

The modern research lines of the Department of Organic Chemistry have strong historical roots. First of all, studies in the field of acetylene and diacetylene derivatives, originating from A.E. Favorskii's works, should be noted. These studies are intensively conducted in the groups of professors I.A. Balova and A.V. Vasilyev. The pioneering work of I.A. D'yakonov on the chemistry of diazo compounds, carbenes, and small cycles was continued and developed by professors R.R. Kostikov, M.A. Kuznetsov, A.P. Molchanov, V.A. Nikolaev, M.S. Novikov, L.L. Rodina, A.F. Khlebnikov, and their students. The legacy of B.V. Ioffe and A.A. Potekhin in the field of organic derivatives of hydrazine and chemistry of heterocyclic compounds is being developed by the groups of M.A. Kuznetsov and associate professors P.S Lobanov and V.V. Sokolov, and analytical topics of B.V. Ioffe are multiplied by the works of professors I.G. Zenkevich and L.A. Kartsova.

In addition to the Department of Organic Chemistry, the Department of Physical Organic Chemistry, Department of the Chemistry of High Molecular Weight Compounds, and Department of the Chemistry of Natural Compounds are also parts of the so-called "organic bush" of the Institute of Chemistry (until 2014, the Chemical Faculty).



The emergence of the Department of the Chemistry of High Molecular Weight Compounds is associated with the name of **Sergei Vasil'evich Lebedev** (1874–1934), A.E. Favorskii's student, creator of domestic synthetic rubber. In 1900 he graduated from the St. Petersburg University. After that, he worked at a soap

factory, and then joined the Commission for the Study of Rail Steel; for his work therein, he received the gold medal of the International Railway Exhibition in Milan. In 1902, S.V. Lebedev returned to the university as a laboratory chemist in the department of technical chemistry and quantitative analysis, but in 1904 he was called up to the army, whence he returned to the university. In 1913, S.V. Lebedev defended his master's thesis "Research in the field of polymerization of diethylene hydrocarbons" and took the post of private docent of the University. At the same time he was elected professor of the Psychoneurological Institute, and he lectured chemistry of heterocyclic compounds at the university. In 1915, S.V. Lebedev became professor of the Women's Pedagogical Institute and read the course of inorganic chemistry at the Institute of Communication Engineers, and since 1917 took charge of the Department of Chemistry at the Military Medical Academy.

In 1925, S.V. Lebedev began working at the Chemical Department of the Faculty of Physics and Mathematics of the university, where he headed specialization in petroleum chemistry and organized a laboratory to develop a method for the synthesis of divinyl (butadiene) from petroleum and its transformation into rubber. Later, S.V. Lebedev developed a method for the preparation of butadiene from ethyl alcohol, which was implemented in industry. In 1929, S.V. Lebedev was elected corresponding member of the Academy of Sciences for his services in the field of preparation of synthetic rubber, and in 1932 he became full member of the Academy of Sciences.

In 1938, the name of S.V. Lebedev was awarded to the Laboratory of High Molecular Weight Compounds created at the Faculty of Chemistry and headed by A.E. Favorsky. In October 1944, the first in the Soviet Union department of chemistry of high molecular weight compounds was created on the basis of this laboratory. Students and associates of S.V. Lebedev became first teachers in this department, and his ideas determined for a long time the main direction of research work of the department.

The first head of the department (until 1950) was A.E. Favorskii's student, Corresponding Member of the Academy of Sciences of the USSR, Academician of the Academy of Artillery Sciences Stepan Nikolaevich Danilov (1889-1978), major specialist in the field of organic chemistry and chemical technology of natural and synthetic polymers. Professor Anastasiya Iosifovna Yakubchik (1894-1973), a student and associate of Academician S.V. Lebedev, headed the department in 1950-1973. From 1973 to 1983, the department was headed by Boris Ivanovich Tikhomirov (1933–1983). Under his leadership, studies on the synthesis and properties of polyconjugated polymers were initiated at the department, but the importance of these studies was truly appreciated only after 20 years. From 1984 to 1990, the head of the department was Vyacheslav Sergeevich Ivanov (1925–1995), who made a significant contribution to the development of radiation chemistry of polymers. Since 1990, the department is headed by Aleksandr Yur'evich Bilibin. His work in the field of synthesis of liquid crystalline polymers was internationally recognized. Promising are research lines in the field of chemistry of dendrimers, supramolecular systems, and biodegradable polymers.

In the spring of 1945 A.E. Favorsky proposed S.N. Danilov, who recently took the charge of the Department of the Chemistry of High Molecular Weight Compounds, to organize and head the Department of the Structure of Organic Compounds at the Faculty of Chemistry, which was created largely on the basis of A.E. Favorskii's laboratory in 1946, after his death. In the year of its creation, professors N.A. Domnin, T.A. Favorskaya, and T.I. Temnikova, as well as research workers I.A. D'yakonov, I.A. Favorskaya, K.A. Ogloblin, V.F. Martynov, etc., constituted the staff of the department. Subsequently, many of them headed other departments of the chemical faculty of the university; in particular, I.A. D'yakonov, and after his death K.A. Ogloblin, headed the Department of Organic Chemistry, and V.F. Martynov headed the Department of the Chemistry of Natural Compounds.

S.N. Danilov headed the department from 1946 to 1952. Simultaneously (in 1947–1949), he was director

of the Research Institute of Chemistry at the Leningrad State University, and since 1950 he began to lead the Institute of Macromolecular Compounds of the Academy of Sciences of the USSR. In 1952, **Nikita** 



Andreevich Domnin (1903–1973), a student, colleague, and son-in-law of A.E. Favorsky, took an active part in the creation of the department. In addition, in 1946–1948, and then in 1952–1953, he was dean of the Faculty of Chemistry, rector of the Leningrad State University (1948– 1950), and director of the Research

Institute of Chemistry of the Leningrad State University (1950–1958). Being the rector, he categorically refused to sign the order for the dismissal of teachers and employees of the Faculty of Biology who did not share T.D. Lysenko's views and also objected to unreasonable attacks on teachers of the Faculty of Philology.

From 1965 to 1975 the department was headed by **Tat'yana Ivanovna Temnikova** (1899–1989). Her scientific activity began in 1920 at the Perm University



under the guidance of G.A. Arbuzov (see Section 6). In 1931, at the invitation of A.E. Favorsky, T.I. Temnikova moved to the Faculty of Chemistry of the Leningrad University, and all her subsequent scientific and pedagogical work was connected therewith. Since the 1930s, T.I. Temnikova has become one of the first and most active advocates of using

electronic concepts while describing mechanisms of organic reactions and reactivity of organic compounds. This was reflected in the course of lectures on theoretical foundations of organic chemistry, which she read for several decades, as well as in the textbook "Theoretical Foundations of Organic Chemistry" published in 1959. This textbook was subsequently expanded and revised in 1962 and 1969, and in 1979 was published already in co-authorship with A.D. Dneprovskii.

In 1967, a NMR laboratory was founded at the department, and in 1968, a group of mass spectrometry. Widespread introduction into department's practice of physical methods caused its renaming to the Department of Physical Organic Chemistry in in 1969. **Boris Aleksandrovich Ershov**, a student of T.I. Temnikova, was in charge of the department in 1976–1984, and in 1984–1989 it was headed by I.A. D'yakonov's

student **Rafael Ravilovich Kostikov**. He was succeeded by another disciple of T.I. Temnikova, **Aleksei Samsonovich Dneprovskii** (1939–2003) who headed the department from 1990 to 2003. A.D. Dneprovskii possessed an exceptional teaching talent and felt a spiritual need to impart his knowledge to the youth. In 1966–1972, he taught at boarding school no. 45 (at the Leningrad State University) and was one of the most active organizers of chemistry Olympiads at school. Over 30 years he read lectures on the theoretical foundations of organic chemistry, annually renewing and enriching them with the latest scientific achievements, and was repeatedly recognized as the best lecturer of the faculty.

After the early death of A.D. Dneprovskii, the department was headed for a few years by T.I. Temnikova's student **Vladimir Semenovich Karavan**, and since 2007 it is headed by Corresponding Member of the Russian Academy of Sciences **Vadim Yur'evich Kukushkin**, a specialist in the field of chemistry of coordination compounds and organic synthesis with participation of metal complexes.

Georgii Vasil'evich Pigulevskii

(1888–1964) was at the origin of the Department of the Chemistry of Natural Compounds. He graduated from the St. Petersburg University in 1910 and already in 1911 began teaching at the university. In 1934 he was approved as a professor of the Leningrad State University and en-



trusted with the management of the Laboratory of Biological Products at the Department of Organic Chemistry. Back in 1937 he was the first Soviet organic chemist to use molecular spectroscopy to establish the structure of compounds. During the Great Patriotic War, the syntheses of sulfanilamide, amphetamine, and a number of other medications were implemented under his leadership. From 1943 to 1963, he also worked as a senior research fellow and head of the biochemical laboratory of the Komarov Botanical Institute of the Academy of Sciences of the USSR. In 1957, the laboratory of bioproducts was transformed into a problem laboratory of the chemistry of natural compounds, and in September 1963, the Department of the Chemistry of Natural Compounds was established on its basis. The department was headed by Vyacheslav Fedorovich Martynov (1913-1993) who shortly before (in 1962) defended his doctoral dissertation at the Department of the Structure of Organic Compounds. On his initiative, studies on the synthesis

and properties of biologically active peptides were added to the research of compounds isolated from plants, traditional for the laboratory of bioproducts. This direction has received rapid development after the return of the young staff of the department from training courses in the Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of Czechoslovakia, where European level specialists in the field of peptide chemistry worked. In 1988, the department was headed by V.F. Martynov's student **Aleksandr Grigor'evich Shavva**, who was engaged in the synthesis of modified steroids, and in 2013, by a graduate of the Technological Institute, V.A. Ostrovskii's student, **Rostislav Evgen'evich Trifonov**.

The next in the hierarchy of centers for the development of organic chemistry in St. Petersburg is undoubtedly the oldest technological institute in Russia, the St. Petersburg State Institute of Technology (Technical University), which was founded on November 28, 1828, by the decree of Emperor Nicholas I, and was officially opened on October 11, 1831. Already from 1834, analytical and organic chemistry began to be studied at the institute along with inorganic chemistry. G.H. Hess opened a chemical laboratory where in the course of practical work students prepared a number of chemical compounds, including organic ones. Since 1863, D.I. Mendeleev taught a course in organic chemistry and supervised the chemical laboratory, and since 1866 it was headed by Fedor Fedorovich Beilstein (1838–1906).



The classical "Russian German" **F.F Beilstein** was born, graduated from school, and died in St. Petersburg, but he received chemical education (R.W. Bunsen, Heidelberg; J. Liebig, Munich; F. Wöhler, Göttingen) and the title of professor (Göttingen, 1865) in Germany. In

1865 he was invited to the St. Petersburg Institute of Technology, where he headed the chemical laboratory in 1866. In the same year he became a professor at the St. Petersburg University and also lectured in chemistry at the Nikolaevsky Engineering Academy. Since 1883, F.F Beilstein was Corresponding Member, and since 1886, Academician of the St. Petersburg Academy of Sciences. He created a handbook on organic chemistry (Beilsteins Handbuch der organischen Chemie) which brought him world fame. In 1867, Beilstein accepted Russian citizenship, but he transferred the rights to publish his handbook to the German Chemical Society.

The creation of the Department of Organic Chemistry at the Technological Institute is considered to be in 1896, since Mikhail Dmitrievich L'vov (1848-1899), a student of A.M. Butlerov, lectured here from 1896 to 1897 and was a professor of organic chemistry. From 1897 to 1908 the department was headed by A.E. Favorskii. In 1899 the construction of a new chemical laboratory, the Mendeleev Corps, was started, where the Department of Organic Chemistry is currently located. From 1909 to 1922 the department was headed by the outstanding scientist Lev Aleksandrovich Chugaev (1873-1922) who left a bright trace in various fields of chemistry, and since 1923 heads of the department were again A.E. Favorskii and his disciples: since 1934 till 1948, Julii Sigizmundovich Zal'kind (1875-1948), and since 1948 till 1950, Elfrida Davydovna Venus-Danilova (1890-1968).

From 1951 to 1987 the department was headed by **Anatolii Aleksandrovich Petrov** (1913–1992). In

1931 he enrolled in the chemistry department of the Voronezh State University, from which he graduated externally in 1933. In 1936, A.A. Petrov defended candidate's dissertation, and already in 1941 (at 28 years!), doctoral dissertation, whose official opponents were academicians A.E. Favorskii and B.A. Kazanskii, A.A. Petrov was



Professor of the Leningrad Institute of Aviation Instrumentation (1945), Professor of Leningrad Institute of Technology (1951), and Corresponding Member of the Academy of Sciences of the USSR (1966). In 1965, A.A. Petrov founded Zhurnal Organicheskoi Khimii (Journal of Organic Chemistry of the USSR) and was its first editor-inchief. After departure of A.A. Petrov from the head of the department, the latter was headed by his students, from 1987 to 1999, by Miroslav Dmitrievich Stadnichuk (1934–2013), from 1999 to 2003, by Vladimir Alekseevich Galishev (1946-2011), and since 2004, by Mikhail L'vovich Petrov.

The research carried out at the department was connected with the chemistry of unsaturated compounds, in particular aromatic hydrocarbons and their derivatives (Beilstein), ethylene derivatives (L'vov), and acetylenes (Favorskii and his disciples). With the arrival of A.A. Petrov, the tradition was not broken, and the main subjects of study were highly unsaturated compounds. During this period, the first in the country

laboratory of physical methods in organic chemistry which dealt with specific problems of structural organic chemistry, was created at the department. Here, pioneering works was carried out in the field of heteronuclear double magnetic resonance. Professor of the department B.I. Ionin, Doctor of Sciences A.I. Kol'tsov (Institute of Macromolecular Compounds), and Professor B.A. Ershov (Leningrad State University) wrote the book "NMR Spectroscopy in Organic Chemistry" (1967) which was published in English in 1970 in the USA. A basic textbook on organic chemistry for chemical and technological higher schools was created at the department and reissued five times, and "A Collection of Tasks and Exercises in Organic Chemistry" and "Laboratory Works on Organic Chemistry" were published.

Under the leadership of M.D. Stadnichuk, methods were developed for the synthesis of 1,3-diene, enyne, and divne organosilicon and organogermanium compounds, and the possibility of using them in various polymerization processes was studied. They were also used as model compounds to study mechanisms of addition to conjugated multiple bonds. Unsaturated organotin compounds (V.S. Zavgorodnii's group) formed the basis for the preparation of various acetylene, vinylacetylene, and diacetylene derivatives via transmetalation. Vinylacetylene derivatives containing trialkylstannyl groups at the acetylenic carbon atom were obtained for the first time. A new research line, the chemistry of unsaturated organophosphorus compounds, emerged and was headed by B.I. Ionin and A.V. Dogadina). Original methods for the synthesis of phosphorus-containing heterocycles have been developed on the basis of reactions of acetylenic phosphonates with nucleophiles.

**M.L. Petrov**'s group works in the field of unsaturated sulfur compounds and their selenium and tellurium analogs. Basic factors determining the reactivity of unsaturated derivatives of this type have been revealed, and methods have been developed for the synthesis and functionalization of heterocyclic systems based on 1,2,3-thia- and -selenadiazoles with the goal of obtaining medicines and pesticides.

Two other departments of the St. Petersburg State Institute of Technology that are closely related to organic chemistry have pointedly "civil" names. These are the Department of Chemistry and Technology of Organic Nitrogen Compounds and the Department of Chemistry and Technology of Macromolecular Compounds. However, for many years these units had only their own numbers, and due to the closed nature of almost all studies conducted there, it is difficult to count on the complete coverage of their activity to this day. Both of them were created at the Leningrad Institute of Chemical Technology in the early 1930s to solve the personnel problems of the Soviet defense industry.

Department of Chemistry and Technology of Organic Nitrogen Compounds [98]. Training of engineering personnel in the specialty "Chemistry and Technology of Explosives" was started in 1926 in a special laboratory of explosives at the Faculty of Chemistry of the Leningrad State University, as well as in the Scientific and Technical Laboratory of the Maritime Administration. In 1930, a number of chemical faculties of Leningrad universities merged into a single Leningrad Institute of Chemical Technology, and a special (military-industrial) faculty was created on the basis of the university laboratory of explosives for training of engineers and technologists for the defense industry. In 1932 a department was founded for this purpose at the Leningrad Institute of Chemical Technology, which was headed by D.I. Mendeleev's disciple Semen Petrovich Vukolov (1863-

1940). Initially, the department had a code "D" and trained specialists in the field of explosives, ammunition, and pyrotechnics. In 1934, it received an arbitrary code "Department 34," from 1959 to 1976, "Department 0814," and then it became known as the Department of

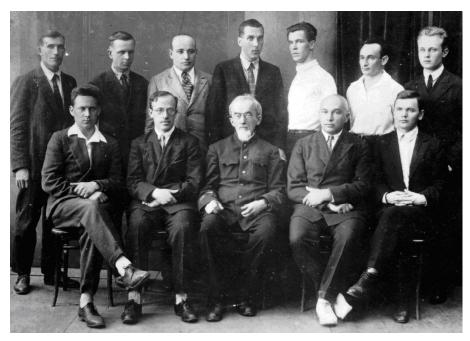


Chemistry and Technology of Organic Nitrogen Compounds. To this day, the department retains its name.

Although S.P. Vukolov did not live up to the beginning of the Great Patriotic War, his contribution to the future victory cannot be overestimated: thanks to his pedagogical talent, he, in addition to his inventions and scientific works, trained a whole cohort of highclass specialists in explosives. His student, a major specialist in the field of chemistry of high-energy compounds, **Lev II'ich Bagal** (1897–1978) headed the

department from 1940 to 1968 and continued S.P. Vukolov's works. He created scientific schools that actively work at present, and his studies determined the main directions of the development of chemistry and technology of nitro compounds of the aliphatic, aromatic, and heterocyclic series.





Department of Chemistry and Technology of Organic Nitrogen Compounds in 1934. Front row: from left to right: V.S. Shpak, L.I. Bagal, and S.P. Vukolov.



Among students of S.P. Vukolov and associates of L.I. Bagal, it is necessary to mention Hero of Socialist Labor Academician Vladimir Stepanovich Shpak (1909–2009). Under his leadership, a technological process for the manufacture of hexogen was developed and put into

operation during the war in Kazan, many high-energy compounds of various classes were synthesized, and technologies for their production and practical application were developed. V.S. Shpak was one of the founders of a new branch of the Soviet chemical industry, production of organofluorine compounds. In 1948, V.S. Shpak was appointed deputy director of the State Institute of Applied Chemistry, and in 1953 he became its director but remained at the department as the second job.

Since 1953, after the Resolution of the Council of Ministers of the USSR on the development of new powerful explosives for strategic weapons systems, work has begun on the synthesis and technology of the production of polynitroalkanes and nitramines. In 1960s a new research line was formed at the department: synthesis and technology of high-density cage explosives based on adamantane and other polycyclic hydrocarbons. Methods for the synthesis of polynitroadamantanes have been developed. Synthetic routes to polycyclic nitramines were intensely sought for. In 1971, the department was the first to receive tetranitroglycoluryl, a powerful high-density explosive, and bicyclic nitramines, including 1,1'-bi(1,3,5-trinitrohexahydro-1,3,5-triazine) that is the dimer of standard explosive hexogen.

A student of V.S. Shpak and L.I. Bagal, **Boris Veniaminovich Gidaspov** (1933–2007), headed the department from 1969 to 1977. For many years he worked in the field of chemistry and technology of nitro-



gen-containing compounds. On the basis of his work, several large-scale production facilities were created, which provided the country with energetic compounds and materials important for its defense. Under the direction of B.V. Gidaspov, pioneering studies of polynitrogen compounds (nitrogen heterocycles, azo, diazo, and azido compounds) as explosives, components of rocket and specialty fuels, and thermobaric weapons were carried out. Polynitroalkylnitramines, powerful explosives and oxidants for mixed solid propellants (MSP), were synthesized for the first time, and pilot production of new environmentally friendly oxidants for mixed propellants, dinitramide salts, was launched. In 1976, for work in this field, B.V. Gidaspov, together with his colleagues, was awarded the Lenin Prize. In 1977, he was appointed General Director of the State Institute of Applied Chemistry, replacing V.S. Shpak in this post. From 1977 to 1988, the department was

headed by Valentin Dmitrievich Nikolaev, who continued the traditions laid down by L.I. Bagal and B.V. Gidaspov.

The disciple of L.I. Bagal Igor Vasil'evich Tselinskii was in charge of the Department of Chemistry and Technology of Organic Nitrogen Compounds from 1988 to 2013. His works cover a wide range of problems related to physical chemistry, kinetics, and reactivity of organic nitrogen compounds, chemistry and technology of nitro, azido, and azoxy compounds of the aliphatic, fatty-aromatic, and heterocyclic series, as well as of organoelement compounds. In the early 1960s, in connection with the problem of creation of high impulse solid propellants, studies were carried out under the guidance of B.V. Gidaspov and I.V. Tselinsky on the synthesis and properties of aliphatic azides as MSP components, and extensive development of methods of synthesis and primary technologies for the manufacture of aliphatic polyazido compounds was performed. Particular attention was paid to azides containing nitro and nitroxy groups.

The structure and reactivity of azido compounds, in particular their 1,3-dipolar cycloaddition reactions, were studied in parallel. Studies of the mechanisms of



sextet rearrangements, carried out under the guidance of **Grigorii Isakovich Koldobskii** (1933–2009), were recognized worldwide. As far back as on the initiative of L.I. Bagal, chemistry and technology of heteroaromatic polynitrogen compounds, tri- and tetrazoles, oxadi-

azoles, and their *N*-oxides, began to develop at the department. The staff of the department is among the recognized world leaders in the field of tetrazole and 1,2,4-triazole chemistry, where G.I. Koldobskii, V.A. Ostrovskii, M.S. Pevzner, and T.P. Kofman worked fruitfully.

Vladimir Aronovich Ostrovskii initiated a largescale correction of research work at the department toward the design and synthesis of pharmaceutics. In particular, in continuation of studies on polyazido compounds, a technology for the manufacture of an efficient anti-HIV drug has been developed. The "Azoles" flexible production system was created with participation of scientists of the department and "Technologist" Special Construction Technological Bureau, which ensured small-tonnage production of more than twenty nitrogen heterocycles for use in medicine, agriculture, and industry. After 2013, the Department of Chemistry and Technology of Organic Nitrogen Compounds was headed by Valerii Yur'evich Dalmatov and Boris Mikhailovich Laskin. Since 2017, Aleksandr Aleksandrovich Kiryushkin is in charge of the department.

The foundation and development of the Department of Chemistry of Macromolecular Compounds is associated with the name of Stepan Nikolaevich

**Danilov**. In 1930, he created the first in the Soviet Union department of artificial fiber technology, which in 1933 was combined with the Department of Powder Technology. The latter was created in 1930 along with the above mentioned Special Military Chemical Faculty of the



Leningrad Institute of Chemical Technology. The department was headed by a major expert in the powder industry **Nikolai Akimovich Golubitskii** (1874–1938) who worked previously as head of the Central Plant Laboratory, chief chemist of the Tambov and Okhtinskii powder plants, and head of the gunpowder department in the Military Chemical Research Institute. The united department of Chemical Cellulose Processing (then the Department of Chemistry and Technology of Macromolecular Compounds) graduated specialists in the chemistry and technology of polymer compositions, powders, and solid propellants. Its head was S.N. Danilov until 1972, and he remained the scientific leader until the end of his life (1979).

As the leading scientist in the field of cellulose, S.N. Danilov was constantly involved in research on the use of cellulose nitrates in ammunition. So, back in 1923–1931, he worked as a chemical engineer at the Institute of Applied Chemistry, and was a consultant to the Okhta Chemical Factory. Together with the staff of the department, he created new modifications of pyroxylin and ballistic powders for small arms and artillery and participates in the creation of ballistic fuels for reactive systems. The significance of the contribution of S.N. Danilov to the solution of these problems follows from the fact that in 1947 he was elected full member of the Academy of Artillery Sciences.

The profile of specialists graduated from the department varied according to the industry requirements. Until 1933, powder gun engineers of a relatively narrow profile were trained. Since 1933, the department provided extensive training in chemical processing of cellulose and its esters. After the war, the department began teaching in two directions and graduated engineers technologists specializing in nitrocellulose powders and researchers specializing in the technology of solid nitrocellulose propellants. Since the second half of the 1950s, work has begun on the creation of a new type of energetic condensed systems, mixed solid propellants for intercontinental strategic missiles. This required proper selection of energy-rich, strong, and elastic binders. The department began to specialize in this field and for a short time it turned into one of the authoritative scientific centers of this profile.

In 1972, Doctor of Engineering Nikolai Grigor'evich Rogov (1930–2002) was elected head of the department. Since 1995, the department is headed by Mikhail Alekseevich Ishchenko. The following traditional directions can be distinguished in the research conducted at the department: synthesis, modification, and development of technology of preparation of new components of propellants and solid propellants; development of formulations and study of properties of gunpowders, solid propellants, and mixed solid propellants; research and search for opportunities to regulate the ballistic characteristics of gunpowders and solid propellants.

After exposition of the history of the two largest centers of teaching and research in the field of organic chemistry, we turn to the **Department of Chemistry of the Imperial Medical Surgical Academy** (since 1881, **Military Medical Academy**) founded in 1798 and having old and glorious traditions.

After the sudden death of A.P. Borodin in 1887, the head of this department was his student and sonin-law, Aleksandr Pavlovich Dianin (1851-1918), whose scientific heritage is rather small. Nevertheless, he entered the history of chemistry as the author of his own reaction (condensation of phenols with ketones, Dianin's reaction) and a whole class of organic compounds, dianic epoxy resins. In 1890, the Department of Chemistry divided into two: the Department of Inorganic, Analytical, and Organic Chemistry and the Department of Medical Chemistry (subsequently the Department of Biochemistry). Unfortunately, a number of reforms undertaken by the military ministry in the late XIXth century and subsequently abolished led to a noticeable drop in the level of teaching fundamental disciplines in the academy.

In 1916, A.P. Dianin was dismissed "in connection with the expiration of the length of service," and in early 1917 the head of the department was already

mentioned S.V. Lebedev. The assessment of the situation at this moment is given by Lebedev himself: "The placement and equipment of the departments of both chemistries is not only completely unsatisfactory, but it is directly humiliating for an institution with such high traditions as the academy. If during the world-famous N.N. Zinin in 1863 the chemical laboratory was exemplary in Russia, at present it is at least the worst in St. Petersburg ..." And just a year after coming of S.V. Lebedev to the department, the country was plunged into the ruin of the civil war. A rigid saving of reagents was introduced, and it was necessary to work on kerosene lamps instead of gas.

S.V. Lebedev personally "knocked out" the necessary equipment. The staff of the department together with S.V. Lebedev at the head went to the Neva to get ice for cooling reaction mixtures. The efforts undertaken by the head of the department pursued two goals, to ensure a high level of comprehensive chemical training of doctors and revive the former glory of the department as a scientific center in the field of organic chemistry, and they quickly led it out of stagnation and provided the basis for later remarkable discoveries of S.V. Lebedev. The crowning point of his activity was the synthesis of artificial rubber from domestic raw materials, which was performed in the framework of the world competition announced by the USSR Supreme Economic Council in 1926.

S.V. Lebedev left the department in January 1934, just a few months before his death. The best part of his creative life and the most significant discoveries that glorified his name and the entire national science are forever associated with the Department of Chemistry of the Military Medical Academy. Lebedev's name is given to the street in St. Petersburg, where the main building of the academy is located.

The departure of a bright talented personality like S.V. Lebedev could not pass painlessly. In early 1934 the leadership of the department passed into the hands of **Nikolai Nikolaevich Andreev** (1879–1961), and since 1926 he taught a course in physical and colloid chemistry. Unfortunately, N.N. Andreev was not interested in organic chemistry, which led to a conflict with the collective formed in the times of Lebedev. In this regard, some employees left the department, and the others tried to continue the works of S.V. Lebedev individually.

Internal tension was resolved by the next division of the team into the Department of Inorganic and Analytical Chemistry with a course of physicochemical chemistry and the Department of Organic Chemistry which was headed by **Petr Aleksandrovich Ashmarin** (1888–1941), a student of A.E. Favorskii. The war time and the first post-war years were characterized by frequent changes in the leadership of both departments and mutual transitions of employees between them. Therefore, it is not surprising that in 1951 they were reunited in the Department of Chemistry under the guidance of the S.V. Lebedev's student **Yakov Mikhailovich Slobodin** (1904–1994). This was already the fourth (!) appointment of Ya.M. Slobodin to the post of head of department.

In 1953, Ya.M. Slobodin returned to the post of senior lecturer, and Isaak Solomonovich Ioffe (1900-1973) was appointed as head of the Department of Chemistry. I.S. Ioffe graduated from the Leningrad Institute of Chemical Technology and in 1935, first in the USSR, defended his dissertation for the degree of Doctor of Chemical Sciences (before that, the Doctor of Sciences degree was conferred on the basis of total works). In 1956, the Military Medical Academy was merged with the Naval Medical Academy; as a result, the corresponding chair of the Naval Medical Academy joined the Department of Chemistry of the Military Medical Academy, and I.S. Ioffe was also entrusted with the leadership of the unified department. His area of research was chemistry of organic dyes and medicines. I.S. Ioffe is author of a textbook on organic chemistry for medical schools, which has survived three editions and has been translated into Romanian and Hungarian.

After the death of I.S. Ioffe, B.V. Ioffe's student Kirill Nikolaevich Zelenin (1938-2004) received the leadership of the Department of Chemistry of the Military Medical Academy. In 1963 he came to a position of assistant lecturer from the Leningrad University after postgraduate school and defense of his candidate's dissertation. In 1968 he became an associate professor of the department, and a decade later, a professor. His arrival gave a powerful impetus to the development of scientific research using the newest physical and chemical methods. The research was mainly focused on the synthesis and structure and properties of organic hydrazine derivatives in order to obtain new physiologically active compounds. K.N. Zelenin did a lot to improve the teaching of chemistry to the huge at that time number of students. In 1998, he wrote and published an original textbook for future doctors (K.N. Zelenin, Chemistry. A Textbook for Medical High Schools), the second edition of which appeared in 2003 (K.N. Zelenin and V.V. Alekseev, *General and Bioorganic Chemistry*. *A Textbook for Students of Medical High Schools*). The scientific authority of K.N. Zelenin is also confirmed by the fact that, not being a physician, he was elected academician of the Military Medical Academy almost for the first time after N.N. Zinin and A.P. Borodin.

In 2004, K.N. Zelenin was replaced by his student, graduate of the Department of Physical Organic Chemistry of the Leningrad State University Valery Vladimirovich Alekseev (1957–2013), who continued the traditions and topics set by K.N. Zelenin. However, he suddenly died at the age of 56, and at present the department is headed by Nikolai Nikolaevich Khimich, a graduate of the Department of Organic Chemistry of the Leningrad State University.

The history of teaching of organic chemistry in the **St. Petersburg Forest Technical University** is not much shorter, and its traditions were laid by many well-known scientists. The genealogy of this educational institution dates back to the Tsarskoye Selo Forestry School founded in 1803, which was soon renamed the Forest Institute and changed its name many times. In 1837, the Forest Institute was transformed into the Forest and Landmark Institute, and in 1862, to the Forest Academy, which a year later turned to the Agricultural Institute. On October 1, 1863, the reading of the chemistry course was entrusted to the adjunct professor of the Medical Surgical Academy A.P. Borodin. In 1864 another N.N. Zinin's student, **Aleksandr Nikolayevich Engelgardt** (1832–1893)

was invited to the position of professor of chemistry. Prior to this, A.N. Engelgardt together with N.N. Sokolov opened the first private paid chemical laboratory in Russia, which functioned from 1857 to 1860, and also founded a chemical



journal (The Chemical Journal of N. Sokolov and A. Engelgardt) which was published from 1859 to 1860. In this magazine, in addition to the publishers, D.I. Mendeleev, A.M. Butlerov, and others published their works.

In 1868, Engelgardt introduced teaching of a special course of organic chemistry. At the same time, he was the first to begin extensive chemical research at the Agricultural Institute. In 1870, A.N. Engelgardt was awarded the Lomonosov Prize for his studies on the structure–property relations in the aromatic series. However, in 1870, A.N. Engelgardt was dismissed for the participation in student unrest, and in 1871 **Nikolai Nikolaevich Sokolov** (1826–1877), a disciple of J. Liebig, was invited to the professor position.

After the death of N.N. Sokolov, teaching of chemistry was entrusted to his and Engelgardt's student **Pavel Aleksandrovich Lachinov** (1837–1891), who worked at the Forest Institute from 1877 to 1891, continuing reading a special course of organic chemistry and performing research in the field organic chemistry. In the last period of his life, P.A. Lachinov performed fundamental works on the structure of cholesterol and bile acids.



Since 1891, Professor **Mikhail Grigor'evich Kucherov** (1850– 1911), who studied chemistry under the guidance of A.N. Engelgardt and N.N. Sokolov, became a professor of chemistry. M.G. Kucherov continued reading the course of lectures on organic chemistry to students of the forestry faculty and also conducted

scientific research. His main works were devoted to the synthesis of biphenyl and some of its derivatives, conditions for the conversion of vinyl bromide to acetylene, and catalytic hydration of acetylenic hydrocarbons discovered by him in 1881 (Kucherov's reaction). The hydration of acetylene was used as the basis for the large-scale production of acetic aldehyde and acetic acid. The first plant for the production of acetic aldehyde according to Kucherov was built in Canada in 1912.

After the departure of Kucherov from the Forest Institute in 1910, Evgenii Vladislavovich Biron (1874-1919), a physical chemist graduated from the St. Petersburg State University, was appointed to the position of professor of chemistry on his recommendation. However, in 1915–1917, at the request of the military department, he headed research on the analysis of chemical warfare agents (mustard gas), during which he received serious poisoning, fell ill, and died at the age of 45. In the period of his illness (1917-1919) lectures on inorganic and organic chemistry to students of forestry specialties were read by A.E. Favorskii's student Vladimir Nikolaevich Krestinskii (1882-1939), who in 1909 held the position of assistant. In 1921 V.N. Krestinskii became an associate professor of the Forest Institute. From 1925 to 1928, he also worked as an assistant professor at the St. Petersburg Polytechnic Institute, where he read a special course of terpene and carbohydrate

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

chemistry. In addition, in 1920 V.N. Krestinskii was elected professor of the St. Petersburg Pedagogical Institute, where he lectured on general and special organic chemistry and supervised students' theses until 1928.

In December 1921, the famous chemist and historian of chemistry, professor of the St. Petersburg Polytechnic Institute **Boris Nikolaevich Menshutkin** 

(1874–1938), the son of N.A. Menshutkin, became the head of the Department of Chemistry of the Forest Institute. B.N. Menshutkin graduated from the St. Petersburg University, and since 1901 he worked at the St. Petersburg Polytechnic Institute, where he headed a department for the rest of his life.



In 1927, in view of the forthcoming transformation of the Forest Institute into the Forest Technical Academy (LTA), it was decided to allocate an independent department of organic chemistry. In 1927 **V.N. Krestinskii** was elected professor of this depart-

ment, and on September 1, 1929, he took the position of its head (approved in 1930). He received his doctorate degree in chemistry in 1935 without defending dissertation. V.N. Krestinskii made a great contribution to the chemistry of acetylenic



and organomagnesium compounds, as well as to the study of the composition of turpentine, turpentine oils, resin acids, and rosin; he is the author of a textbook on the chemistry of terpenes.

After the death of V.N. Krestinsky, **Dmitrii Vyacheslavovich Tishchenko** (1886–1969), professor

of the Leningrad State University, was invited in the Forest Technical Academy. Since September 1, 1940, D.V. Tishchenko headed the Department of Organic Chemistry. In December 1941, he was evacuated to Moscow, where until September 1945 he worked as deputy director for research of the Central Research



Forest Chemical Institute. Since 1942, D.V. Tishchenko studied the composition and use of resins obtained by thermolysis of wood. This line of research formed the basis for the creation of a problem laboratory of pyrogenic resins at the Forest Technical Academy. Based on the structural similarity of terpene hydrocarbons with alkenes, he proposed a scheme for chlorination of terpenes to give allylic chlorides, which opened up prospects for the development of fundamentally new methods for the synthesis of homoterpene derivatives. In 1951, these works were awarded with the State Prize. Since 1953, extensive research has been carried out in the field of lignin chemistry under the guidance of D.V. Tishchenko. In 1964, the degree of Doctor of Chemical Sciences was conferred on D.V. Tishchenko without doctoral thesis. From the latest works of D.V. Tishchenko, studies on the synthesis of rosin substitutes have great theoretical and practical interest.

From 1969 to 1972, Vitalii Borisovich Foliadov (1919–1984) was the head of the department. The main direction of his research was the chemistry of terpenes. From 1972 to 2011, the department was headed by Mikhail Yakovlevich Zarubin. In 1954 he graduated with honors from the Faculty of Chemistry and Technology of the Forest Technical Academy, and in 1954–1957 he was a postgraduate student; candidate of sciences since 1961, doctor of chemical sciences since 1978, and professor since 1979. From September 1967 to July 1971, he was teaching at the Institute of Oil and Gas in Algiers. From 1980 to 1985, he was dean of the Faculty of Chemistry and Technology of the Forest Technical Academy, and in 1985-1996 he worked as a vice-rector for academic work of the Forest Technical Academy.

At this time, research on pyrogenic wood resins, neutral components of sulfate soap, and wood extracts was conducted at the Department of Organic Chemistry. New methods of wood delignification were developed. The structure, composition, and ways of utilization of industrial wastes (hydrolysis lignin) were also studied.

Since 2011, the Department of Organic Chemistry (since 2014, the Department of Chemistry) of the St. Petersburg State Forest Technical University (until February 2011, Forest Technical Academy) is headed by **Aleksandr Viktorovich Vasilyev**. In 1992 he graduated from the Department of Organic Chemistry at the St. Petersburg State University and entered postgraduate studies at the Department of Organic Chemistry of the Forest Technical Academy. Since 1994 he worked at the department and defended his candidate (1996) and doctoral dissertations (2010). Since 2011 he also works as a professor at the Department of Organic Chemistry of the St. Petersburg State University. Areas of his scientific interests include organic synthesis based on electrophilic activation of molecules, chemistry of cations and radical cations, chemistry of acetylenic compounds, organic synthesis based on the basis of renewable plant resources.

The younger universities, at which research in the field of organic chemistry and its teaching began already in the Soviet era, include the Pedagogical Institute, Chemical and Pharmaceutical Academy, and St. Petersburg State University of Industrial Technology and Design (until February 2016, St. Petersburg State Technological University of Plant Polymers).

Outstanding chemists and organic scientists of the XXth century, V.N. Ipat'ev and S.V. Lebedev, were at the origins of teaching of organic chemistry at the **Herzen State Pedagogical University of Russia** (at that time, Imperial Women's Pedagogical Institute, and then Third Petrograd Pedagogical Institute). In different years they lectured on organic chemistry at its chemical department.

The Department of Organic Chemistry at the Herzen State Pedagogical University of Russia was founded in 1929. Its first head was A.E. Favorskii's student **Yu.S. Zal'kind**; since 1934, he was also in charge of the Department of Organic Chemistry of the Leningrad Institute of Technology. Yu.S. Zal'kind initiated research in the field of chemistry of acetylenic hydrocarbons at the department.

A new stage in the development of organic chemistry at the Herzen University (Herzen Leningrad State Pedagogical Institute) began in 1949, when the department of organic chemistry was headed by the student

of Academician A.E. Porai-Koshits Vsevolod Vasil'evich Perekalin (1913–1998) who initiated extensive studies of nitro compounds and amino acids. The obtained results led to the foundation of the problem laboratory of nitro compounds (1959). This important milestone in the development of the department has determined the main directions



for further scientific and pedagogical work of the staff of the two divisions existing as a whole. V.V. Perekalin headed the department and laboratory for more than 40 years (1949–1992) and created a team of highly professional teachers and researchers who are keen on organic chemistry and its teaching.

Since 1992, the Department of Organic Chemistry and the Problem Laboratory of Nitro Compounds was led by Valentina Mikhailovna Berestovitskaya, a talented student of V.V. Perekalin (1940–2017), who preserved and continued successful development of the main lines of research held at the department, as well as the traditions established by V.V. Perekalin in teaching organic chemistry. In 2017, after the death of V.M. Berestovitskaya, the department was headed by her student, Doctor of Chemical Sciences **Sergei** Valentinovich Makarenko.

ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS

Long-term fundamental and applied research in the field of chemistry of nitro compounds and amino acids led to the formation of a scientific school known in the country and abroad. In 1997, it was recognized as the Leading Scientific School of Russia [99].

From the middle of the last century to the present, the priority of this scientific school is the chemistry of nitrogen-containing compounds, such as functionalized nitroethenes, organoelement and heterocyclic compounds, and amino acids. These topics are closely related to the problem of creating domestic effective drugs structurally close to brain metabolites and genetically related to each other, i.e., y-aminobutyric acid (GABA), glutamic acid, and  $\alpha$ -pyrrolidone. Based on these studies, general methods for the preparation of GABA and glutamic acid and original methods for the synthesis of novel GABA derivatives, spiropyrrolidones, and N- and C<sup>3</sup>-substituted derivatives of  $\alpha$ -pyrrolidone have been developed, as a result of which these substances have become available for extensive pharmacological studies.

The most significant result of the research was the creation at the end of the last century, together with pharmacologists of the Volgograd State Medical University and Bekhterev Research Institute and specialists of the *Biolar* research and industrial association (Latvia), of the original domestic nootropic drugs *Phenibut* and *Phenylpiracetam* that are widely used in medical practice. These works have made a significant contribution to the development of organic and pharmaceutical chemistry and provided an innovative breakthrough in the design of a new class of drugs, nootropics. In recent years, a series of patented substances possessing neuroprotective properties and cardiovascular activity have been obtained and recommended for industrial implementation.

Fundamental research in the field of functionalized nitroethenes, sulfur- and nitrogen-containing heterocyclic nitro compounds, and various derivatives of amino acids and  $\alpha$ -pyrrolidone is also successfully developing.

The Department of Organic Chemistry of the St. Petersburg State Chemical and Pharmaceutical Academy was founded in 1919 and was one of the first to appear in the newly opened Petrograd Chemical and Pharmaceutical Institute. The first head of the department was the first director of the Petrograd Chemical and Pharmaceutical Institute, a graduate of the University of Warsaw, Aleksandr Semenovich Ginzberg (1870–1937). He headed the department until 1937. From 1947 to 1951, the department was headed by associate professor Nikolai Vasil'evich Kashkin, a graduate of the Department of Physics of the Leningrad State University. From 1951 to 1964, the department was headed by Professor Iosif Fedorovich Suknevich, who graduated from the chemical department of the Faculty of Physics and Mathematics of the Leningrad State University, and from 1964 to 1979, by Professor Leonid Borisovich Dashkevich, who graduated from the special faculty of the Lensovet Leningrad Institute of Technology (1937-1941) and from the Military Academy of Chemical Defense (1941-1943) and did a lot to study methods of synthesis of carbon suboxide and its use in the synthesis of biologically active compounds. In 1979, the department was headed by a graduate of the Leningrad Institute of Technology Boris Aleksandrovich Ivin (1936-2014) who was engaged in the chemistry of heterocyclic compounds. At first he was offered to head the department of pharmaceutical chemistry, but he accepted an invitation to the Leningrad Chemical and Pharmaceutical Institute only when it became possible to head the department of organic chemistry. In parallel with this, since 1974 he supervised the laboratory of organic synthesis of the Research Institute of Oncology of the Ministry of Health Protection of the RSFSR.

Since 2007, the department is headed by a graduate of the Leningrad Institute of Technology, **Igor' Pavlovich Yakovlev**, a specialist in the field of chemistry of heterocyclic compounds and chemistry of biologically active compounds. From 1997 to 2010 he was dean of the Faculty of Industrial Technology of Medicines, and from 2010 to 2015, Vice-Rector for scientific work of the St. Petersburg State Chemical and Pharmaceutical Academy. Extensive research on the synthesis, structure, chemical properties, and biological activity of 1,3-oxa- and thiazines, pyrimidines, pyranones, 1,3,4-oxa- and thiadiazines, 1,4,2-dioxazines, 1,2,4-triazoles, pyranocoumarins, oxazinocoumarins, and amidines is now performed in the department. The Department of Organic Chemistry in the Higher School of Technology and Energy of the St. Petersburg State University of Industrial Technologies and Design was founded in 1946 as a result of reorganization of the Department of Organic, Physical, and Colloidal Chemistry of the Molotov Leningrad Institute of Technology, which was headed by Professor Boris Nikolaevich Dashkevich.

Since the creation and until 1954, the department was headed by **Vyacheslav Venediktovich Yanovskii**, a graduate of the Leningrad Institute of Chemical Technology and a specialist in the field of carbohydrates. From 1954 to 1972 the department was headed by a graduate of the Bestuzhev Courses, professor **Tat'yana Evgen'evna Zalesskaya**. The main scientific activity of T.E. Zalesskaya is related to isomerizations of fatty aromatic ketones.

In 1972, Viktor Nikolaevich Chistokletov (1932-2006), a disciple of A.A. Petrov (Lensovet Leningrad Institute of Technology) was invited to head the department. In 1973 he defended his doctoral dissertation. Together with A.A. Petrov, he was the first to formulate new principles for the construction of 1,3-dipolar systems containing elements of higher periods. These principles were subsequently widely used to synthesize a variety of heterocyclic compounds. Since 1973 the department has received a powerful impetus for further development. New laboratories for the synthesis of organic compounds and studying their properties by modern physicochemical methods were organized. In a fairly short time, the staff of the department was updated by young promising employees and postgraduate students, who now form the core of the department. Since 1991, works on deep chemical processing of turpentine and by-products of sulfate cellulose production have been carried out. As a result, in 1993, the technology of pinane production by hydrogenation of pinene was implemented on an industrial scale, as well as technology for the production of pinane hydroperoxide (together with the Voronezh branch of the All-Russian Research Institute of Synthetic Rubber).

Since 2004, the department is headed by a disciple of V.N. Chistokletov and A.A. Petrov, **Yurii Georgievich Trishin**, who developed a new general approach to the synthesis of phosphorus-containing heterocyclic compounds by reaction of  $\alpha$ , $\beta$ -unsaturated trivalent phosphorus compounds with difunctional reagents.

Concluding this section, we note that due to the limited volume of the article, we could not mention in

it the works of the great chemist, the creator of the Russian chemical industry and the "father of American petrochemistry," Academician V.N. Ipat'ev (1867–1952), his foster brother L.A. Chugaev (1873–1922), Academician A.E. Porai-Koshits, and a number of other outstanding scientists. Unfortunately, the department of dyes of the St. Petersburg State Institute of Technology and the activities of such institutions such as the State Institute of Applied Chemistry, Institute of Macromolecular Compounds, All-Russian Research Institute of Synthetic Rubber, etc. remained beyond the scope of the present review.

## 4. ORGANIC CHEMISTRY IN MOSCOW UNIVERSITIES

## 4.1. History of Organic Chemistry in the Moscow University

**4.1.1. Organic chemistry in the Moscow University in the "pre-Markovnikov" period.** The history of organic chemistry in the Moscow University dates back to the first years of its existence. When in August 1754 the Empress Elizaveta Petrovna signed a decree establishing the University in Moscow, it consisted of three faculties: philosophical, legal, and medical; the latter also included the department of "physical and pharmacological" chemistry with a laboratory in the building of the "Pharmacy House" at the Voskresenskii Gate.

According to the statute of 1804, the faculties of the university were reorganized into four departments, and the Department of Chemistry was included into one of which, the physics and mathematics department. Private docent F.F. Reuss (1778–1852), the most famous in the history of chemistry for his work on electrophoresis, was invited from Hannover to a position of head of the department [100]. In the chemical



"Red Chemical Building" (chemical laboratory building of the Moscow University on Mokhovaya street).

laboratory of the university, Reuss was the first to start experiments in organic chemistry, which were aimed at studying drugs [101], in particular, at extracting active substances from the cinchona bark [102].

After F.F. Reuss, since 1833, the head of the department of chemistry (from 1833 to 1850, the physics and mathematics department of the Faculty of Philosophy; since 1850, the Faculty of Physics and Mathematics) was R. Heimann (1802-1865). He read a course of chemistry for students of the Department of Physical and Mathematical Sciences, which included general organic chemistry. The course of lectures was combined with practical exercises: students practiced "in carrying out chemical experiments and solving problems of chemical proportions" (1835-1836) and chemical analysis (1840-1850). In 1837, on the initiative of R. Heimann, a chemical laboratory was built with an auditorium (the main part of the subsequently known "Red Chemical Building" on Mokhovaya Street), where lectures for students, as well as very popular "public lectures" for manufacturers and artisans, were read. The laboratory was considered at that time exemplary in equipment. In this laboratory, R. Heimann carried out research on stearin, "firearm cotton paper" (nitrocellulose), various paints, coal, and "ways of impregnating wood with various substances" to make it colored and prevent decay [103, 104].

After the resignation of R. Heimann, from 1854 to 1871 the Department of Chemistry of the Faculty of Physics and Mathematics was headed by Professor Nikolai Erastovich Lyaskovskii (1816-1871), who previously taught pharmacy and pharmacognosy to students of the Faculty of Medicine. In 1846-1847 Lyaskovskii read a public course of lectures "The System of Newest Organic Chemistry," which was one of the first courses in physiological chemistry in Russia. N.E. Lyaskovskii is known primarily for his work in the chemistry of proteins: he was the first to correctly determine the composition of the most important protein substances such as fibrin and egg and vegetable albumins, and also proved the inconsistency of the Mulder theory which dominated at that time and implied the existence of a single protein radical. This was a turning point in the development of modern theory of proteins [105]. N.E. Lyaskovskii also studied volatile and nonvolatile constituents of the Limburger cheese and identified butyric, valeric, and caproic acids therein (together with P.A. Il'yenkov) [106, 107]; he also determined the margarine formula [108].

After the death of N.E. Lyaskovskii in 1871, the Department of Chemistry was briefly led by D.K. Ki-

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

rillov, and in 1872 rector S.M Soloviev invited Professor V.V. Markovnikov to the position of head of the Department of Chemistry.

**4.1.2. Organic chemistry in the Moscow University under V.V. Markovnikov (1872–1893).** By the beginning of the 1870s, there was a difficult situation with teaching of chemistry in the Moscow University. The level of teaching was not high, N.E. Lyaskovskii's lectures on chemistry were designed for a wide range of listeners, including those who were not sufficiently trained (now we would call such lectures *popular science*). These lectures, like practical exercises, were not systematic, and they ceased in 1871. By this time, research work stopped almost completely [109].

V.V. Markovnikov is rightfully called the creator of the methodology of chemical university education in Russia. Working at Moscow University from 1873 until the end of his life, he, in fact, performed a radical reform of the teaching of chemistry [110].

Vladimir Vasil'evich Markovnikov (1838–1904),

a graduate of the Kazan Chemical School, a student of A.M. Butlerov, is the creator of the theory of mutual influence of atoms in organic molecules and the author of the famous rule on the regioselectivity of electrophilic addition to unsaturated compounds [111]. This rule entered



the science so that it is indicated only by the first letter of the author's surname, "M" [112–117].

The early period of V.V. Markovnikov's life was associated with Kazan; it has already been described in Section 2. In 1871–1872 he was a professor at the Novorossiysk University in Odessa, where he lectured on organic chemistry, headed a chemical laboratory, and directed all practical chemistry classes, and then received a proposal from the Novorossiysk University Council to head the department of chemistry. In 1872, after long hesitation, V.V. Markovnikov accepted the offer to move to Moscow.<sup>25</sup>

The first innovation of V.V. Markovnikov in the curriculum was the division of the general chemistry course into inorganic, organic, and analytical chemistry. Such attempts were made earlier by F.F. Reuss and R. Heimann; however, at that time no real division

<sup>&</sup>lt;sup>25</sup> The reason for Markovnikov's hesitation is clear: in Odessa he had a well-equipped laboratory, whereas at the Moscow University there was only an old building built in 1838, and it was clear that it would have to do a lot of work to bring the laboratory into working condition.



Founders of the Russian Chemical Society (members of the First Congress of Russian Naturalists and Physicians, who issued a resolution on its establishment on January 4, 1868). Standing from left to right: F.R. Vreden, P.A. Lachinov, G.A. Shmidt, A.R. Shulyachenko, A.P. Borodin, N.A. Menshutkin, N.A. Sokovnin, F.F. Beilstein, K.I. Lisenko, D.I. Mendeleev, F.N. Savchenkov; sitting: V.Yu. Rykhter, S.I. Kovalevskii, N.P. Nechaev, V.V. Markovnikov, A.A. Voskresenskii, P.A. Il'enkov, P.P. Alekseev, A.N. Engelgardt (the signatures were made by D.I. Mendeleev's hand).

of the courses took place. V.V. Markovnikov was the first to introduce lecturing in organic chemistry for three semesters, and in the additional semester, socalled "Repeat course of organic chemistry" was read to improve assimilation of the subject; other lecturers were often instructed to read this part of the course. V.V. Markovnikov read the main course of organic chemistry for students of the Faculty of Physics and Mathematics for twenty years (until 1893), and for students of the Medical Faculty, until 1878 (later this course was considered too extensive for physicians).

In 1875, a department of inorganic chemistry was founded at the chemical laboratory. Since the beginning of the 1880s, the two branches existed largely apart from each other, and they were named the Laboratory of Organic and Analytical Chemistry and the Laboratory of Inorganic Chemistry. In 1899, the latter was renamed to the Laboratory of Inorganic and Physical Chemistry.

V.V. Markovnikov's lectures on organic chemistry included two sections. The first section dealt with nonaromatic compounds and contained chapters on saturated and unsaturated hydrocarbons, alcohols, aldehydes and ketones, acids, nitrogen-containing derivatives of hydrocarbons, carbohydrates, and organometallic compounds of Zn, Hg, Al, Sn, and Pb. The second section described aromatic compounds (monoand polynuclear) and alkaloids. Since 1886, on the initiative of V.V. Markonnikov a large number of special courses began to be read at Faculty of Physics and Mathematics (1–2 h a week). Such special courses were read by M.I. Konovalov ("Methods for determination of the structure of organic compounds" and "Polyhydric alcohols and carbohydrates"), A.N. Reformatskii ("Organic chemistry. aromatic Series"), and N.M. Kischner ("Methods of transformations of organic compounds in relation to their structure").

In 1887, V.V. Markovnikov introduced practical classes in organic chemistry; since this year, a new chemical laboratory was opened at the cost of his enormous efforts[118]. V.V. Markovnikov believed that "...a library and a quiet office are not sufficient for a chemist to work productively; he needs a laboratory, materials, and money."<sup>26</sup>

<sup>&</sup>lt;sup>26</sup> V.V. Markovnikov was never a "desk scientist," and he always worked with his students. Each topic given by V.V.Markovnikov to the student for research "was made available to all working in the laboratory. Everyone could participate spiritually, if not materially, in the work of neighbors: these works were discussed between students and, undoubtedly, that such a discussion "together" brought tremendous benefit to all involved."

Practical training in organic chemistry consisted in preliminary synthesis of 2–3 compounds and further in performing a research. The V.V. Markovnikov system virtually implied rapid (without special preliminary preparation) involvement of students in research work [119]. From 1874 to 1884, practical exercises in analytical chemistry were also conducted in V.V. Markov-nikov's laboratory<sup>27</sup> [120].

V.V. Markovnikov set independent work of students at the head of his teaching system. He did not consider numerous preliminary preparative works necessary, believing that students would acquire necessary skills duering the research process [121]. Good illustrations of this attitude are his well-known quotations: "In every training it is essential to provide the greatest possible scope for student's self-activity"; "You should never squeeze fried pigeons into the mouth"; "You should let a student into a deep place: who swims, it means sense."<sup>28</sup>

In the late 1870s, for the first time at the Moscow University, V.V. Markovnikov organized scientific colloquiums with participation of students at the Department of Chemistry. Such activity of V.V. Markovnikov led to the fact that the number of people engaged in chemistry at the Moscow University, as well as the number of scientific works published by them, began to increase continuously. Students who wanted to devote themselves to scientific work remained laboratory assistants; among them there were such well-known scientists as A.N. Reformatskii. M.I. Konovalov, A.M. Berkengeim, N.M. Kischner, I.A. Kablukov, N.Ya. Dem'yanov, and many others. Through the efforts of V.V. Markovnikov at the Moscow University, the largest national school of chemists was created, and by the end of the XIXth century the Moscow University itself became one of the most important scientific chemical centers.



V.V. Markovnikov reads a lecture for students in the Large Chemical Lecture Room of the Red Building.

The main scientific achievements of V.V. Markovnikov are the following [122]:

(1) Discovery of the isomerism in the series of alcohols and fatty acids;

(2) Development of the concept of mutual influence of atoms in organic molecules, formulation of a rule on the direction of cleavage, substitution, addition to double bond, and isomerization reactions, depending on the structure (Markovnikov's rule, 1869 [113]);

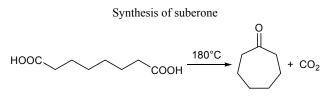
(3) Ascertainment of peculiarities of double and triple bonds in unsaturated compounds, specifically their greater strength in comparison with single bonds but not equivalence to two or three single bonds (1860–1870);

(4) First synthesis of cyclobutanedicarboxylic acid (together with G.A. Krestovnikov, 1879);

(5) Discovery of a new class of organic compounds, naphthenes (alicyclic hydrocarbons, 1880s);

(6) First studies of the composition of Russian oil, which gave rise to the development of a new independent science, petrochemistry (since 1880);

(7) Proof of the existence of cyclic compounds with 3 to 8 carbon atoms in the ring; the first synthesis of suberone (cycloheptanone) by pyrolysis of cork acid (1889);



(8) First isomerization of cyclic hydrocarbons with ring contraction (cycloheptane to methylcyclohexane) (1880–1890).

1319

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

<sup>&</sup>lt;sup>27</sup> The following order was established: "The time of classes was not determined, but the laboratory was at the service of students from 9 am to 7 pm. Since laboratory assistants had state apartments then, with the exception of lunch time, they had to stay in the laboratory for total time of lessons. The professor himself stayed in the laboratory from 10 am to 5 pm, and later, when he had a state apartment near the laboratory, he sometimes worked in the evenings" [111].

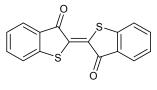
<sup>&</sup>lt;sup>28</sup> The fact that the techniques for synthetic works were not given to students in an explicit form also contributed to the independence and development of students' activity since they had to find them themselves in German journals and translate. As a result, "the students immediately saw that further study of chemistry is impossible without the knowledge of foreign languages, and they gradually got to know independent methods of research from the original articles of various scientists."

From the beginning of the 1890s, V.V. Markovnikov began to systematically study composition of the Caucasian oils of Russia. It is interesting to note that this new direction in the research work of V.V. Markovnikov at first did not meet sympathy among some Russian chemists who expressed regret at the fact that he engaged in oil and thus "betrayed pure chemistry." In 1883, V.V. Markovnikov and V.N. Ogloblin submitted an extensive article entitled "Study of Caucasian Oil" to the Department of Physics and Mathematics of the St. Petersburg University. This article was a summary of all studies performed on this topic in the laboratory of the Moscow University [113], and the authors came to the conclusion that the Caucasian (Baku) oil consists by no less than 80% of hydrocarbons called *naphthenes* at the suggestion of V.V. Markovnikov. To identify the position of naphthenes in a number of other classes of organic compounds, he isolated a large number of individual compounds from the Caucasian oil and studied their physical and chemical properties. Simultaneously, in order to clarify the structure of naphthenes, he synthesized a large number of polymethylene compounds. At the same time, he developed many original methods of synthesis of both polymethylene hydrocarbons and their derivatives such as cyclic ketones, naphthenic acids, and others. In 1892, studies on the chemistry of naphthenes were summarized in [123].

V.V. Markovnikov was not a scientist closed in his specialty. In 1880 he studied mineral waters of Narzan and salt lakes in the Caucasus and Astrakhan province. He was interested in problems of the chemistry of minerals and geology, as well as in finding Glauber's salt in the Volga salt lakes and the origin of such lakes.

During the Russian–Turkish War of 1877–1878, V.V. Markovnikov developed an exceptionally intensive activity in organizing sanitary assistance of the active army. In July 1877, he was sent to Romania and beyond the Danube for the organization of disinfection business. During the inspection in the Kursk region, he was severely ill with typhus (1878). At the same time V.V. Markovnikov refused to receive 400 rubles in gold per month (the reward assigned to all professors sent to the theater of operations).

V.V. Markovnikov's laboratory was one of the first where women were involved in chemical research. In 1870–1880, **Yu.V. Lermontova**, a close friend of Sophia Kovalevskaya, one of the first Russian women who received doctor's degree in chemistry, engaged in research in the field of deep decomposition of petroleum and petrochemicals, as well as in the field of organic synthesis, worked there. In particular, she developed a convenient method for the preparation of 1,3-dibromopropane [124] (Yu.M. Lermontova also performed studies in St. Petersburg in collaboration with A.M. Butlerov). The alkylation of olefins with halogen derivatives, discovered during this work, became a name reaction (Butlerov–Lermontova– El'tekov reaction). However, with time Lermontov's name disappeared from the reference books on name reactions, and today the reaction is called *Butlerov– Eltekov* [125]. Also, E.A. Fomina-Zhukovskaya, Doctor of Physical Sciences of the University of Geneva, worked in the laboratory; until 1893 she was a private assistant professor and was engaged in research on the synthesis of sulfur analogs of indigo.



2,2'-Bis(benzothiophene)indigo

V.V. Markovnikov was in charge of the main department of chemistry of the Faculty of Physics and Mathematics and of the laboratory of organic and analytical chemistry from 1872 to 1890 when he left the position of full-time professor for "30 years of service" but actually supervised it until 1893. In 1893, V.V. Markovnikov handed over the laboratory and the official apartment to N.D. Zelinskii, who replaced him in the department of analytical and organic chemistry; the latter remained formally without a leader since 1890.

V.V. Markovnikov experienced very hard the dismissal from the laboratory, the creation of which cost him enormous efforts and with which his entire life was connected. Here is what he wrote about this: "It's so hard for me to talk about this ... in my life it's a disaster that has knocked me out of the rut ... it's a terrible insult that hit me to the smallest of the fibers of my heart ... It's not insulting for myself alone, but for science in Russia and for its unfortunate representatives, who are turned into serfs" [126]. Nevertheless, V.V. Markovnikov was able to save 12 positions in the laboratory of organic and analytical chemistry at his disposal for life [127]. In the year of 1894-95, these positions formed the "Department of the Honored Professor V.V. Markovnikov" where he conducted practical studies and research in organic chemistry; this department was abolished in 1904. V.V. Markovnikov's teaching activity was noticeably reduced, but the research related to Caucasian oil became even more intense.

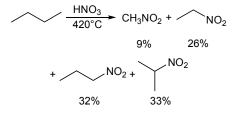
**4.1.3. Students of V.V. Markovnikov. Markovnikov School.** The pedagogical activity of V.V. Markovnikov who created the famous "Markovnikov" school of chemists, was exceptionally fruitful. Many of his students subsequently became famous scientists with world names, in particular M.I. Konovalov, V.N. Ogloblin, I.A. Kablukov, N.M. Kischner, and others.



Mikhail Ivanovich Konovalov (1858–1906) graduated from the Moscow University in 1884 and in 1884–1896 continued working within its walls; in 1896–1899 he was Professor of the Moscow Agricultural Institute; since 1899, professor, and in 1902–1904, rector of the Kiev Polytechnic Institute.

M.I. Konovalov's main works were devoted to the action of nitric acid on organic compounds. In the 1880s, he discovered the nitrating effect of dilute nitric acid on aliphatic compounds (Konovalov's reaction [128]) and alicyclic and fatty aromatic hydrocarbons and developed methods for the synthesis of oximes, alcohols, aldehydes, and ketones from fatty nitro compounds (1888–1893). M.I. Konovalov used nitration reactions to determine the structure of hydrocarbons and developed methods for the isolation and purification of a number of naphthenes (1889).

Konovalov reaction (nitration of butane as an example)



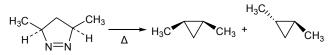


Nikolai Matveevich Kischner (1867–1935) graduated from the Moscow University in 1890; in 1894–1901, he lectured at the Moscow University and simultaneously taught at the Alexander Military School. In 1901–1913 he was professor of the Tomsk Technological Institute (see Section 5), and in

1914–1917, of the Shanyavskii People's University in Moscow. Since 1918, N.M. Kischner was the scientific

director of the "AnilTrest" Research Institute in Moscow, Basic research fields of N.M. Kischner were devoted to organic synthesis and properties of organic compounds discovered by him. He showed (1894) that hydrogenation of benzene with hydroiodic acid produces methylcyclopentane. This observation was the first experimental proof of isomerization with ring contraction. He was the first to prove the existence of aliphatic diazo compounds (1900) and developed a method for the preparation of organic hydrazine derivatives. In 1910, he discovered the transformation of the carbonyl group of aldehydes and ketones to methylene via catalytic conversion of the corresponding hydrazones [129]. Simultaneously, the same reaction was described by the German chemist Ludwig Wolff [130] and is known as the Wolff-Kischner reaction (a method for the synthesis of individual highpurity hydrocarbons; see Section 5). By applying the catalytic decomposition method to pyrazoline bases, N.M. Kischner in 1912 discovered a universal method for the synthesis of hydrocarbons of the cyclopropane series, including bicyclic terpenes with a threemembered ring of carane type (Kischner reaction [131, 132]). He made an essential contribution to the chemistry of synthetic dyes and to the creation of the aniline-dye industry in the USSR.

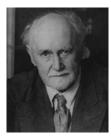
## Kischner reaction



Ivan Alekseevich Kablukov (1857–1942) in 1880 graduated from the Natural Department of the Faculty of Physics and Mathematics of the Moscow University; in 1881– 1882 he worked in A.M. Butlerov's chemical laboratory at the St. Petersburg University and then continued

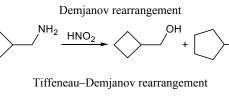


to work at the Moscow University under the guidance of V.V. Markovnikov. In 1882–1884 he taught at the Higher Women's Courses in Moscow, and since 1885 he was a private docent of the Moscow University. In 1889 he worked at the Leipzig University in the laboratory of W. Ostwald under the direction of S.A. Arrhenius. Since 1899, he was professor of the Moscow Agricultural Institute, and since 1903, professor of the Moscow University. The works of I.A. Kablukov are mainly related to electrochemistry of nonaqueous solutions. In his master's thesis (1887) "Glycerols, or trihydric alcohols, and their derivatives," he tried to substantiate Markovnikov's theory of mutual influence of atoms from the viewpoint of thermochemical data. Together with V.F. Luginin, he found (1893) that the heat of addition of bromine to ethylene hydrocarbons decreases in going from lower to higher homologs. In 1886–1888, he lectured at the Moscow University on private chemistry courses in organic chemistry: "Organic Chemistry (Nitrogenous Aromatic Compounds)" and "History and Criticism of the Theory of the Structure of Chemical Compounds."

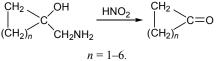


**Nikolai Yakovlevich Demjanov** (1861–1938) graduated from the Faculty of Physics and Mathematics of the Moscow University; since 1887, he was laboratory assistant of Prof. G.G. Gustavson in the Petrovskaya Agricultural Academy (now Timiryazev Agricultural Academy),

in which he worked until the end of his life. In January 1900, he defended his doctoral thesis "On the action of nitric anhydride and nitrogenous oxide on hydrocarbons of the ethylene series" at the Moscow University. He read a course of organic chemistry at the Moscow University, and later, a course of the chemistry of plants and physicochemical basis of biological chemistry. In 1908–1917 he lectured organic chemistry at the Higher Women's Agricultural Courses. Since 1935, he was in charge of a laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR. The most famous scientific works of N.Ya. Demjanov include the discovery of the allene synthesis (in 1888 together with G.G. Gustavson) by the action of zinc dust on 2,3-dichloropropene [133] and the discovery of ring-expansion isomerization of alicyclic compounds (1902-1903), namely Demjanov [134] and Tiffeneau–Demjanov rearrangements [135].



OH



Aleksandr Nikolaevich Reformatskii (1864– 1937), the brother of S.N. Reformatskii, graduated from the Kazan University. He was a student of A.M. Zaitsev (see Section 2). A.N. Reformatskii worked as professor of the Higher Women's Courses, Second Moscow University (1918), and Moscow Institute of Fine Chemical Technology (since 1930), dean of the Faculty of Physics and Mathematics of the Moscow State University (1919), and dean of the Chemical and Pharmaceutical Faculty of the



Second Moscow State University. Together with V.V. Markovnikov, he studied the composition of rose oil (1894) and aromatic aldehydes (1901). He taught at the Moscow State University from 1889 to 1911 by reading the courses "Historical outline of the development of chemical views over the past 100 years," "Periodic system of elements," "Organic chemistry (aromatic series)," "General (inorganic) chemistry," and "General (organic) chemistry." He is author of the textbook "Organic Chemistry" (1904) which was reprinted seven times.

**4.1.4. Organic chemistry in the Moscow University under N.D. Zelinskii (1893–1938).** In 1893, the laboratory of organic and analytical chemistry was headed by **N.D. Zelinskii**, a private docent of the Novorossiisk (Odessa) University, who was appointed an extraordinary professor. From 1893–94 he began to read the general course of organic chemistry and at the same time conduct practical classes in organic chemistry. In 1921–1929 N.D. Zelinskii headed the laboratory of organic and analytical chemistry of the Faculty of Physics and Mathematics of the Moscow State University, in 1929–1938, the Department of Organic Chemistry, and in 1938–1953, the Department of Petroleum Chemistry.

N.D. Zelinskii was the first to introduce into the teaching program a large systematic practicum on organic chemistry with a certain program including synthetic methods of organic chemistry. In 1905, during the general expansion and reorganization of university buildings, N.D. Zelinskii managed to increase the premises of the chemical laboratory to 254 workplaces.

Until 1911, Zelinskii conducted practical classes in organic chemistry with students. Compulsory synthesis of about 30 organic preparations was introduced for students specializing in organic chemistry before their independent research began; this practice was very different from the system adopted under V.V. Markovnikov, and it subsequently rooted in the Moscow University. Before 1911, N.D. Zelinskii also read the general course of organic chemistry; in addition to the



N.D. Zelinskii with collaborators and students (pre-revolution period); standing: E.S. Przheval'skii (2nd from the left), I.F. Gutt (3rd from the left); sitting: S.S. Nametkin (1st from the left), V.V. Longinov (?, 3rd from the left).

main course, a large number of private docent courses were lectured in 1886–1911 at the Moscow University. These courses included "Supplementary course in organic chemistry," "Organic chemistry. Nitrogenous organic compounds," and "History and criticism of the theory of the structure of organic compounds" by I.A. Kablukov; "Organometallic compounds," "Polyhydric alcohols and carbohydrates," and "Methods of determination of the structure of organic compounds" by M.I. Konovalov; "Methods of transformations of organic compounds in relation to their structure," "Methods of synthesis of organic compounds," "Repeating course of organic chemistry," etc., by N.M. Kischner; "Organic chemistry. Aromatic series" by A. N. Reformatskii; "Selected chapters of organic chemistry" by S.G. Krapivin (see also Section 13) and N.A. Rozanov; "Recent advances in experimental chemistry," "Chemistry of alkaloids," "Fundamentals of organic chemistry," etc., by A.E. Chichibabin; "Chemistry of organic dyes" by A.A. Yakovkin; and a course of stereochemistry by N.D. Zelinskii. In 1910, S.G. Krapivin published "Practical works on organic chemistry" which included 178 syntheses most often offered to students in the chemical laboratory of the Moscow University.

N.D. Zelinskii continued the traditional research lines related to petroleum chemistry. In 1901–1907, numerous cyclic hydrocarbons with a ring size of 3 to 8 were synthesized in the laboratory of organic and analytical chemistry and were used for artificial modeling of petroleum fractions. Since the beginning of the 1910s, a new research line, organic catalysis, began to develop in the laboratory.

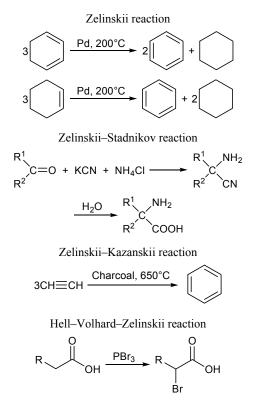
Nikolai Dmitrievich Zelinskii graduated from the natural department of the Faculty of Physics and Mathematics of the Novorossiisk University in 1884 and later improved his education under the guidance of J. Wislicenus at the Leipzig University and of V. Meyer at the University of Göttingen. Since 1888, for four years, he worked at the Novorossiisk University, where in 1888 he passed the master's examination and defended his master's degree (1889) and doctoral dissertation (1891). In 1893-1953, he was Professor of the Moscow University, except for the period 1911–1917 when he left the university together with a group of scientists in protest against the reactionary policy of the tsarist Minister of Education L.A. Kasso (during this period he was director of the Central Chemical Laboratory of the Ministry of Finance in St. Petersburg). In 1935, N.D. Zelinskii actively participated in the foundation of the Institute of Organic Chemistry of the Academy of Sciences of the USSR, where he subsequently headed a number of laboratories. In 1953, this institute has been named after N.D. Zelinskii.

The main areas of research activity of N.D. Zelinskii were several fields of organic chemistry, in particular organic catalysis, chemistry of heterocycles, chemistry of alicyclic compounds, chemistry of proteins and amino acids. He studied isomerism of thiophene derivatives, synthesized a number of its homologs, studied stereoisomerism of saturated aliphatic dicarboxylic acids, discovered methods for the synthesis of five- and six-membered cyclic ketones, and from the ketones thus obtained synthesized cyclic hydrocarbons with a ring size of three to nine carbon

atoms, which allowed artificial modeling of the composition of oil and oil fractions. N.D. Zelinskii was one of the founders of the concept of organic catalysis, discovered dehydrogenation catalysis [136-139] via selective action of palladium and platinum on cvclohexane and aromatic hydrocarbons and showed complete reversibility of the hydrogenation and dehydrogenation reactions, depending only on the temperature, discovered irreversible catalysis (catalytic disproportionation of cyclohexadiene and cyclohexene, 1911) [140], selective catalytic hydrolysis of cyclopentane hydrocarbons, destructive hydrogenation, isomerization, mutual transformations of rings toward both expansion and contraction, experimentally proved the formation of methylene radicals as intermediates in organic catalysis, discovered and carried out pyrogenic and catalytic aromatization of petroleum, proposed the idea of deformation of the reactant molecules on a solid catalyst during the adsorption process, designed a gas mask<sup>29</sup> (together with A. Kummant) [141], and for the first time in the USSR initiated work on the production of chloroprene rubber (together with N.S. Kozlov). Many of Zelinskii's studies were also related to proteins and amino acids: he discovered the synthesis of  $\alpha$ -amino acids from aldehydes and ketones by the action of a mixture of potassium cyanide and ammonium chloride and subsequent hydrolysis of  $\alpha$ -amino nitriles and obtained a number of amino acids and hydroxyamino acids.

In 1918–1919, Zelinskii developed a method for the preparation of gasoline by cracking of solar oil and oil in the presence of aluminum chloride and bromide; the implementation of this method on an industrial scale played an important role in providing gasoline to the Soviet state.

Four name organic reactions bear his name: catalytic disproportionation of cyclohexadiene and cyclohexene (irreversible catalysis, 1911, Zelinskii reaction), synthesis of  $\alpha$ -amino acids from aldehydes and ketones (Zelinskii–Stadnikov reaction, a modification of the Strecker amino acid synthesis), thermal trimerization of acetylene to benzene on activated carbon (Zelinskii–Kazanskii reaction), preparation of  $\alpha$ -halosubstituted carboxylic acids by the action of bromine (or chlorine) in the presence of phosphorus or phosphorus halides (Hell–Volhard–Zelinskii halogenation).



In 1911, a number of activities of the Ministry of Education sharply infringed upon the rights of university professors and teachers. In protest, about 130 professors of the Moscow University, including N.D. Zelinskii and some of his closest colleagues, left the university. The Laboratory of Organic and Analytical Chemistry was temporarily headed by I.A. Kablukov (analytical part) and the regular laboratory assistant I.F. Gutt (organic part). In 1912, I.F. Gutt resigned, and the laboratory of organic and analytical chemistry was headed by Prof. V.V. Chelintsev (for more details, see Section 10) known for his studies on organomagnesium and heterocyclic compounds. He also conducted practical classes in organic chemistry.

After the October Revolution, in 1917, Zelinskii returned to the Moscow University and again took charge of the laboratory of organic chemistry, which he headed until 1929 (before the establishment of the Faculty of Chemistry). The laboratory continued to

<sup>&</sup>lt;sup>29</sup> The first experiments were conducted in the central laboratory of the Ministry of Finance in Petrograd. In a hermetically sealed room, a large piece of sulfur was fired, and the room was filled with toxic sulfur oxide. When the gas concentration became high enough, Nikolai Zelinskii and his collaborators, laboratory assistant Sergey Stepanov and V.S. Sadikov entered the room, breathing through a scarf with calcined coal. Tests have surpassed all expectations. Stepanov was able to stay in a deadly poisonous atmosphere for over an hour, and the other testers, for half an hour. The Tsar personally thanked Nikolai Zelinskii, and his disciple Stepanov was rewarded with a soldier's St. George Cross for showing courage. After that, the Emperor issued an order: to remove all other protection systems and to start large-scale production of Zelinskii's gas mask.

carry out numerous studies in the field of organic catalysis, synthesis, and petrochemistry, and one of the new directions was the chemistry of proteins.

In 1921, a chemical department was established at the Faculty of Physics and Mathematics, and this department existed at the Moscow University for eight years. The number of students entering the first course of the chemical department according to the initial plan was to be 250 people. However, this figure soon had to be increased: in December 1921, the list of students accepted for the first year reached four hundred. In 1923, training of highly qualified chemists has been started through graduate school on the basis of the chemical department.

In 1922, the Research Institute of Chemistry was founded within the framework of the Association of Research Institutes established at the Moscow State University, and this institute directed the entire research work of the university in chemistry. The Research Institute of Chemistry trained postgraduate students, and senior students carried out diploma theses in its laboratories (training workshops for junior students were still held in the faculty laboratories).

In July 1928, the Plenum of the Central Committee of the CPSUadopted a resolution "On improvement of training of new specialists" in the light of Stalin's slogan "cadres decide everything," and reorganization of the higher school toward its professionalization began. At a regular rector's meeting held in May 1929 in Moscow, it was decided to change the management of higher educational institutions, since the Communist Party demanded to speed up training of specialists: the subject commissions were abolished, the main training and production unit became departments with managers appointed personally by the rector. In the course of these reforms, according to the order of the Moscow State University, on October 1, 1929, the Faculty of Chemistry of the Moscow State University was established on the basis of the chemical department of the Faculty of Physics and Mathematics. The Department of Organic Chemistry headed by N.D. Zelinskii was among the first five departments thus created.

The newly created faculty produced chemists in four specialties: inorganic, organic, physical, and analytical chemistry. A significant part (up to 50%) of teachers were young employees. The faculty trained 740 students. From the second course there was a division into two streams: organic and inorganic chemistry. In the fourth year, students acquired a narrow specialization. Initially, the Department of Organic Chemistry included five laboratories: intermediate products and dyes (headed by N.N. Vorozhtsov and A.P. Terent'ev), petroleum (headed by B.A. Kazanskii), cellulose (A.M. Nastyukov), processing of protein substances (N.I. Gavrilov), and catalysis of organic substances (M.I. Ushakov). Already by 1933–1934, the structure of the department had undergone significant changes so that it included six laboratories (organic catalysis, synthetic rubber, petroleum chemistry, organometallic compounds, protein substances, and organic synthesis).

In 1929, the mass media repeatedly discussed the need for a radical restructuring of the educational process at the university on "brigade-consultative" principles. In December 1929, it was stated that it was necessary to "dismember" the university on a production basis to several independent universities with the aim of "screwing science into production." In January 1930, general reorganization of the Moscow State University began, and the "active brigade–laboratory method of training" was introduced on a large scale.

On April 22, 1930, the Department of Chemistry was removed from the Moscow State University and was included as the IVth branch into the Unified Moscow Institute of Chemical Technology which consisted of four chemical universities and started to train research engineers. By 1931, more than 40 new universities and technical colleges had been created in the RSFSR in this way. The reform of higher education has made it possible to shorten the terms of training and increase the capacity of higher education institutions. In April 1931, the Resolution of the Central Committee of the CPSU "On the targets of universities" was issued, according to which universities had to prepare personnel for production (for factory laboratories and research institutes serving certain industries).

However, in January 1933 the Moscow Research Institute of Chemistry (the former Faculty of Chemistry and then the IVth branch of the Unified Moscow Institute of Chemical Technology) rejoined the Moscow State University as a chemical department. The following specialties and departments were established thereat: analytical chemistry (headed by Prof. E.S Przhevalskii), inorganic chemistry (Prof. E.F. Krauze), physical chemistry (Prof. A.V. Rakovskii), organic chemistry (Academician N.D. Zelinskii), and colloid chemistry (Prof. V.A. Naumov). The use of a brigade-laboratory method of training was deemed inexpedient. Collective attestation was abolished, and test periods and exams were re-introduced. In May 1933, the faculty system was restored at the university.

The Petrochemistry (1929) and Organic Catalysis Laboratories (1930) founded on the initiative of N.D. Zelinskii at the Department of Organic Chemistry were later transformed into the Department of Petroleum Chemistry (1938) headed by N.D. Zelinskii and Department of Organic Catalysis (1940) headed by A.A. Balandin.

N.D. Zelinskii created the second large school of organic chemists at the Moscow University, which became widely known already at the beginning of the XXth century. The outstanding students and collaborators of N.D. Zelinskii were A.A. Balandin, L.F. Vereshchagin, B.A. Kazanskii, K.A. Kocheshkov, S.S. Nametkin, A.N. Nesmeyanov, L.A. Chugaev, V.V. Chelintsev, A.E. Chichibabin, N.A. Shilov, and others.

4.1.5. Scientific school of N.D. Zelinskii. Boris Aleksandrovich Kazanskii (1891–1973) graduated



from the Moscow University. Together with N.D. Zelinskii, he was the author of well-known works on catalytic cracking of solar oil with aluminum chloride and a number of heterogeneous catalysts (activated carbon, aluminum oxide). Since 1935, he lectured on organic catalysis, petroleum chemistry, and organic chemistry at the Moscow Uni-

versity. From 1945 to 1960 he was successively deputy head of the Department of Petroleum Chemistry, head of the Department of Organic Catalysis (1949–1953), and then head of the Department of Petroleum Chemistry (1953-1960). Since 1961, professor of the Department of Petroleum Chemistry and Organic Catalysis, since March 1935, a senior scientific specialist in the newly created Institute of Organic Chemistry, from 1954 to 1966, director of the Institute. Working at the institute, he did not interrupt his pedagogical activity at the Moscow University. Along with theoretical research, he carried out applied studies related to the industrial production of synthetic rubber, which was implemented in the USSR. He was one of the founders of the scientific basis of petrochemistry and catalysis and Full Member of the Academy of Sciences of the USSR (1946). He discovered and studied mechanisms of catalytic dehydrocyclization of hydrocarbons, hydrogenolysis of cycloalkane derivatives, and hydrogenation and dehydrogenation of olefins and aromatic compounds. He developed a technological process for the production of benzene from hexane. B.A. Kazanskii is the author of a widely used method of analyzing gasoline mixtures. He discovered three new types of catalytic reactions of hydrocarbons, hydrogenolysis of cyclopentanes (together with N.D. Zelinskii and A.F. Plate [142]), aromatization of paraffin hydrocarbons [143], and their dehydrocyclization to form five-membered rings [144].

Aleksei Aleksandrovich Balandin (1898–1967) in 1923 graduated from the Faculty of Physics and Mathematics of the Moscow State University in specialty physical chemistry. Since 1930, he taught the course "Organic Catalysis" for chemistry students of the Moscow State



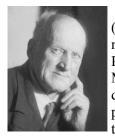
University, and in 1934 he became a professor at the Department of Organic Chemistry of the Moscow



N.D. Zelinskii with co-workers (1940s).

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

State University. In 1939, he organized the organic catalysis laboratory at the Faculty of Chemistry of the Moscow State University. A.A. Balandin is known primarily as the creator of the multiplet theory of catalysis (1929) [145] based on the assumption of structural similarity of reactant molecule and catalyst surface. He gave rise to the new direction "Scientific basis for selection of catalysts" and headed the corresponding Council in the Academy of Sciences. He studied the kinetics and mechanisms of hydrogenation and dehydrogenation of saturated and unsaturated hydrocarbons and was the author of basic works on the theory of catalytic hydrogenation of unsaturated organic compounds. A.A. Balandin published 1200 scientific works, including 8 scientific-theoretical reviews and 4 monographs.



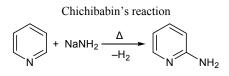
**Vladimir Vasil'evich Chelintsev** (1877–1947) graduated from the natural department of the Faculty of Physics and Mathematics of the Moscow University with a first-degree diploma and was left to prepare for professorship. His diploma thesis "Azo compounds of the aro-

matic series" was carried out under the guidance of Prof. N.D. Zelinsky. He defended his master's thesis "Individual magnesium compounds and their transformations into oxonium and ammonium complexes" at the Moscow University (1908). Since 1912 he read the general course of organic chemistry and also conducted practical classes in this discipline. From 1912 to 1917, Prof. V.V. Chelintsev was in charge of the laboratory of organic and analytical chemistry. In 1918 he was appointed professor of the Saratov State University, with which all his subsequent activities are connected (see Section 10). Thermochemical studies carried out by V.V. Chelintsev made it possible to correct the earlier formulas of a number of oxonium coordination compounds and to compile a complete table of thermochemical data on higher valencies of all major groups of organic compounds. In his subsequent studies of chlorophyll he succeeded in ascertaining the position of magnesium in the pyrrole rings and the nature of the tetrapyrrole group, as well as in solving some issues of the chemistry of chlorophyll assimilation. Since the 1930s, he was engaged in studying furan compounds [146].

Aleksei Evgen'evich Chichibabin (1871–1945) began his scientific career at the natural department of the Faculty of Physics and Mathematics of the Moscow University under the leadership of V.V. Markovnikov and M.I. Konovalov. In 1899–1909 he was assistant professor of chemistry at the Moscow Agricultural Institute; simultaneously, in 1901–1911 he lectured at the Moscow University. The main direction of his scientific activity was the chemistry of pyridine and its



derivatives, as well as of related compounds such as alkaloids and synthetic substances with a strong physiological activity. The synthesis of  $\alpha$ -amino-pyridine by the action of sodium amide on pyridine was named Chichibabin's reaction [147].



Chichibabin's work on triatomic carbon compounds (1902-1912) formed the basis of the free radicals concept (doctoral dissertation "Studies on triatomic carbon and structure of the simplest colored triphenylmethane derivatives" [148]). As the First World War started, he was actively engaged in the creation of technologies for the production of medicines and made a great contribution to the organization of the Russian pharmaceutical industry. Together with his students, he developed the technology of production of salicylic acid and its salts, acetylsalicylic acid, salol, and phenacetin. A.E. Chichibabin together with N.G. Patsukov and V.M. Rodionov initiated production of morphine and codeine. He also worked in the field of organomagnesium synthesis. Chichibabin's book "Basic Principles of Organic Chemistry" published in 1925 [149] withstood repeated reprints and was translated into Czech, Slovak, Hungarian, French, Spanish, English, and Chinese. In the 1930s and 1940s, this course was recommended as the main guide to organic chemistry in many French universities [150]. In 1926, A.E. Chichibabin was elected corresponding member of the Academy of Sciences of the USSR, and in 1928, full member.

In 1930, after the tragic death of his daughter from the oleum burn, A.E. Chichibabin left for Paris, where he first worked in the pharmaceutical laboratory of Prof. M. Tiffeneau in the Hôtel-Dieu and then led the research laboratory of one of the largest chemical concerns Etablissements Kuhlmann. In 1936 he finally refused to return to his homeland and was deprived of the Academician title and USSR citizenship by the decision of the general meeting of the Academy of Sciences. In 1990, the General Assembly of the USSR Academy of Sciences decided to restore Chichibabin to the rank of a full member of the Academy of Sciences [151, 152].

Ksenofont Aleksandrovich Kocheshkov (1894–1978), a disciple of N.D. Zelinskii, graduated from the



Moscow University in 1922. Since 1934 he was professor of the Department of Organic Chemistry. In 1930, together A.N. Nesmeyanov, he created a new lecture course "Chemistry of organoelement compounds," which he read at the Faculty of Chemistry for several years. Since

1944, he was head of the Laboratory of Chemistry of Organoelement Compounds of the Department of Organic Chemistry of the Faculty of Chemistry of the Moscow State University. Since 1951, he headed the Laboratory of Synthesis and Structure of Organometallic Compounds, created by him in the late 1940s, at the Karpov Research Physicochemical Institute.

Scientific works of K.A. Kocheshkov were concerned with the chemistry of organometallic compounds. In 1929, he developed for the first time a method for the synthesis of RSnX<sub>3</sub> compounds and studied their properties. In 1930, together with A.N. Nesmeyanov, he discovered a method for the preparation of organotin compounds through organomercury derivatives. Also, together with A.N. Nesmevanov, in 1935-1948 he used the diazo method to obtain organic compounds of tin, lead, antimony, and other metals. In 1936, K.A. Kocheshkov synthesized for the first time organotin and organolead compounds of the aromatic series with various substituents in the aryl ring directly linked to the metal. In 1944, he synthesized organic compounds of tri- and pentavalent antimony with different numbers of aryl substituents. Subsequently, he obtained polylithium compounds, in particular polylithiated toluene. Many of these reactions are known in the world literature as Kocheshkov's reactions, and they underlie the main method of synthesis of a number of important classes of organometallic compounds on both laboratory and industrial scales [153-157]. K.A. Kocheshkov also

Kocheshkov's reactions $3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl$  $R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2$  $R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3$ 

developed methods for the synthesis of amines, thiols, and other compounds with the use of organometallic compounds.

4.1.6. Department of Organic Chemistry of the Moscow University in 1938–1944 (headed by Academician Sergei Semenovich Nametkin). In 1938, the department of organic chemistry was headed by a student of N.D. Zelinskii, Sergei Semenovich Nametkin. He is known for his work on determination of the structure of bicyclic hydrocarbons, studies of terpene compounds, and the discovery (together with L.Ya. Bryusova) of the camphene rearrangement of the second type (Nametkin's rearrangement; see Section 4.2), which made it possible to explain mechanisms of many transformations in the chemistry of terpenes.

Sergei Semenovich Nametkin (1876–1950) graduated from the Faculty of Physics and Mathematics of the Moscow University in 1902. The places of his future work were the Second Moscow State University (1918–1924, professor, dean, rector), State Research Petroleum Institute at the Supreme Soviet of the National



Economy (1924-1934), Mining Academy (1927-1930), and Moscow Institute of Fine Chemical Technology (1930–1938). Since 1938, he was professor of the Moscow State University, and since 1939, director of the Institute of Petroleum of the Academy of Sciences of the USSR. He studied catalytic hydropolymerization of unsaturated hydrocarbons, developed methods for determination of unsaturated hydrocarbons in petrochemicals, methods of oil desulfurization, a number of petrochemical synthesis methods, including direct oxidation of hydrocarbons to alcohols and aldehydes. He also carried out research in the field of synthesis of detergents, fragrances, and plant growth stimulants. Since 1927, he was the first in Russia to read a systematic course of petroleum chemistry. He lectured for several years on organic chemistry for students of biology and geology and later on the chemistry of alicyclic compounds and essential oils for chemists at the Moscow University. S.S. Nametkin showed an active interest in the history of chemical science; he was the author of articles devoted to the life and work of D.I. Mendeleev, A.M. Butlerov, N.D. Zelinskii, L.A. Chugaev, N.M. Kischner, and V.E. Tishchenko. Doctor of chemical sciences B.A. Krentsel' remembered S.S. Nametkin: "I had to see and hear a

lot of big scientists, but the chemical erudition of S.S. Nametkin, perhaps, did not know equal. Nevertheless, during the years of our joint work, I have never heard from him any references to scientific superiority, experience, and authority. Respect for the opponent, the spirit of tolerance and freedom of scientific thought, and friendly attention to the comrade are those traits of his character and his appearance that remained in my memory forever as a model, which I want to imitate" [158].

Under the guidance of S.S. Nametkin, the Department of Organic Chemistry began a series of works on the synthesis of fragrant substances and plant growth stimulants. In view of production requests, an organic analysis laboratory was founded in 1938 at the Research Institute of Chemistry of the Moscow State University, where a special practicum was carried out and organic analyses were performed under contracts with enterprises.

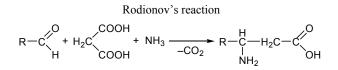
In the autumn of 1941, because of the Great Patriotic War, a part of teachers, researchers, and students of the Department of Organic Chemistry was evacuated to Tashkent and then to Ashgabat (later some professors moved to Sverdlovsk). The head of the Ashgabat group was Prof. Aleksandr Petrovich Terent'ev. In 1942–1944, **Vladimir Mikhailovich Rodionov** (1878–1954), the discoverer of Rodionov's



reaction, was invited to manage the remaining part of the department in Moscow; he was known for his work on the chemistry of amino acids, dyes, alkaloids, vitamins, fragrances, and physiologically active substances. V.M. Rodionov was corresponding member of the Academy of

Sciences of the USSR and one of the organizers of the aniline-dye and pharmaceutical industry in our country (for more details, see Section 4.4). During the war, the department of organic chemistry produced saccharin and medicinal preparations (sulfidine, diphenylisopropyl alcohol, etc.), and works were carried out to determine the octane number of aviation gasoline. During the war, the Moscow group continued to conduct training sessions.

By the end of 1943, the evacuated staff of the department returned to Moscow, and the department



was again headed by S.S. Nametkin. In the beginning of 1944, the Department of Special Organic Synthesis and Analysis separated from the Department of Organic Chemistry and was headed by S.S. Nametkin; A.N. Nesmeyanov headed the Department of Organic Chemistry and soon became the dean of the Faculty of Chemistry.

4.1.7. Department of Organic Chemistry of the Moscow University in 1944–1978 (headed by Academician Aleksandr Nikolaevich Nesmeyanov). Aleksandr Nikolaevich Nesmeyanov (1899–1980)

graduated in 1922 from the Natural Department of the Faculty of Physics and Mathematics of the Moscow University, specializing in physical chemistry. At the suggestion of N.D. Zelinskii, he was left at the university to prepare for professorship. From that moment his whole life was connected with the Moscow



University. In 1924 he became an assistant, in 1930 he received the title of associate professor, and in 1934, doctor of chemical sciences and professor. In 1939 he was elected corresponding member, and in 1943, full member of the Academy of Sciences of the USSR. In 1944, A.N. Nesmeyanov headed the Department of Organic Chemistry at the Faculty of Chemistry of the Moscow State University, in 1945–1948 he was dean of the Faculty of Chemistry, and in 1948 he became rector of the university. In 1951–1961 A.N. Nesmeyanov was President of the Academy of Sciences of the USSR.

Immediately after returning from the evacuation, the department included four laboratories: organic synthesis headed by Yu.K. Yur'ev (after 1945, by R.Ya. Levina), chemistry of organoelement compounds (K.A. Kocheshkov, later A.N. Nesmeyanov), chemistry of proteins (N.I. Gavrilov), and lecture demonstration (N.K. Kochetkov), as well as a student practicum on organic chemistry. In 1950, a laboratory of antibiotics (headed by N.D. Zelinskii with A.B. Silaev and A.P. Terent'ev as deputies) was founded at the department.

In the post-war period, the Department of Organic Chemistry conducted large-scale chemical studies on the development of new methods of synthesis of acetylene, ethylene, paraffin, and cycloparaffin hydrocarbons, oxygen-containing heterocycles, and derivatives of antibiotics. Academician A.N. Nesmeyanov and K.A. Kocheshkov began research in the field of



A.N. Nesmeyanov (on the right) at the construction site of new buildings of the Moscow State University (autumn 1950).

organoelement compounds (derivatives of tin, mercury, gold, magnesium, phosphorus, arsenic, etc.), which then developed into a special field of organic chemistry. Since 1952, a new field of research has been developed, chemistry of sandwich compounds of transition metals, in particular, ferrocene derivatives. In 1960–1970, together with the Institute of Organoelement Compounds of the Academy of Sciences of the USSR, possibilities of creating synthetic food products were studied.

Despite the enormous workload on the leadership of the Moscow University, Academy of Sciences, and Institute of Organic Chemistry (1939–1954), A.N. Nesmeyanov himself was very intensively engaged in scientific research. His works in the field of a new chemical discipline, chemistry of organoelement compounds, brought him world fame and recognition; A.N. Nesmeyanov is one of the creators of the chemistry of organoelement compounds.<sup>30</sup>

Scientific interests of A.N. Nesmeyanov included the development of synthetic methods and study of the properties of organic compounds of non-transition and transition metals, organic synthesis (synthetic methods based on the transformations of  $\beta$ -chlorovinyl ketones [161], synthetic chemistry of polyhalogen derivatives, etc.), theoretical organic chemistry (tautomerism and dual reactivity), ways of synthesis of artificial food from the simplest and accessible substances (carbohydrates, nitro compounds, aldehydes), amino acids and protein products, and imitators of smells and taste of food products [162–165] (see also Section 4.4).

A.N. Nesmeyanov was one of the authors and editors (jointly with K.A. Kocheshkov) of serial publications "Synthetic Methods in the Field of Organometallic Compounds" (1945–1950) and "Methods of Organoelement Chemistry" (1963–1976). In spite of his enormous organizational work, A.N. Nesmeyanov for many years read a course of lectures on organic chemistry at the Faculty of Chemistry, which gathered all scientific Moscow.<sup>31</sup>

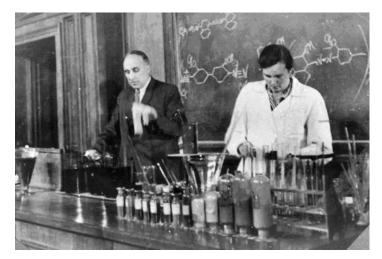
In 1953–1954, a complex of new buildings of the Moscow State University was built on the Leninskie Gory, one of which was occupied by the Faculty of Chemistry. It is the name of Nesmeyanov, with which organization of the new construction of the Moscow University is connected. "As soon as I became a rector, I immediately started talking about the construction, but at this time not only of the Faculty of Chemistry

<sup>&</sup>lt;sup>30</sup> From the memoirs of Professor Yu.A. Ustynyuk: "The ability to catch a new idea, assess its capabilities, and immediately join was cultivated by A.N. Nesmeyanov. Yu.G. Bundel once said: "He (Nesmeyanov) is like a thoroughbred dog that smells the hot blood and rushes along the hot trail." I have always admired the ability of him and I.P. Beletskaya to generate and recognize such ideas. In my opinion, it was this orientation toward the cutting edge of world science that made the department headed by A.N. Nesmeyanov the center of scientific thought in the country."

<sup>&</sup>lt;sup>31</sup>From the memoirs of Prof. Yu.A. Ustynyuk: "In the Southern Chemical Auditorium, the first rows were usually filled with venerable scientists who came to the lecture long before it began. The auditorium has always been crowded. The manner of reading of A.N. Nesmeyanov conquered and fascinated listeners at once. He never resorted to spectacular poses and techniques. He spoke very clearly, calmly, and not very loudly, as though thinking out loud, never used any notes or abstracts, clearly and accurately drew complex formulas and reaction equations on the board. The students were given the impression that the lecturer's knowledge and thoughts were born in his head before their eyes. They themselves, as it were, became complicit in this creative process. Impeccable logic, interesting examples, beautiful experiments ... A whole galaxy of brilliant professors was brought up at these lectures. In a conversation with me, his lecture assistant, Aleksandr Nikolaevich somehow explained: "Of course, I know my subject in details, and my memory is not bad. But I still worry about every lecture. Yes, I'm worried, like an artist who goes on stage. There is nothing more honorable, more beautiful, and more complex than this meeting with the audience filled with those who will replace us in science. How many shining eyes! I should not deceive them. You say that the best satisfaction is given to you by a well-conducted study. Yes, I understand you well. But think, let you get an important result and publish an article in a prestigious journal. At best, it will be read by four dozen colleagues, but only a dozen will refer to it in their publications. But two or three years will pass, and they will simply forget about it. If you read a good course of lectures, then hundreds of your students will remember these lectures for the rest of their lives, and even tell their children about them. How not to worry here !?"



A part of the staff of the Department of Organic Chemistry (1967).



A.N. Nesmeyanov reads a lecture on organic chemistry at the Faculty of Chemistry (on the right: lecture assistant T.P. Tolstaya).

but of the entire Moscow State University. Yu.A. Zhdanov said that he will find out how things are going and give me a signal at the right time. This moment came very soon. Yurii Andreevich told me that a decision was made to build several high-rise buildings in Moscow and that I should (I do not know whether he received this instruction from I.V. Stalin or A.A. Zhdanov) to request one of such buildings for the needs of the Moscow State University. Then we began to write a letter to Stalin. Proceeding from the estimates I made with M.A. Prokofiev (associate professor of the chemical faculty, secretary of the party committee of the Moscow State University) of the necessary areas for the Faculty of Chemistry and "on aggregate indicators" and proportionally increasing the cubature, it was easy to tentatively determine the needs of the Moscow State University. Since the figures turned out to be quite impressive, we decided not to

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

calculate them for a while for the humanitarian faculties of the Moscow State University, since the buildings left on the Mokhovaya street would have been abundant enough for this. The huge number (1600000 m<sup>3</sup>) thus obtained was included in a short note-request addressed to Stalin with roughly the following content: please draw the construction of one of the high-rise buildings for the needs of the Moscow State University. The demand is 1600000 m<sup>3</sup>" [166]. A.N. Nesmeyanov personally engaged in the interior design of new laboratories. On his initiative, one of the rooms in the Institute of Organic Chemistry of the Academy of Sciences of the USSR was equipped as a pattern of the future laboratories of the Faculty of Chemistry of the Moscow State University. Fume hoods without middle racks and a new model of chemical workbench were designed. Nesmeyanov tried them many times and asked his staff whether the

height of the table and stools and the location of sanitary ware were convenient.

After moving to the new buildings, the Department of Special Organic Synthesis, which was headed by A.P. Terent'ev after the death of S.S. Nametkin in 1950, was transformed into a laboratory of special organic synthesis at the Department of Organic Chemistry. The main direction of the research in this laboratory was synthesis and study of optically active and inner-complex compounds. In 1957, the laboratory of theoretical problems of organic chemistry was created and headed by O.A. Reutov.

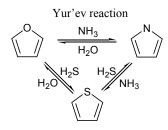
At the end of 1965, the Department of Chemistry of Natural Compounds was founded on the basis of the Laboratory of Protein Chemistry of the Department of Organic Chemistry. The first head of the department was Corresponding Member of the Academy of Sciences of the USSR M.A. Prokof'ev, an outstanding scientist and statesman and Minister of Education of the USSR in 1966–1984.

In the post-war years, many outstanding scientists and teachers worked at the department, in particular Yu.K. Yur'ev, R.Ya. Levina, N.A. Kochetkov, A.P. Terent'ev, A.N. Kost, I.F. Lutsenko, and many others.



**Yurii Konstantinovich Yur'ev** (1896–1965) known for his work on mutual catalytic transformations of five-membered heterocycles (the Yur'ev reaction) [167] was the first head of the laboratory of the chemistry of heterocyclic compounds. Yu.K. Yur'ev began to read for the

first time at the department a special course "Chemistry of heterocyclic compounds," as well as the original general course "Synthetic methods of organic chemistry," which, according to the program he compiled, was later read in a number of other higher educational institutions of the country. Yu.K. Yur'ev and co-workers wrote the textbook "Practical works on organic chemistry" and developed a program of an extensive practicum on organic chemistry, which for



many years became a model for all chemical faculties at higher school.

**Roza Yakovlevna Levina** (1900–1970) and her colleagues developed methods for the synthesis of various difficultly accessible hydrocarbons and discovered the acetylene–diene rearrangement, as well as opening of cyclopropanes under the action of mercury salts [168]. She was a student of N.D. Zelinskii and one of the first postgraduate students of the Faculty of Chemistry. In 1943–1970, she headed the laboratory of organic synthesis. In 1941–1943, she was evacuated in Sverdlovsk (now Yekaterinburg), where she lectured on organic chemistry and founded the Ural school of chemistry of hydrocarbons. R.Ya. Levina read the special courses "Selected chapters of organic chemistry" and "Methods of organic synthesis" at the department.

Cyclopropane ring opening by the action of mercury salt

$$\begin{array}{c} \searrow \overset{CH_{3}}{\longleftarrow} + \text{Hg(OAc)}_{2} \xrightarrow{\text{THF}-H_{2}O} \xrightarrow{H_{3}C} \overset{CH_{3}}{\xrightarrow{I}} H_{3}C \xrightarrow{CH_{2}} \overset{CH_{3}}{\xrightarrow{I}} H_{2}CH_{2}HgOAc \xrightarrow{I} H_{3}C \xrightarrow{I} H$$

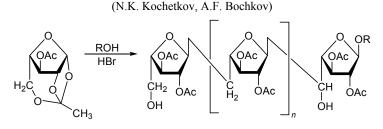
Nikolai Konstantinovich Kochetkov (1915–2005), a graduate of the Moscow Institute of Fine Chemical Technology (see Section 4.2), assistant since 1945, associate professor since 1951,

and professor of the Department of Organic Chemistry of the Faculty of Chemistry of the Moscow State University since 1955. From 1959 to 1966 he was deputy director and head of a laboratory of the Institute of Chemistry of Natural Compounds of the Academy of Sciences of the



USSR, from 1966 to 1988, director of Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR, and since 1988, honorary director of the institute and scientific leader of the Laboratory of Carbohydrate Chemistry. He developed the chemistry of  $\beta$ -chlorovinyl ketones, and since the mid-1950s he began to perform extensive research on the carbohydrate chemistry. N.K. Kochetkov discovered natural oligosides and developed methods for their isolation and structure determination [169]. In the late 1950s and early 1960s, he developed and studied methods for the synthesis of monosaccharides and their derivatives, deoxy sugars, higher sugars, keto deoxy aldonic acids, amino sugars, glycosides, and glycopeptides [170]. He developed a method for the extension of the carbon chain of monosaccharides by two bonds, as well as new methods for creating

Synthesis of polysaccharides by polycondensation of ortho esters



glycoside bonds, in particular, the orthoester method (1965) and cyanoethylidene condensation (1976). N.K. Kochetkov proposed methods for the synthesis of antitubercular, anticonvulsant, and antiallergic drugs (cycloserine, beclamide, mebhydrolin, etc.) and of a number of antibiotics (in the 1990s). N.K. Kochetkov took part in the development of physicochemical methods for structural analysis of complex carbohydrates (mass spectrometry, NMR spectroscopy with computer-assisted analysis of the spectra); he developed approaches to the preparation of artificial antigens used as diagnostic means. In 1958-1959 he was the first in the Moscow State University to create an original course on the chemistry of nucleic acids and wrote (with co-authors) the first textbook on the chemistry of nucleic acids [171]. In the early 2000s, N.K. Kochetkov was one of the most cited chemists in our country.

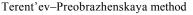
Aleksandr Petrovich Terent'ev (1891–1970), corresponding member of the Academy of Sciences of

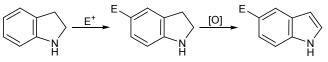


the USSR since 1953, in 1941–1942 headed the Department of Organic Chemistry in Ashgabat, and in 1950– 1953 was head of the Department of Special Organic Synthesis and Analysis at the Faculty of Chemistry. He created a new method for the sulfonation of acidophobic com-

pounds with sulfur trioxide complexes (State Prize, 1948) [172]. At the Department of Organic Chemistry he read the courses "Analysis and study of organic compounds," "Structural theory of organic compounds," "Stereochemistry," "Chemical literature and its use," and "Organic Chemistry." He wrote (in co-authorship with B.A. Pavlov) the textbooks "The course of organic chemistry," which survived eight editions (the first in 1958 [173]) and was translated into foreign languages, "Organic analysis" [174] published in the USA, etc. The scientific activity of **M.N. Preobrazhenskaya**, who later became director of the Gauze Institute of Antibiotics, began under the leadership of A.P. Terent'ev. M.N. Preobrazhenskaya

and A.P. Terent'ev developed the indole-indoline method of electrophilic substitution in the benzene ring of indoles, which went down in the history heterocyclic chemistry as the Terent'ev-Preobrazhenskaya method.





Sulfonation of five-membered heterocycles with sulfur trioxide-pyridine complex

 $\begin{array}{c} & \overbrace{} \\ & & \overbrace{} \\ & & \\ \\ & & \\ \\ & X = O, NR, S. \end{array}$ 

Ivan Fomich Lutsenko (1912–1993) graduated with honors from the Faculty of Chemistry in 1937,

and in 1937–1940 he studied in the postgraduate school, which he successfully finished in 1940 by defending his candidate's dissertation on organomercury compounds. Since 1940 he was an assistant at the Faculty of Chemistry. From June 1941 to 1945, he fought on the fronts of the Great Patriotic War and ended the war in the rank of major.



In 1945 he returned to the Department of Organic Chemistry and passed the way from assistant to professor and deputy director of the Research Institute of Chemistry. In 1962–1969 he was dean of the Faculty of Chemistry. The fields of scientific interests of I.F. Lutsenko were chemistry of organoelement compounds and dual reactivity problems. Together with his students he discovered elementotropic tautomerism in the series of organogermanium and organotin compounds. I.F. Lutsenko is the founder of the organophosphorus school at the Moscow State University; under his leadership, the chemistry of functionally substituted derivatives of three- and four-coordinate phosphorus acid has been developed [175–177].



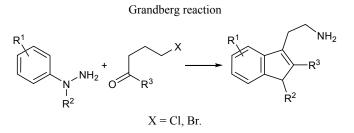
Staff of the laboratory of organophosphorus compounds. In the middle: head of the laboratory, dean of the Faculty of Chemistry of the Moscow State University I.F. Lutsenko (October 1967).



Professor Aleksei Nikolaevich Kost (1915–1979), a student of A.P. Terent'ev and veteran of the Great Patriotic War, in 1969 headed the laboratory of chemistry of nitrogenous bases founded by him at the Faculty of Chemistry of the Moscow State University. He developed (with

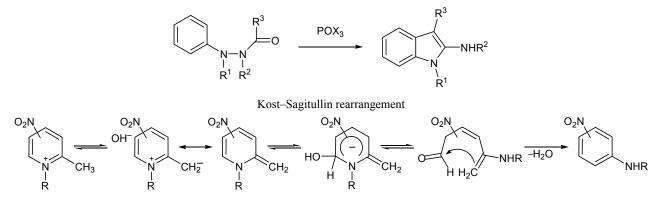
co-authors) convenient methods for the preparation of a number of derivatives of fatty and aromatic amines and heterocyclic nitrogen bases [178], methods of electrophilic substitution in the indole series, and methods of synthesis of fused heterocyclic systems [179]. In 1975 he discovered a new method for the preparation of amines of the indole series by cyclization of acylhydrazines (the Kost reaction [180]), and (together with R.S. Sagitullin) isomerization recyclization of nitrogenous heteroaromatic compounds (Kost– Sagitullin rearrangement). This rearrangement is registered in the state register as discovery no. 205 (see also Section 14). A.N. Kost was editor of the Russian translation of the third edition of Becker's "Organikum. Organisch-chemisches Grundpraktikum" [181].

One of the most talented students of A.N. Kost was Prof. **Igor' Ioganovich Grandberg** (1930–2011) who since 1995 (for 30 years) led the Department of Organic Chemistry in the Timiryazev Agricultural Academy. He discovered the original method for the synthesis of tryptamines (Grandberg reaction) from arylhydrazines and  $\omega$ -halocarbonyl compounds [182].



**P.B. Terent'ev** (1930–2014), a companion of A.N. Kost, created for the first time a group of organic mass spectrometry at the department.

Kost reaction



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017



I.P. Beletskaya. Defense of doctoral dissertation.

Irina Petrovna Beletskaya graduated from the Faculty of Chemistry of the Moscow State University in 1955. Doctor of Chemical Sciences (1963), professor of the Department of Organic Chemistry, corresponding member of the Academy of Sciences of the USSR (since 1974), full member of the Russian Academy of Sciences (since 1992). He is in charge of the Laboratory of Organoelement Compounds of the Department of Organic Chemistry. Fields of scientific interests of I.P. Beletskaya include organic synthesis with organometallic compounds as reagents and catalysts, organic chemistry of early transition metals and lanthanides, carbanion chemistry, and mechanisms of organometallic reactions. Early research refers to physical organic chemistry. In 1960-1966, she studied electrophilic and radical substitution reactions at a saturated carbon atom and mechanisms of nucleophilic aromatic substitution, formulated S<sub>E</sub>1/S<sub>E</sub>2 mechanisms, and carried out fundamental research on the chemistry of carbanions, ambident ions, and their ion pairs [183-185]. I.P. Beletskaya developed methods of synthesis of new classes of organic lanthanide compounds and showed the possibility of their widespread use in organic synthesis and catalysis [186]. Current research is devoted to metal-complex catalysis of the formation of carbon-metal and carbon-element bonds [187-189], nanocatalysis [190], and catalysis by copper salts and complexes [191, 192].

Many outstanding scientists graduated from the Department of Organic Chemistry in this period, namely Academician G.B. Elyakov (1952), founder and director (1964–2001) of the Pacific Institute of Bioorganic Chemistry in Vladivostok, Prof. M.N. Preobrazhenskaya (1954), director of the Gauze Research Institute of New Antibiotics (2003–2007), Academician V.A. Tartakovskii (1955), director of the Zelinskii Institute of Organic Chemistry (1988– 2002), Academician Yu.N. Bubnov (1957), director of the Nesmeyanov Institute of Organoelement Compounds (1996–2013), Academician M.P. Egorov (1976), director of the Zelinskii Institute of Organic Chemistry since 2003, Academician N.S. Zefirov (1958), head of the Department of Organic Chemistry of the Moscow State University (1994–2014) and director of the Institute of Physiologically Active Compounds of the Russian Academy of Sciences (1989–2006), and Prof. K.Yu. Novitskii who was for many years director of the Scientific Research Chemical and Pharmaceutical Institute.

4.1.8. Department of Organic Chemistry in 1978–1994 (headed by Academician O.A. Reutov). From 1978 to 1994, the Department of Organic Chemistry was headed by Academician Oleg Aleksandrovich Reutov. During his leadership at the department, research was conducted on the mechanisms of nucleophilic and electrophilic substitution reactions at a carbon atom in various valence states, and various types of rearrangements and tautomeric transformations were studied. O.A. Reutov and his coworkers began for the first time an extensive study of the mechanisms of reactions of organometallic compounds with the use of the most modern methods and concepts of physical chemistry.

**Oleg Aleksandrovich Reutov** (1920–1998) enrolled in the Faculty of Chemistry of the Moscow State University in 1937; in 1941, after the fourth year, he volunteered for the front. He finished the Great Patriotic War in the rank of major in the position of deputy chief of the chemical department of the 4th Ukrainian



Front for operational investigation. After demobilization, he returned to the Faculty of Chemistry of the Moscow State University, where he worked as an assistant, and then assistant professor and professor of the Department of Organic Chemistry. In 1957 O.A. Reutov founded and headed a laboratory of theoretical problems of organic chemistry in the Moscow State University, which later became a laboratory of physical organic chemistry. He headed the laboratory until 1988. Since 1978, he was head of the Department of Organic Chemistry.<sup>32</sup>

<sup>&</sup>lt;sup>32</sup> For a while O.A. Reutov studied in graduate school in philosophy at the future academician of the Academy of Sciences of the USSR B.M. Kedrov. Reutov considered the study of philosophy to be extremely useful for a natural scientist, and a deep acquaintance with dialectics is necessary. In his view, the years spent studying philosophy paid a hundredfold to him later in carrying out scientific research.



O.A. Reutov and employees of the Department of Organic Chemistry (1980s).

Being a disciple of A.N. Nesmeyanov, O.A. Reutov began his scientific path from the study and development of the diazo method proposed by A.N. Nesmeyanov for the synthesis of various organometallic compounds and extended it to the synthesis of organic derivatives of mercury, arsenic, antimony, and bismuth. The main scientific works of O.A. Reutov were connected with physical organic and organometallic chemistry, molecular rearrangements, CH acidity, stereochemistry, and mechanism of hydroxymercuration. For many years, one of the most significant series of studies performed by O.A. Reutov, which also involved many employees of his laboratory, was research on the mechanism of electrophilic substitution at a saturated carbon atom [193, 194].

In 1950–1960, together with his colleagues, O.A. Reutov developed more than 30 new methods for the synthesis of organometallic compounds, established the mechanisms of the most important syntheses of organometallic substances through diazo compounds, discovered new types of isotope exchange reactions of covalently bonded organometallic compounds, and discovered and investigated the phenomenon of nucleophilic catalysis in electrophilic substitution.

Together with Academician A.N. Nesmeyanov, O.A. Reutov read the general course of organic chemistry for students of the Faculty of Chemistry (1948– 1970). An important role in the teaching of chemistry at the Faculty of Chemistry was played by the course of theoretical foundations of organic chemistry he had created which he had been reading for more than 30 years.<sup>33</sup> O.A. Reutov wrote the books "Theoretical Problems of Organic Chemistry" (1956, the first Russian textbook on this topic) and "Theoretical Foundations of Organic Chemistry" (1964). He was the founder of a large scientific school (15 of his students became professors and doctors of sciences). "All those who worked with Oleg Aleksandrovich mark his unique ability to lead the work and the very style of this leadership. He did not restrict anyone, did not impose his opinion, did not command, but he was able to direct young scientists," T. Voitovich noted in an article devoted to O.A. Reutov [195].

During this period, outstanding scientists and teachers worked at the department: A.N. Kost, V.M. Potapov, E.G. Perevalova, Yu.K. Shabarov, Yu.G. Bundel', Yu.A. Ustynyuk, A.L. Kurts, K.P. Butin, N.N. Magdessieva, T.A. Smolina, V.A. Sazonova (she supervised a large series of works on the chemistry of ferrocene and cymantrene), N.S. Shusherina, L.A. Kazitsyna (together with N.B. Kupletskaya, the author of the textbook "Application of IR, UV, and NMR Spectroscopy in Organic Chemistry" [196], which has grown more than one generation of chemistry students at the Moscow State University and many others). **M.A. Volodina** headed the laboratory of organic analysis.

<sup>&</sup>lt;sup>33</sup> O.A. Reutov specially took lessons in speech technique at the House of Scientists from the artists of the Maly Theater. The lessons were not in vain for the academician: he lectured without a microphone in a large auditorium of the Faculty of Chemistry, while his diction remained clear.



**Viktor Mikhailovich Potapov** (1917–1988). In 1970–1988, V.M. Potapov was head of the laboratory of special organic synthesis, he used for the first time in the country the spectropolarimetric method in organic chemistry, and for many years he read the original

courses "Stereochemistry" and "Chemical Information" at the Faculty of Chemistry. V.M. Potapov wrote the textbook "Stereochemistry" [197], which was reprinted several times, and the popular reference book "Chemical Information. Where and How to Find Necessary Information for a Chemist" [198].



Emiliya Georgievna Perevalova (1922–2012) in 1945 graduated with honors from the Faculty of Chemistry of the Moscow State University, in 1948 she defended her candidate's dissertation "Study of some compounds of the triphenylmethane series" under the leadership of A.N. Nesmeyanov, and in 1962, doctoral dissertation on the chem-

istry of ferrocene. After the death of A.N. Nesmeyanov in 1980, she headed the laboratory of organometallic compounds and remained head of the laboratory for many years. E.G. Perevalova is author of more than 200 publications on organometallic compounds. She developed a special course on the chemistry of organometallic compounds for senior students.



Yurii Aleksandrovich Ustynyuk graduated with honors from the chemical faculty of the Moscow State University in 1958. In 1962 he defended his candidate's dissertation under the guidance of A.N. Nesmeyanov, and in 1974, doctoral dissertation. In 1968, he organized

a nuclear magnetic resonance laboratory at the Faculty of Chemistry of the Moscow State University, which he headed until 2012. He read lectures on NMR spectroscopy, physical methods of studying the structure of organic molecules, and chemistry of organoelement compounds at the Faculty of Chemistry of the Moscow State University, Higher Chemical College of the Russian Academy of Sciences, and Faculty of Chemistry of the Peoples' Friendship University of Russia. Yu.A. Ustynyuk is author of the currently published book series "Lectures on Organic Chemistry" [199]. The range of his scientific interests includes such areas as NMR spectroscopy, quantum chemistry, catalysis, chemistry of organometallic compounds, and supramolecular chemistry. He proved the generality of metallotropic rearrangements of organometallic compounds (1968–1978) [200], discovered a new type of metallotropy (1976–1996) [201], and developed basic principles of <sup>199</sup>Hg NMR spectroscopy (1988–1996) [202].

Yurii Sergeevich Shabarov (1919–2005), Honored Professor of the Moscow State University and brilliant lecturer who read for 25 years! (1968-1993) the general course of organic chemistry to students of the Faculty of Chemistry (this is the rarest case in the history of the faculty). He is author of a two-volume textbook on organic chemistry [203], manuals "Practical works on organic chemistry," "Laboratory works in organic practicum," "Mono- and disaccharides," and "Tasks and exercises in organic chemistry." The last book was written in co-authorship with other lecturers of the Department of Organic Chemistry and was translated into English and Spanish and used in educational institutions of several countries. Yu.S. Shabarov's research work was related to the chemistry of small carbocycles, and he was the founder of the chemistry of arylated cyclopropanes in Russia. Yu.S. Shabarov discovered the unique properties of a small carbocycle linked to an aromatic nucleus (ortho effect of cyclopropane in nitration, ipso attack of an electrophile on the position occupied by cyclopropyl radical, the ability to initiate intramolecular rearrangements and transformations) [204].

Prof. V.R. Skvarchenko (a student of R.Ya. Levina), who was known for her work in the field of triptycene chemistry, fruitfully worked for many years in Yu.S. Shabarov's laboratory [205]. V.R. Skvarchenko, together with R.Ya. Levina and Yu.S. Shabarov, published a number of methodological manuals on organic chemistry. She read a special course "Selected chapters of organic synthesis" for 20 years.

Yurii Glebovich Bundel' (1929– 2001) graduated from the Faculty of Chemistry of the Moscow State University in 1952; he headed the laboratory of biologically active organic compounds. Yu.G. Bundel', together with the laboratory staff, discovered new types of carbocation



rearrangements, studied their stereochemistry, formulated multiple migration patterns. He discovered the phenomenon of reaction center transfer under the action of electrophiles on benzyl derivatives of metals, a new method for synthesizing benzyl derivatives of mercury and tin, a fundamentally new method for the synthesis of indole derivatives via recyclization, as well as the formation of donor–acceptor complexes in the reaction of halogens with a metal–carbon bond.

Professor Aleksandr Leonidovich Kurts (1937–2003), a graduate of the Mendeleev Moscow Institute



of Chemical Technology, defended the candidate and doctoral dissertations at the Department of Organic Chemistry of the Moscow State University under the guidance of I.P. Beletskaya. He read for many years the general course of organic chemistry for third-year students of the Faculty of Chemistry of the

Moscow State University. The revised program of this training course is now accepted as a base for chemistry students in Russian universities. He is the author of two scientific monographs (including co-authorship with O.A. Reutov and I.P. Beletskaya in "Ambident Anions" published by Consultants Bureau in 1983), a four-volume textbook on organic chemistry (co-authored with O.A. Reutov and K.P. Butin and repeatedly republished) which is now the basis for teaching the general course of organic chemistry at the Faculty of Chemistry, and the problem book "Problems in Organic Chemistry with Solutions" [206]. Research interests of A.L. Kurts were related to the chemistry of ambident anions and dual reactivity [207].

**Kim Petrovich Butin** (1936–2005), a graduate of the Mendeleev Moscow Institute of Chemical Technology, finished postgraduate courses at the Moscow State University under the guidance of I.P. Beletskaya and headed a laboratory of theory and mechanisms of organic reactions. For many years, he lectured at the



Research team of Prof. K.P. Butin (1980s).

Department of Organic Chemistry and read the course "Theoretical problems of organic chemistry," advanced course of organic chemistry for postgraduate students, and the course "Theoretical stereochemistry." His scientific interests were related to mechanisms of chemical reactions, metal complexes, organometallic compounds, electrochemistry, and bioorganic chemistry [208]. He discovered "organic calomels" and created an electrochemical acidity scale for very weak CH acids, including methane. Experiments on organic and organoelement electrochemistry, electrochemical modeling of active sites of metalloenzymes, studies of short-lived intermediates, and electrocatalytic activation of small molecules were carried out in K.P. Butin's laboratory [209]. Such topics of common interest as the contribution of sulfur to biology, non-innocent ligands, electron sponges, redox antennas, long-range electron transfer, and conformational polymorphism, were studied in the laboratory [210]. K.P. Butin was co-author of the monograph "CH Acids" and fourvolume textbook "Organic Chemistry" (together with O.A. Reutov and A.L. Kurts).

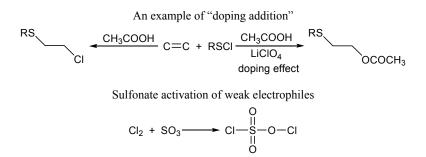
A great role in the preparation of highly skilled organic chemists was played in the 1960–1990s by the glorious galaxy of associate professors A.E. Agronomov, G.A. Golubeva, R.A. Gracheva, V.M. Dem'yanovich, Z.S. Novikova, O.A. Ptitsyna, S.V. Ponomarev (Gryuner), N.K. Sadovaya, T.P. Tolstaya, E.V. Uglova, and V.L. Foss. They brought up not only a large number of students but also the next generation of lecturers who was taught by them while working together in a practical course or attending their master classes.

4.1.9. Organic chemistry at the Faculty of Chemistry of the Moscow State University in 1994– 2014. In these years, the Department of Organic Chemistry was headed by Academician Nikolai Serafimovich Zefirov (1935–2017), a student of Prof. Yu.K. Yur'ev. N.S. Zefirov graduated from the Faculty of Chemistry of the Moscow State University in 1958.

He completed his diploma thesis and candidate's dissertation in the field of furan chemistry under the guidance of Prof. Yu.K. Yur'ev. In 1970– 1971 he trained at Princeton University (USA). Since 1971, he was head of the laboratory of chemistry of heterocyclic compounds, since 1994, head of the Department of Organic

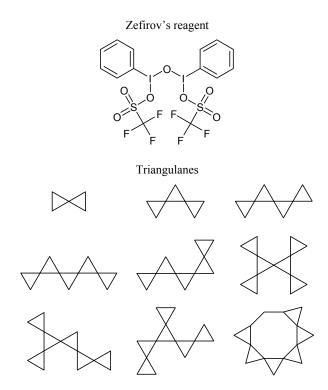


Chemistry, and from 2015 to 2017, head of the Department of Medical Chemistry and Fine Organic



Synthesis created by him. From 1989 to 2001, he was director of the Institute of Physiologically Active Compounds of the Russian Academy of Sciences. N.S. Zefirov initiated establishment of a new specialization, *medicinal chemistry* [211].

The basic research of N.S. Zefirov was related to organic synthesis and theoretical organic chemistry. Together with his colleagues, N.S. Zefirov developed new methods for the synthesis of various previously unknown or difficultly accessible cage and polycyclic hydrocarbons and their derivatives (heteroadamantanes, dihomocubanes, bicyclo[3.3.1]nonanes, tricyclodecanes), various sulfur compounds, crown ethers, etc. He discovered the phenomenon of doping addition, which made it possible to enhance the effective electrophilicity of weak electrophiles [212, 213], as well as a number of new conformational effects ("hockeystick" effect) [214–217]. He introduced the concept of stereocontrol in ion-pair reactions and developed



(jointly with A.S. Koz'min and N.V. Zyk) a method of sulfonate activation of weak electrophiles.

N.S. Zefirov created a number of new reagents for organic synthesis, one of which was named Zefirov's reagent ( $\mu$ -oxobis[(trifluoromethanesulfonato)-(phenyl)iodine]) [218], proposed (together with S.S. Trach) a new formal logical approach to the description of molecular structure and reactions of organic compounds [219], developed general principles for the computer generation of organic structures and reactions, discovered (together with T.S. Kuznetsova's group) a new class of spiro cyclopropane structures (triangulanes), and developed general methods for the synthesis of chain, branched, and cyclosubstituted triangulanes [220].

Within the specialization "medicinal chemistry" N.S. Zefirov was engaged in research on creating ligands for glutamate, melatonin, and other receptors as potential drugs.<sup>34</sup>

During this period, the department conducted educational work on teaching the basic course of organic chemistry at the 7 faculties of the Moscow State University (chemical, biological, soil science, material sciences, geological, bioengineering and bioinformatics, and fundamental physicochemical engineering). Annually, about 40–50 students of the

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

<sup>&</sup>lt;sup>34</sup> From the memoirs of Prof. N.V. Zyk: "It was very interesting to work with him (Zefirov), but also not easy. It was necessary to always be in good shape. It often happened that during the discussion of a scientific problem, this problem was already becoming very clear to Nikolai Serafimovich, and he could not understand why it was not clear to another. He thought quickly, acutely feeling what would be relevant and in demand a few years later. He was quickly ignited with a new task, grasped the very essence of the problem and for 2-3 years came to the world level. After 5-7 years, he could catch fire with a new idea, and then largely lost interest in the previous topic and trusted its further development to students. Stereochemistry, electrophilic agents, cage hydrocarbons, QSAR, mathematical modeling, medicinal chemistry were among scientific interests of Nikolai Serafimovich, which impressed with their diversity. He could insert 1-2 phrases into an article written by colleagues, and they immediately became key to all the work."

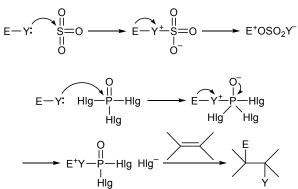
fifth year completed the diploma thesis. In 2009, special courses were taught to students specializing at the department: "Introduction to the Specialty" (Academician N.S. Zefirov), "The Strategy of Organic Synthesis" and "Synthetic Methods of Organic Chemistry" (associate professor V.P. Dyadchenko), "Theoretical Foundations of Organic Chemistry" (Prof. T.V. Magdesieva), "Chemistry of Organoelement Compounds (Prof. D.A. Lemenovskii), "Physicochemical Methods of Analysis of the Structure of Organic Compounds" (Prof. V.S. Petrosyan), "Chemistry of Heterocyclic Compounds" (leading researcher M.A. Yurovskaya), "Medicinal Chemistry" (associate professor O.N. Zefirova), "Methods of Organic Chemistry in the Design of Medicines" (Prof. L.G. Tomilova, associate professors O.N. Zefirova, E.D. Matveeva, and V.M. Dem'yanovich), "Metals in biomolecular chemistry" (Prof. E.R. Milaeva), "Computer Modeling and QSAR" (leading researcher V.A. Palyulin and others).

In 1996, a laboratory of organometallic coordination compounds under the guidance of Prof. D.A. Lemenovskii was organized at the department, where new types of cage organometallic compounds with unusual coordination and valence state of the metal atoms, including those with intracomplex hypervalent interactions (such as additional hypervalent metal-covalently bound ligand and ligandligand interactions) in the coordination sphere of transition, post-transition, and non-transition metals, were studied.

In the 1990s, The chemistry of organic derivatives of silicon, germanium, and tin was studied in the laboratory of physical organic chemistry (until 1957, the laboratory of theoretical problems of organic chemistry) under the guidance of Prof. **Valerii Samsonovich Petrosyan** who headed the laboratory after O.A. Reutov. To date, a large number of hypercoordinate tin compounds exhibiting interesting structural features and unusual reactivity [221] have been described and studied in detail by NMR spectroscopy. From the 1980s to the present, the laboratory also conducts research on ecotoxicology. Much attention was paid to the organization of work of the Open Environmental University at the Moscow State University, founded in 1987 by Prof. V.S. Petrosyan.

A number of new highly reactive electrophilic chlorinating, sulfenylating, aminosulfenylating, selenating, sulfosulfenylating, nitrating and nitrosating agents were discovered under the guidance of Prof. **Nikolai Vasil'evich Zyk**. Original preparative procedures for the synthesis of bifunctional biologically active compounds have been developed [222, 223].

Activation of weak electrophiles with SO3 and POHlg3



After reorganization in the late 1980–1990s, the department included 8 laboratories (laboratory of organic reagents which combined practicums on organic chemistry and research laboratories of organic synthesis, organoelement compounds, physical organic chemistry, biologically active organic compounds, organometallic coordination compounds, bioorgano-element chemistry, and nuclear magnetic resonance).

In the early 2000s, research groups engaged in computer modeling and design of new compounds, as well as in the design and synthesis of antitumor and neuroprotective agents were formed at the department. In 2005, about 190 employees worked at the department, among them 2 full members of the Russian Academy of Sciences, more than 30 doctors of science, and more than 90 candidates of science. In addition, about 50 postgraduate students took part in the research performed therein.<sup>35</sup>

In 2005, a laboratory of supramolecular chemistry and nanotechnology of organic materials was organized at the department under the guidance of corresponding member of the Russian Academy of Sciences **Sergei Panteleimonovich Gromov** who graduated from the Faculty of Chemistry of the Moscow State

<sup>&</sup>lt;sup>35</sup> From the memoirs of Professor I.V. Alabugin: "I can not help mentioning the "Zefirov seminars" held weekly in 1980–1990 for the staff and graduate students of his laboratory. For the first time I got to such a seminar, being a second-year student. One of the elders was making a report on a sophisticated scientific article which at that time was beyond my comprehension. Then N.S. Zefirov stood up, pronounced one phrase, and the meaning of the article became clear and obvious at once. This ability to convey to the listener the most complex idea in simple and understandable words has always fascinated me in Academician Zefirov."

University in 1975. The subject of research at the laboratory was synthesis of organic ligands and tectones for the construction of organic and coordination supramolecular ensembles, study of self-assembly and selforganization in solution, crystal, liquid crystals, and gels, study of photophysical properties and photochemical transformations of supramolecular nanosized systems and organic materials based thereon, photoswitchable molecular devices and photocontrolled molecular machines, and design, synthesis, and use of ligands for radiopharmaceutics, organic electronic devices, and biovisualization.

In 2008, a laboratory of bioorganoelement chemistry was created under the guidance of Prof. Elena Rudol'fovna Milaeva on the basis of the Laboratory of Theory and Mechanisms of Organic Reactions; this laboratory is currently a laboratory of the Department of Medicinal Chemistry and Fine Organic Synthesis of the Faculty of Chemistry. The possibilities of using metal complexes with organic ligands in biology and medicine were studied in this new laboratory.

During the years of perestroika (1990–2000), a number of employees and postgraduate students of the department became professors in prestigious universities in the US and Europe. Among them, V.A. Samoshin (professor of the Pacific University, California), A.G. Kutateladze (currently dean of the University of Denver, USA), T.G. Kutateladze (professor of the Faculty of Pharmacology, Denver University), I.V. Alabugin (professor at the University of Florida), E.E. Nesterov (professor of the University of Louisiana), A.N. Khlobystov (professor of Nottingham University, Great Britain), A. Yudin (University of Toronto, Canada), etc. **4.1.10. Modern period.** Since 2014, the Department of Organic Chemistry is headed by Prof. **Valentin Georgievich Nenajdenko** (born in 1967),

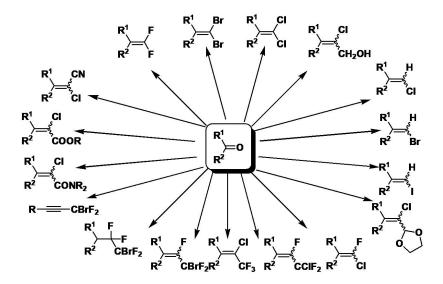
a student of Prof. E.S. Balenkova; fields of his scientific interest are organic synthesis, chemistry of heterocyclic and sulfur- and fluorinecontaining compounds, metal complex catalysis, asymmetric synthesis, and medicinal chemistry. He introduced into the synthetic practice



catalytic olefination, i.e., reaction N-unsubstituted hydrazones with haloalkanes in the presence of CuCl to give substituted alkenes [224–228].

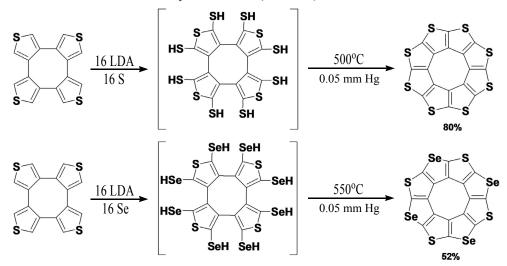
A new class of compounds has been discovered, heterocyclic circulenes [229–231], that are representatives of fused polycyclic thiophenes [232] and are of great interest as materials for electronics. On the basis of fluorine-containing building blocks, effective approaches have been developed that allow the construction of molecules having a fluorine atom or a fluorinecontaining substituent in the strictly prescribed position [233–236]. Another research line developed in V.G. Nenajdenko's laboratory is multicomponent reactions based on isocyanides, which ensure efficient synthesis of peptides and peptidomimetics [237–239].

The department includes 7 laboratories: organoelement compounds (headed by Academician I.P. Beletskaya), organic synthesis (Prof. V.G. Nenajdenko), physical organic chemistry (Prof. V.S. Petrosyan), organometallic coordination compounds (Prof. D.A. Lemenovskii), biologically active organic compounds (Prof. N.V. Zyk), supramolecular chemistry and nanotechnology of organic materials (corresponding



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

Heterocyclic curculenes (sulflowers)



member of the Russian Academy of Sciences S.P. Gromov), physicochemical methods of analysis (Prof. A.T. Lebedev), and organic reagents (Prof. V.I. Terenin). Currently, the department has about 100 employees, including 3 full members of the Russian Academy of Sciences, 25 doctors of science, 59 candidates of science, and about 30 postgraduate students.

Priority directions of the research performed at the department are as follows:

(1) Molecular design of organic structures and reactions, targeted search, synthesis and testing of practically important organic compounds;

(2) Organoelement compounds as reagents and catalysts in the synthesis of organic and organometallic compounds;

(3) Catalysis, surface physicochemistry, supramolecular chemistry, photochemistry;

(4) Modern methods of analysis of organic substances, ecology, and environmental chemistry.

The basis of the educational process at the department is the general course and general practicum on organic chemistry. More than two hundred students of the Faculty of Chemistry and about three hundred students of related faculties (biological, bioengineering and bioinformatics, basic medicine, material sciences) goes through the practicum each semester. In addition, students of special schools, boarding schools, and chemical circles are engaged in the practicum at the department.

Starting from 2015, the school-conference of young scientists in organic chemistry "Markovnikov

Readings" is held annually by the Department of Organic Chemistry in Krasnovidovo village (Moscow oblast). The conference organizes educational minicourses read by world's leading scientists. In addition, its program includes plenary reports of leading scientists of Russia and of the far and near abroad, as well as oral and poster reports of young scientists. In 2017, a commemorative medal of V.V. Markovnikov conference was established to be awarded to Russian and foreign scientists for outstanding achievements in the field of organic chemistry. The first winners were academicians I.P. Beletskaya, B.A. Trofimov, and O.N. Chupakhin.



V.V. Markovnikov's medal.

In October 2015, International Congress "Kost-2015" on the chemistry of heterocyclic compounds, dedicated to the 100th anniversary of the birth of the honored worker of science and technology of the RSFSR, Professor Aleksei Nikolaevich Kost, was held at the Moscow State University by the Department of Organic Chemistry. Between May 29 and June 3, 2016, the Organic Chemistry Department of the Faculty of Chemistry of the Moscow State University and the Department of Chemistry of the North Caucasus Federal University with participation of the Karachaevo-Cherkessk State University successfully held a cluster of conferences on organic chemistry "Dombai-2016" (Dombay Organic Conference Cluster DOCC-2016) (see also Section 14).

## 4.2. History of Organic Chemistry in the Moscow Institute of Fine Chemical Technologies

The history of the Department of Organic Chemistry of the Institute of Fine Chemical Technologies of the Moscow Technological University began with the foundation of the Moscow Higher Women's Courses in 1900 [240]. Although organization of individual departments was not initially intended, the teaching staff of related disciplines was grouped into subject commissions. The Laboratory of Organic Chemistry was founded by Nikolai Dmitrievich Zelinskii (1861-1953), Academician of the Academy of Sciences of the USSR (1929), one of the founders of organic catalysis and petrochemistry and organizers of the Institute of Organic Chemistry of the Academy of Sciences of the USSR. During the 1900/1911 academic year he lectured on organic chemistry for students. In 1910, on the recommendation of Prof. N.D. Zelinskii, Sergei Semenovich Nametkin (1876-1950), a graduate of the Moscow University and an employee of N.D. Zelinskii's laboratory, was invited to the position of senior assistant in the department and the laboratory of organic chemistry of the Moscow Higher Women's Courses (see also Section 4.1). After defending his master's thesis "On the action of nitric acid on saturated hydrocarbons" [241] in 1911, he left the Moscow University as a result of the "Kasso case" and for many years his activity was associated with the Higher Women's Courses. In 1912 he was elected professor of the Faculty of Physics and Mathematics of the Higher Women's Courses and headed the laboratory and the Department of Organic Chemistry until 1938. In 1916 S.S. Nametkin published a scientific monograph "Studies in the field of bicyclic compounds" [242] which was presented to the St. Petersburg University as a doctoral dissertation. After public defense in 1917, he was awarded a doctor degree in chemistry. All 28 years spent by S.S. Nametkin at the head of the laboratory (department) were marked by great scientific successes. Already from 1913, publications of the laboratory, mainly devoted to transformation of saturated bicyclic hydrocarbons, began to appear on a regular basis in the Journal of the Russian Physicochemical Society [243-246]. The research performed in the laboratory (department) significantly

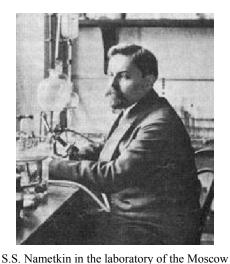
In 1912–1913 S.S. Nametkin read the course "Organic Chemistry" (4 h a week) for students of the 3rd and 4th semesters of the natural science department and the course "Selected Chapters" for students

theoretical and experimental data.

of the 5th and 6th semesters (2 h a week). Practicum was conducted in the 5th to 8th semesters for 4 h a week. In 1914-1915, additional practical classes on organic chemistry were introduced in the 7th and 8th semesters.

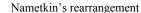
Initially, the staff of the laboratory was formed mainly by students of the Moscow Higher Women's Courses, who wished to remain there at the end of their study and devote themselves to scientific and teaching activities. Some of them should be noted separately.

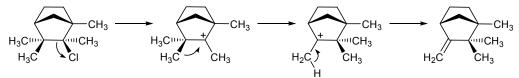
Lidia Yakovlevna Bryusova (1888–1946) enrolled in the History and Philosophy Department of the Moscow Higher Women's Courses. After a year of study, she moved to the natural department, from which she graduated in 1917 with a first-degree diploma in chemistry [247, 248]. Her graduate thesis was experimental study of diazo esters. On the recommendation of S.S. Nametkin and A.N. Reformatskii, L.Ya. Bryusova was left at the courses for research and teaching [248, 249]. She made a great contribution to the chemistry of camphor by discovering (together with S.S. Nametkin) [250, 251] isomerization of terpenoids via migration of one of the geminal methyl groups to the neighboring carbon atom under acid catalysis. This isomerization was called the camphene rearrangement of the second type or Namektin rearrangement and was included into both domestic [252] and world monographs on name reactions [253].



Higher Women's Courses.

enriched the organic chemistry of terpenes with new





In the 1920s and 1930s, L.Ya. Bryusova taught at the Second Moscow State University and the Moscow Institute of Fine Chemical Technology which was created as a result of reorganization of the Chemical and Pharmaceutical Faculty of the former. She read the course "Terpenes." While evaluating the scientific and pedagogical activity of L.Ya. Bryusova, S.S. Nametkin noted in 1931 that "her erudition in the chosen specialty, obtained as a result of persistent and systematic work ... meets the most stringent requirements" [254]. Later, as an assistant to the director of the institute, she performed a great work on the organization of the educational process. In addition to her pedagogical work, L.Ya. Bryusova, being already closely associated with industry, paid much attention and effort to the synthesis of fragrances on the basis of the pyrolysis products of ricinoleic acid ester, synthesis of dihydrojasmone, and synthesis of enanthic acid and heptyl alcohol (used in perfume and other industries) by the Cannizzaro reaction of enanthole [255]. In the period of her work as professor of the Department of Organic Chemistry (mid-1930s) she composed the 5th section "Fragrant substances" in the practicum of Prof. A.M. Berkengeim on synthetic medicinal and fragrant substances, conducted at the related department of fine organic technology [256].

Anna Mikhailovna Khukhrikova (1890–1944) studied at the Courses in 1908–1915 [248, 257]; under the supervision of S.S. Nametkin, she performed a separate work on the structure of camphenylone [258, 259]. Later she worked in the laboratory of organic chemistry under the guidance of S.S. Nametkin, mainly in the field of camphor derivatives [250, 260]. In the 1920s, A.M. Khukhrikova moved to Kiev, where she worked in a medical institute (now Bogomolets National Medical University) and received the title of professor. During the evacuation of the Institute in Chelyabinsk (1941–1944), she headed the Department of General Chemistry [248].

Antonina Sampsonovna Zabrodina (1898–?) studied at the Courses in 1915–1918 [261] and worked with S.S. Nametkin in the laboratory of organic chemistry of the Second Moscow State University in the field of nitration of alicyclic hydrocarbons [262, 263]

and camphor derivatives [264]. In parallel, she worked at the State Research Petroleum Institute, and also as an assistant professor at the Moscow Institute of Steel and Alloys. Since 1938, A.S. Zabrodina moved to work in the Institute of Organic Chemistry of the Academy of Sciences of the USSR [265].

Anna Kuz'minichna Ruzhentseva (1891–?) studied at the mathematical department of the Courses in 1908–1912 [266]. Later, she worked with S.S. Nametkin in his laboratory at the Second Moscow State University, studying chemistry of fenchylene [267] and isofenchone derivatives [268]. In the summer of 1930, she worked in the laboratory of organic analysis with Prof. Hermann Staudinger in Freiburg (Germany). She headed the Department of Organic Chemistry at the Moscow Chemical and Technological Institute of Meat Industry (currently the Moscow State University of Food Production) [269]. Later, she moved to work at the Scientific Research Chemical and Pharmaceutical Institute [270].

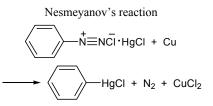
In 1918, the Higher Women's Courses were transformed into the **Second State University**, where the Chemical and Pharmaceutical Faculty was established [271]. The years of civil war and post-war devastation (1919–1922) were hard, and there were not enough reagents, glassware, and fuel. According to M.F. Matveeva (an employee of the department), there was not even hydrochloric acid which "had to be transported from the Dorogomilovskii plant on the red grassy\* ... And there was a time that there was no water and no gas ... So we carried water from the house in sleds and used primus, but L.Ya. Bryusova and A.K. Ruzhentseva did not stop the work (\*the red grassy is a horse whose forage consisted only of grass)" [272].

From 1918 to 1924, S.S. Nametkin held the posts of professor and head of the department of organic chemistry, and in 1919–1924, rector of the university. In addition to the basic course of organic chemistry, S.S. Nametkin conducted special courses on "Stereochemistry," "Chemistry of Camphor and Essential Oils," and "Methodology of Organic Chemistry" [241]. From 1922 to 1929, he was a full-time member of the Scientific Research Institute of Chemistry and professor of the Faculty of Chemistry of the First Moscow State University. The staff of the department remained virtually unchanged: Prof. S.S. Nametkin was head of the department, A.K. Ryzhentsova was senior assistant, private docent, and head of the chemical library, L.Ya. Bryusova was senior assistant, lecture assistant, and supply and maintenance manager, S.I. Sergievskaya was junior assistant and privatedocent, etc. In the late 1920s, S.S. Nametkin organized a department of organic chemistry at the oil department of the Moscow Mining Academy (later the Moscow Petroleum Institute). During this time, several generations of organic chemists, who worked in various institutes not only in the capital but also in other cities of the country, was brought up: A.I. Shavrygin, N.N. Mel'nikov, V.V. Nekrasov, D.N. Kursanov, etc. Thus, S.S. Nametkin's disciple D.N. Kursanov, corresponding member of the Academy of Sciences of the USSR (1953), professor and head of the Department of Organic Chemistry of the Moscow Textile Institute (1935–1953) recalled that with the scarcity of the then equipment and supplies, "Sergei Semenovich persistently taught us to "respect" the test substances and treated their characterization with great rigor. No any constant of a substance left the laboratory without being personally verified by Sergei Semenovich. With the same rigor he checked all the conclusions drawn from the experimental data. Sergei Semenovich demanded from himself and from others that the conclusions were solidly justified and ruthlessly dismissed any hasty conclusions reckoned on spectacular effect" [273].

In 1930, the People's Commissariat of Education decided to unite the chemical departments of all (!) chemical universities in Moscow into one giant Unified Moscow Institute of Chemical Technology. The Second Moscow State University was also among those that "fell under the wheel" of the reform [274]. The non-viability of the Unified Moscow Institute of Chemical Technology became clear already during the first months of its existence, and S.S. Nametkin led a delegation of employees of the institute, who turned to the People's Commissar of Heavy Industry G.K. Ordzhonikidze for help. The People's Commissar helped S.S. Nametkin to retain the Institute of Fine Chemical Technology [273]. In December 1931, a commission consisting of professors, teachers, and staff of the institute (A.N. Reformatskii, S.S. Nametkin, Ya.K. Syrkin, E.V. Rakovskii, A.M. Berkengeim, S.L. Rykov, L.Ya. Bryusova, and others), examined the conditions in which they had to work, and came to

the conclusion that normal functioning of educational institution in such a cumbersome bureaucratic system is impossible [275]. In 1932, the Unified Moscow Institute of Chemical Technology was abolished, and the **Moscow Institute of Fine Chemical Technology** was established on the basis of the Faculty of Chemistry of the Second Moscow State University.

Since 1938, after the departure of S.S. Nametkin to the Moscow State University, with a break in 1946, the Department of Organic Chemistry of the Moscow Institute of Fine Chemical Technology was headed by Aleksandr Nikolaevich Nesmeyanov (1899-1980, see Section 4.1). His students I.F. Lutsenko, V.A. Sazonov, and K.A. Pecherskaya together with their teacher passed from the Moscow State University to the Moscow Institute of Fine Chemical Technology. R.Kh. Freidlina also joined them, leaving the Institute of Organic Chemistry of the Academy of Sciences of the USSR. Together with the lecturers A.I. Shavrygin and A.P. Stukov, they were the whole teaching staff of the department [276]. The diazo method of synthesis of aromatic organomercury compounds developed by A.N. Nesmeyanov [277] entered into practice and was used in many organic laboratories.



From 1941 to 1943, A.N. Nesmeyanov was evacuated in Kazan with the Zelinskii Institute of Organic Chemistry of Academy of Sciences of the USSR headed by him. During his absence (1941-1943), the department was headed by Prof. Aleksei Il'ich Shavrygin (1898-1951), who defended in 1934 his candidate's dissertation on the transformations of tertiary propylbornyl alcohol under the guidance of S.S. Nametkin [278]. A.I. Shavrygin is the author of a number of works on the chemistry of camphor [279, 280]. E.M. Cherkasova, who worked as an assistant at the department after defending her candidate's dissertation in 1939, recalled that during the Great Patriotic War (1941-1945) "classes continued. The department rendered great assistance to the specialty of rubber technology in the synthesis of vulcanization accelerators." In 1942-1943, E.M. Cherkasova was also in evacuation in Chelvabinsk in the position of alternate assistant professor in the evacuated Kiev Medical Institute, while working as head of a department of a research laboratory at the Drugstore Department, where she was engaged in the production of sulfanilamide and sulfidine.

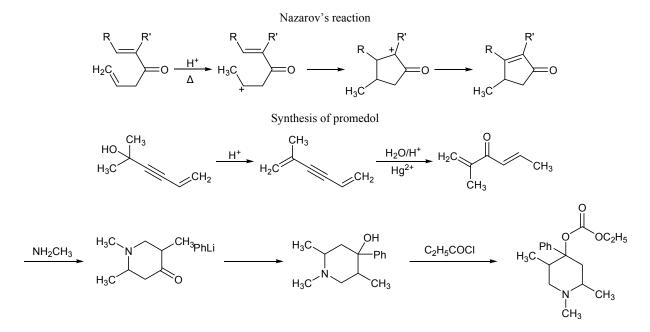
From 1944 to 1947, the department was headed by **Sergei Sergeeveich Medvedev** (1891–1970), a graduate of the Faculty of Physics and Mathematics of the Moscow State University, full member of the Academy of Sciences of the USSR since 1958, known for his works on oxidation mechanisms and polymerization theory.

Ivan Nikolaevich Nazarov (1906-1957), a student of the outstanding Russian organic chemist A.E. Favorskii (Leningrad State University), headed the department from 1948 to 1957 and had a huge influence on the formation of the scientific and pedagogical school at the department. I.N. Nazarov, full member of the Academy of Sciences of the USSR (1953), gained world fame thanks to his works on the chemistry of acetylene and vinylacetylene. He discovered the cyclization of allyl vinyl ketones to cyclopentenones under the action of acids [281, 282], which received the name Nazarov's reaction and entered many domestic [283] and foreign [284, 285] monographs of organic name reactions. In the 1950-1951 academic year, the theoretical course was 350 h long, and a large practicum took 250 h [272]. Under the leadership of I.N. Nazarov, a large research work was carried out in the field of synthesis of heterocyclic compounds by transformations of acetylenic and vinylacetylenic alcohols; graduate and postgraduate students actively participated in this research.

The staff of the Department of Organic Chemistry of the Moscow Institute of Fine Chemical Technology and of the Laboratory of Unsaturated Compounds of the Institute of Organic Chemistry of the Academy of Sciences of the USSR, headed by I.N. Nazarov, developed synthetic routes to a broad spectrum of hormone-related compounds and representatives of the most important classes of natural compounds from major products of basic organic synthesis (acetylene, ketones, etc.). Studies of the addition of nucleophiles to divinyl ketones resulted in the creation and implementation in medical practice of the analgesic promedol (trimeperidine) which has a less pronounced side effect and surpasses the analgesic effect of morphine [286, 287].

After the sudden death of I.N. Nazarov, the department was headed from 1957 to 1964 by **Sergei Vasil'evich Vasil'ev** (1899–1967), a graduate of the Timiryazev Moscow Agricultural Academy [288], author of a series of papers on the action of nitrogen tetroxide on various unsaturated compounds [289–292]. Works started by Academician I.N. Nazarov at the Department of Organic Chemistry were continued by professors B.V. Unkovskii, S.M. Makin, V.B. Mochalin, and E.M. Cherkasova (a student of S.S. Nametkin, who worked at the Institute from 1939 to 1996), who later brought up a galaxy of highly qualified specialists: professors A.I. Kuznetsov, E.Ya. Borisova, A.D. Shutalev, and many others.

From 1968 to 1991, the department was headed by Prof. Boris Vladimirovich Unkovskii (1922–1992),



a graduate of the Moscow Institute of Fine Chemical Technology, Doctor of Chemical Sciences, Honored Worker of Science and Technology of the RSFSR. In 1941, he was called to the front of the Great Patriotic War. After demobilization from the army in 1946 [293], he successfully defended his candidate (under the guidance of I.N. Nazarov) [294] and then doctoral dissertation [295]. During this period, several scientific groups were formed at the department [296].

The group of Professor **Boris Vladimirovich Unkovskii** and Associate Professor Evgenii Trofimovich Golovin, including Yu.F. Malin, L.A. Ignatov, I.P. Boiko, T.D. Sokolov, K.I. Romanov, A.I. Kuznetsov, O.T. Burdelev, A.D. Shutalev, and many others, was engaged in research of five- and six-membered heterocyclic systems, search for new ways of their synthesis, preparation of new compounds, and study of their useful properties [297–300] in active and fruitful cooperation with many research institutions.

The group of Professor **Sergei Mikhailovich Makin** (1929–1993) (O.A. Shavrygina, R.I. Kruglikova, M.I. Berezhnaya, Yu.E. Raifeld, T.P. Kolobova, A.I. Pomogaev, L.A. Kundryutskova, O.V. Kharitonova, E.K. Dobretsova, N.N. Lonina, and others) developed the chemistry of acetals and enol esters in various directions, creating on their basis a whole spectrum of different classes of practically useful substances from cyanine dyes to carotenoids and carbohydrates [301–303]. The cooperation of Prof. S.M. Makin with research institutes and industrial enterprises within the framework of economic contracts led to large-scale implementation of a number of inventions, for example, of unique IR sensitizers for photographic materials [304–305].

The group of Doctor of Chemical Sciences Professor **Elena Mikhailovna Cherkasova** (1907– 1996) (E.Ya. Borisova, S.V. Bogatkov, etc.), who worked at the department from 1939 to 1996, successfully performed syntheses and study of new potential drugs of the amino alcohol, amino ester, and amino amide series [306–308], in particular, of those affecting the cardiovascular system (for example, the patented drug nibentan [309]).

The group of Doctor of Chemical Sciences Professor **Vsevolod Borisovich Mochalin** (1931– 2012), who as early as 1953 started under the guidance of Academician I.N. Nazarov developing new methods for the synthesis of fragrances from acetylenic compounds [310–312], subsequently worked in the field of synthesis and investigation of the reactivity of heterocyclic compounds of the tetrahydropyran series [313, 314] and aziridines [315, 316].

The group of Doctor of Chemical Sciences Professor **Anatolii Ivanovich Kuznetsov** carried out research in the field of cage compounds. The study of the chemistry of azaadamantanes led to the emergence of a new scientific trend related to new heterocyclic systems, azahomoadamantanes [317–320]. The newgeneration disinfectant teotropin was patented [321].

From 1991 to 1992, the department was headed by **Eduard Prokof'evich Serebryakov**, Corresponding Member of the Russian Academy of Sciences, Head of the Laboratory of Low-Molecular Bioregulators of the Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR, who made a great contribution to the teaching and methodological work of the department. It was at this time that foundations of modern academic disciplines, taught at the department at the present time, were laid.

From 1992 to 1997, the department was headed by Doctor of Chemical Sciences, **Professor Vyacheslav Vladimirovich Samoshin** (currently a professor at the Pacific University, USA), who brought a new line, design of macrocyclic compounds, molecular switches, etc., to the research work of the department [322–324].

From 1997 to 2017, the department was headed by associate professor Aleksandr Il'ich Pomogaev and professors Anatolii Ivanovich Kuznetsov, Vitalii Rafailovich Flid, and Anatolii Dmitrievich Shutalev.

Doctor of Chemical Sciences Professor Elena Yakovlevna Borisova, a student of Prof. E.M. Cherkasova and Academicians M.I. Cherkashin and G.A. Tolstikov, at this time successfully supervises works on the creation of a new generation of antiarrhythmics and anesthetics and a new research line in the chemistry of arylaliphatic and heteroaliphatic amino amides. A large series of studies has been carried out on the synthesis, structure, properties, and new applications of polymeric quaternary salts and transition metal complexes with nitrogen- and oxygencontaining ligands was carried out [325–329].

In the best traditions of the department, extremely fruitful are works performed by the group of Doctor of Chemical Sciences Professor **Anatolii Dmitrievich Shutalev**, whose diverse studies are related to the synthesis and reactivity of hydrogenated nitrogen-containing heterocyclic compounds [330–334]. As a result of these studies, general methods for the synthesis of previously inaccessible or unknown classes of compounds, including seven-membered heterocycles and macroheterocycles, have been developed [335–337].

During the history of the department, dozens of hundreds of its graduates and employees have continued their scientific and teaching activities in different cities of the country. Thus, Nikolai Sergeevich Prostakov (1917-2007), a student of A.I. Shavrygin and I.N. Nazarov, for many years (1960-1989) headed the Department of Organic Chemistry of the Peoples' Friendship University of Russia (see Section 4.5). Another postgraduate student of I.N. Nazarov, Stepan Grigor'evich Matsoyan (1923-2010), after defending his candidate's dissertation, worked in the Academy of Sciences of Armenia and from 1967 to 1988 headed the Institute of Organic Chemistry of the Academy of Sciences of the USSR; since 1982, he was Academician of the Academy of Sciences of the Armenian SSR. Leonora Gyulievna Babaeva defended her dissertation under the guidance of Prof. V.B. Mochalin and currently holds the position of associate professor of the Department of Physical and Organic Chemistry of the Dagestan State University in Makhachkala. Students of Prof. S.M. Makin are widely represented in the regions of Russia: Boris Konstantinovich Kruptsov in 1974-1980 headed the Department of Technology of Polymer Materials at the Kalinin Polytechnic Institute (currently Tver State Technical University); Yurii Vasil'evich Morozhenko is now a professor at the Bivsk Technological Institute. Students of Prof. B.V. Unkovskii work now in many cities of Russia; namely, Aleksandr Semenovich Fisyuk is head of the Department of Organic Chemistry of the Omsk State University (dean of the Faculty of Chemistry in 1993-1997; see section 14); Fil'za Nizamutdinovna Latypova is an associate professor of the Department of General, Analytical, and Applied Chemistry of the Ufa State Petroleum Technological University; Sergei Ivanovich Filimonov is an assistant professor of the Department of General and Physical Chemistry of the Yaroslavl State Technical University.

## 4.3. Organic Chemistry at the Department of Chemistry of the Pirogov Russian National Research Medical University

During the long history of the Pirogov Russian National Research Medical University, fundamental chemical disciplines were taught at one or several chemical departments, whose names changed quite often in accordance with changes in the requirements for the content of specific chemical disciplines. Chemical departments in the initial period (1890–1945). The history of the chemical departments of the Pirogov Russian National Research Medical University began much earlier than the Medical Faculty was founded (1906) at the Moscow Higher Women's Courses (1872–1918). As early as 1890, the famous chemist Aleksandr Nikolaevich Reformatskii (1864–1937), was elected professor at the depart-

ment of chemistry, and he headed the department in 1893–1930. A.N. Reformatskii, Honored Scientist of the RSFSR, was dean of the chemical and pharmaceutical faculty of the Second Moscow State University. His brilliant lectures with demonstrations of carefully thought-out and



spectacular experiments gathered a huge number of students not only from the medical but also from other faculties. He wrote a number of textbooks on chemistry, including "Inorganic Chemistry" (1903), which survived 26 editions, and also specially for students of the medical faculty the textbook "Organic Chemistry" (1904) [338], which was reprinted seven times and was translated into many languages of the Union Republics [339].

The Department of Organic Chemistry of the Moscow Higher Women's Courses at the Second Moscow State Medical Institute was founded in 1907. Its first head (1907–1912) was Professor (later Academician) Nikolai Dmitrievich Zelinskii (1861– 1953) [340].

During the long history, chemical departments were repeatedly combined and separated, in particular were combined with the department of biochemistry. In 1918, the **Second Moscow State University** was established on the basis of the Moscow Higher Women's Courses. It was reorganized in 1930, and its medical faculty was transformed into the **Second Moscow State Medical Institute** (later Second Moscow Lenin's Order State Medical Institute, Russian State Medical University; now Pirogov Russian National Research Medical University). After the creation of the Second Moscow State University, the department of inorganic chemistry continued to be headed by A.N. Reformatskii.

Many bright scientists in chemistry and practical educators such as already mentioned Professor A.N. Reformatskii and Academician N.D. Zelinskii and Academicians Sergei Semenovich Nametkin (1876–1950) and Vladimir Mikhailovich Rodionov (1878–1954) worked in the Second Moscow State University.

**S.S. Nametkin** (see also Sections 4.1, 4.2), professor of the Moscow Higher Women's Courses since 1912, headed the chemical departments in 1912–1925. In 1918–1930 he was professor of the Second Moscow University, rector (1919–1924) and professor (1930–1938) of the Moscow Institute of Fine Chemical Technology, professor of the Moscow State University (since 1938), and director of the Institute of Petroleum of the Academy of Sciences of the USSR (since 1948). S.S. Nametkin was in charge of the Department of Organic Chemistry from 1912 to 1925, and from 1925 to 1930 it was headed by Prof. **Yakov Ivanovich Mikhailenko** (1864–1943) whose main scientific interests were related to chemical analysis and solution theory.

In 1930, the Department of Organic Chemistry of the Second Moscow State University (Second Moscow State Medical Institute) was merged with the Department of Biological Chemistry under the leadership of



**Boris II'ich Zbarskii** (1885–1954). B.I. Zbarsky was a major biochemist, director of the Laboratory at the Lenin Mausoleum, academician of the Academy of Medical Sciences of the USSR. He headed the Department of Biochemistry until 1934. His main works were devoted to biochemistry of protein. At that time,

the Department of Inorganic Chemistry continued to be headed by A.N. Reformatskii.

In 1939–1943 the Department of General Chemistry of Second Moscow State Medical Institute was headed by **V.M. Rodionov** (see also Sections 4.1, 4.2), and the course of organic chemistry was transferred from the Department of Biochemistry to the Department of General Chemistry. During the time of V.M. Rodionov's work in the Second Moscow State Medical Institute (1939–1954), the manual for practical studies in organic chemistry compiled by lecturers of the department and edited by V.M. Rodionov was published [341] and repeatedly reprinted, many works on the synthesis and properties of  $\beta$ -amino acids and other biologically important compounds were published, and 8 candidate's dissertations were defended.

The head of the Department of General Chemistry of the newly organized (1930) Second Moscow State Medical Institute was Prof. Abram Moiseevich Berkengeim (1867–1938), who headed the department until 1938. A.M. Berkengeim began his pedagogical activity in 1909 at the Department of Chemistry of the Moscow Higher Women's Courses under the leadership of Prof. A.N. Reformatskii. In 1930–1938, lectures on inorganic, analytical, organic, physical, and colloid chemistry were read at the



department. A.M. Berkengeim was one of the first in Russia to introduce electronic concepts into organic chemistry [342, 343]. Under his leadership, the staff of the department was engaged not only in obtaining new medicinal substances (atophan, novocaine, dionin, coumarin, etc.) but also in industrial implementation of methods of their synthesis [344], which freed the country from the need to import these medicines. At the same time, much effort and attention was given to the teaching and methodical work. From 1931 to 1939, the lecturers of the department composed practicums on inorganic, analytical, physical, and colloidal chemistry [345]. In 1937, when the construction of the new main educational building of the Second Moscow State Medical Institute on M. Pirogovskaya Street was completed, the Department of General Chemistry received specially equipped chemical laboratories for the educational process and scientific work.

In 1943, the Department of General Chemistry of the Second Moscow State Medical Institute was divided into departments of general chemistry (inorganic and analytical chemistry) and organic chemistry (organic, physical, and colloid chemistry), and V.M. Rodionov remained head of the Department of Organic Chemistry. Doctor of Chemical Sciences, Professor Ekaterina Aleksandrovna Nikitina, a major specialist in the field of heteropoly compounds, was elected head of the Department of General Chemistry. Under the leadership of E.A. Nikitina (1943–1957), the main scientific direction of the Department of General Chemistry was synthesis and study of the properties of heteropoly compounds. A significant contribution to the scientific and pedagogical work of this department in the first post-war years was made under the leadership of professors Stanislav Iosifovich Papko and Anatolii Stepanovich Lenskii (1910-2004).

**S.I. Papko** headed the department from 1957 to 1971. He took an active part in the development of programs for chemical disciplines for students of medical schools and was chairman of the Medical Section of the Joint Scientific and Methodological Council for teaching of chemistry in



non-chemical institutes of the Ministry of Higher and Specialized Secondary Education of the USSR and RSFSR. Under the guidance of S.I. Papko, extensive research was continued at the department; in particular, oxidation of ammonia in aqueous solutions with ozonized oxygen was studied.



**A.S. Lenskii** headed the Department of General Chemistry from 1971 to 1982. During the Great Patriotic War A.S. Lenskii made a significant contribution to strengthening the defense capability of the USSR by creating effective smoke-forming compositions on the basis of chloro-

sulfonic acid [346]. Later he was engaged in scientific research in the chemistry and technology of phosphorus fertilizers, as well as in therapeutic use of nitrogen iodide; in particular, together with Prof. **Vladimir Viktorovich Teplov**, he studied positive effect of nitrogen iodide microexplosions in the treatment of psoriasis.

In 1982, due to significant change in the content of training, both chemical departments changed their name. As a result, the Department of Bioinorganic and Biophysical Chemistry headed by A.S. Lenskii (1982–1988) and the Department of Bioorganic and Biophysical Chemistry appeared (see below). Such enhanced "biologization" and "medicalization" of chemical disciplines required careful selection of the content of training and appropriate methodological support. A.S. Lenskii wrote the textbook "Introduction to Bioinorganic and Biophysical Chemistry" [347] with a pronounced medical–biological orientation. This textbook in the revised form is currently used in the educational process [348].

Since 1954, after the death of V.M. Rodionov, the Department of Organic Chemistry was headed until 1961 by Prof. Nikolai Sergeevich Drozdov (1902–1963), and then by associate professors V.V. Monblanova (1961–1963) and A.N. Mashentsev (1963–1965). In 1965, the disciplines studied at the department were again transferred to the Department of Biochemistry.

From 1968 to 1973, the re-established Department of Organic, Physical, and Colloid Chemistry was headed by Vasilii Antonovich Rudenko, and since 1973, Doctor of Chemical Sciences, Professor, Laureate of the State Prize of the Russian Federation, Full Member of the Russian Academy of Natural Sciences **Yurii Ivanovich Baukov** took charge of the depart-

ment. Yu.I. Baukov was a student of Academician A.N. Nesmeyanov and Prof **I.F. Lutsenko**, who previously worked at the Moscow State University. In 1982, in view of enhancement of medical and biological orientation of chemical disciplines, the department was renamed (see above) to the Department of Bio-



Yu.I. Baukov

organic and Biophysical Chemistry. Yu. I. Baukov in collaboration with Prof. **Nonna Arsen'evna Tyukavkina** (Sechenov First Moscow Medical Institute) wrote a textbook on a new discipline for medical schools, bioorganic chemistry [349], which survived 8 editions and is actively used for teaching students [350].

In addition, the department issued a number of methodological materials and instructions for students, including three original manuals on biophysical chemistry devoted to various sections of the course, which were written by Prof. Igor' Viktorovich Kolosov [351].



Employees of the Department of General and Bioorganic Chemistry of the Russian State Medical University (2002).

A great contribution to the teaching and methodical work of the department of Prof, Viktor Nikolaevich Sergeev should also be noted. Together with assistant professor L.S. Smirnova, he wrote a handbook on surface phenomena, disperse systems, and environmental protection [352] and then a textbook on colloid chemistry [353] for students of medical higher schools.

In 1988, both chemical departments were united under the leadership of Yu.I. Baukov to a single Department of General and Bioorganic Chemistry.

**Department of Experimental and Theoretical Chemistry of the Medical and Biological Faculty**. Immediately after the establishment of the Medical and Biological Faculty in 1963, teaching of chemical disciplines began thereat, and the course system of teaching was first adopted. The first lecturers in inorganic and analytical chemistry were associate professor S.S. Olenin, senior lecturer S.P. Arkhangel'skaya, and assistant O.D. Men'kova. The administration of the Pirogov Second Moscow Lenin's Order State Medical Institute decided soon to organize a department at which all chemical disciplines should be taught. Professor Lev Aleksandrovich Nikolaev



(1913–2001), head of a department in the Moscow Institute of Transport Engineers, author of more than 10 textbooks and manuals, including those with medical and biological orientations [354, 355], was invited to head the new department as parttime manager. Teaching of physical and colloid chemistry began in

October 1964, and of organic chemistry, in 1965. Since that time the full-scale work of the Department of Experimental and Theoretical Chemistry has started.

In 1969, associate professor Viktor Nikolaevich Zakharchenko (1937–2012) was appointed as head of



the department, and he headed it with interruptions until 2011. He wrote a number of teaching and methodical manuals, including a textbook on colloid chemistry [356].

Since the foundation, scientific research has been carried out at the Department of Experimental and

Theoretical Chemistry. Under the guidance of L.A. Nikolaev, systems simulating the action of enzymes via proton transfer, peroxide oxidation processes in aqueous systems, and influence of low frequencies on protein solutions were studied. V.N. Zakharchenko developed a method for studying the viscosity of blood using a rotational viscometer with a freely floating cylinder (which was created by him), as well as a new method for separating blood into plasma and a concentrated suspension of blood corpuscles using nuclear filters, which has found application in clinical practice.

The merger of chemical departments started in 1988 by Yu.I. Baukov was completed in 2011 by Professor of the Russian Academy of Sciences Vadim Vital'evich Negrebetskii. Thus, a single department

of chemistry was formed from the Department of General and Bioorganic Chemistry of the Therapeutic Faculty and the Department of Experimental and Theoretical Chemistry of the Faculty of Medicine and Biology. V.V. Negrebetsky, a graduate of the Mendeleev Moscow Insti-



tute of Chemical Technology, has been working in the Russian National Research Medical University since 1992. He continued the tradition of creating modern textbooks [357, 358] and made a decisive contribution to the organization of teaching of a number of new chemical disciplines at the Pharmaceutical Faculty, which was founded in 2008 in the Russian National Research Medical University. In general, over the last five years, more than 60 different tutorials have been published and republished, and most of the latest methodological materials were created for students of the Pharmaceutical Faculty [359].

At that time, the material and technical base of the department was significantly renewed, the use of multimedia equipment in the educational process was extensively developed, and recording of video lectures for medical students was started [360].

At present, the basis of the educational process at the department is the course of chemistry for students of Therapeutic, Pediatric, and Dentists' Faculties. A laboratory practicum was organized for students of these faculties, through which about 2000 students from the majority of faculties pass each semester.

> 4.4. History and Scientific Achievements of the Department of Organic Chemistry of the Mendeleev University of Chemical Technology of Russia

Teaching of organic chemistry at the Mendeleev Moscow Institute of Chemical Technology (since 1993, Mendeleev University of Chemical Technology of Russia) has started in the 1923–1924 academic year. In that year the staff of the department consisted of only two employees. The first head of the department was Professor **Ivan Dmitrievich Smirnov**, and his assistant in the organization of the first academic year was lecturer Ya.Ya. Makarov-Zemlyanskii. In the first years, training sessions were conducted in one of the laboratories of the Department of Chemistry and Technology of Intermediate Products and Dyes. This laboratory was designed for a laboratory practicum of 19 students.

In 1925, the Department of Organic Chemistry of the Mendeleev Institute was headed by Academician P.P. Shorygin (1881–1939), and he should be considered the founder of the scientific and pedagogical school of the Department of Organic Chemistry, widely known for his fundamental research in the field of organic chemistry, organization of the educational process, and high level of educational work determined by the preparation of educational and methodical publications.

**Pavel Polievktovich Shorygin** graduated from the Chemical Faculty of the Imperial Moscow Technical School in 1903 with the title of engineer-technologist. His first teacher in the field of organic chemistry and technology was Vasilii Vasil'evich Sharvin. In 1903, together with V.V. Sharvin, P.P. Shorygin published the first study "Stereoisomeric oximes of unsymmetrical aromatic ketones" [361]. In the same year, P.P. Shorygin entered Freiburg University (Germany), where he worked for 3 years under the guidance of the famous chemist Professor Ludwig Gatterman.

In 1906, P.P. Shorygin passed his doctoral examinations and presented Ph.D. thesis "On chemical luminescence. Crystalloluminescence and triboluminescence." Upon his return to Russia, P.P. Shorygin received (1906) the post of assistant at the Department of Chemistry at the Moscow Technical School, where he worked until 1911 by conducting pedagogical and



From left to right: Ya.Ya. Makarov-Zemlyanskii, P.P. Shorygin, I.P. Losev (1926).

research work. In 1909–1910 he passed his master's examinations and in December 1910 he defended his thesis at the Moscow University, having obtained master's degree in chemistry. In 1932 Professor P.P. Shorygin was elected a corresponding member, and in 1935 the Higher Attestation Commission and the Presidium of the Academy of Sciences of the USSR awarded him the degree of Doctor of Chemical Sciences without defending a dissertation. In 1939, P.P. Shorygin became a full member of the Academy of Sciences of the USSR.

Already in the 1930s the Department of Organic Chemistry had two large laboratories for student's practicum and 6 laboratories for scientific work of the staff. From the first years, a students' scientific circle actively worked at the department, and post-graduate students appeared soon; among the latter, there were two future academicians **Aleksandr Vasil'evich Topchiev** and **Vasilii Vladimirovich Korshak** and four future professors Ivan Platonovich Losev, Vladimir Nikolaevich Belov, Anatolii Pavlovich Kreshkov, and Alfred Anisimovich Berlin.

While forming the staff of the department, P.P. Shorygin required that each teacher conducted experimental work oriented to practice. At that time such works were those the results of which were needed by the developing chemical industry. The first person to join such a work was associate professor **Yakov Yakovlevich Makarov-Zemlyanskii**; he was engaged in developing technology for the synthesis of camphor by oxidation of borneol.

Back in 1918, after reading the course of chemistry of explosives in the Moscow High Technical School, P.P. Shorygin began work in the field of nitration of organic substances and actively continued this study at the Department of Organic Chemistry. He found conditions for the side-chain nitration of toluene and ethylbenzene and obtained stable glycerol and picric acid dinitrates. Together with the first post-graduate student of the department, Aleksandr Vasil'evich Topchiev, the nitration of aromatic and heteroaromatic compounds with nitrogen oxides was carried out [362].

By the time the second postgraduate student, Vasilii Vladimirovich Korshak, appeared at the department, P.P. Shorygin had met Vache Ivanovich Isagulyants, an enthusiast in the development of fragrance industry in the USSR. Therefore, the dissertation of V.V. Korshak was related to the synthesis and study of hydroxyaldehyde ethers and their acetals. Glycolaldehyde diethyl acetal geraniol ether and geranylacetaldehyde were synthesized; both compounds had a pleasant rose smell. Encouraged by this success, P.P. Shorygin and V.V. Korshak synthesized and studied  $\beta$ -hydroxypropanal acetals [363]. These works predetermined further scientific interests of V.V. Korshak, the leading specialist in the field of polymer chemistry, who was always closely associated with the Mendeleev Institute.

Another future researcher in the field of the chemistry of plastics, Ivan Platonovich Losev came to the Department of Organic Chemistry almost simultaneously with P.P. Shorygin and worked therein first as an assistant and then as an assistant professor. His candidate's dissertation was devoted to catalytic conversion of halogen derivatives and alcohols to aldehydes and ketones. Later, on the initiative of P.P. Shorygin at the Mendeleyev Institute in 1932, the Department of Plastics Technology was organized and headed by I.P. Losev. P.P. Shorygin, jointly with V.V. Korshak and I.P. Losev, studied polycondensation of phenol with methylene chloride and obtained phenol-methylene chloride resin which was not inferior to phenol-formaldehyde resin in its properties [364].

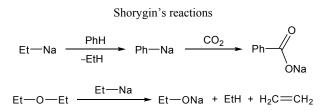
It is worth remembering one more famous student of P.P. Shorygin, Prof. Vladimir Nikolaevich Belov, future head of the Department of Organic Chemistry of the Moscow Institute of Chemical Technology. The interest of P.P. Shorygin to fragrant substances proved to be very stable, and he invited three graduates of the Bauman Moscow High Technical School, employees of the experimental plant of fragrances of the Zhirkost' Trust Vladimir Nikolaevich Belov, Irina Vladimirovna Machinskaya, and Sof'ya Abramovna Skoblinskaya. Their cooperation led to a number of works in the field of organometallic synthesis [365, 366]. V.N. Belov graduated from the Bauman Moscow High Technical School in 1930. However, even before finishing his study thereat, he began scientific work under the guidance of Prof. P.P. Shorygin. In the first joint work, they obtained opianic acid and a number of heterocyclic compounds based thereon [367]. While searching for new raw materials for the synthesis of fragrances, Academician P.P. Shorygin drew attention to the huge amounts of still residues from fusel oil and instructed V.N. Belov to begin a detailed study of their composition. Already in 1933, P.P. Shorygin and V.N. Belov published the results of analysis of the composition of high-boiling fractions of fusel oil [368]. In 1934, P.P. Shorygin and A.P. Kreshkov, by order of the paint and varnish industry, investigated



P.P. Shorygin and A.E. Favorskii (1935–1939). Zelinskii Institute of Organic Chemistry.

mixtures of acids formed in the oxidation of saturated hydrocarbons [369].

P.P. Shorygin also continued his classical studies in the field of organosodium compounds at the Mendeleev Institute. As already mentioned, while preparing his master's thesis he discovered several reactions of organosodium compounds, in particular metalation and decomposition of ethers by the action of organometallic compounds. The most significant of these is the metalation reaction, i.e., substitution of a hydrogen atom in an aromatic hydrocarbon by a metal atom [370]. While studying the properties of ethylsodium, he obtained phenylsodium by exchange reaction with benzene, as evidenced by the formation of sodium benzoate after treatment of the reaction mixture with carbon dioxide. Subsequently, this reaction has become one of the most important organometallic methods widely used in modern organic synthesis for the generation of organolithium and organomagnesium compounds. Another reaction he discovered was decomposition of ethers under the action of alkylsodium [371].



Professor P.P. Shorygin wrote the first textbooks on organic chemistry at the Mendeleev Institute. He prepared three editions of the "Courses of Organic Chemistry" for chemist-technologists (1932 and 1940) and for physicians and biologists (1925), two editions of "Advances in Organic Chemistry" (1928 and 1932), three editions of "Chemistry of Carbohydrates" (1927, 1932, 1938), and 2 editions of "Chemistry of Cellulose" (1936, 1939). He prepared the first programs of the course of organic chemistry, read at the Mendeleev Institute. A large laboratory practicum was organized under the leadership of P.P. Shorygin, which included 18 training syntheses, one literature synthesis, and 7 analyzes.

Being head of the Department of Organic Chemistry at the Mendeleev Institute, Prof. P.P. Shorygin continued to work in the Military Chemical Academy, where the Department of Artificial Fiber (organized by P.P. Shorygin in 1928 as part of the Bauman Moscow High Technical School) was transferred. P.P. Shorygin is the author of more than 150 scientific works [372].

After the death of P.P. Shorygin in 1939, the Department of Organic Chemistry was headed by Prof. V.V. Feofilaktov. The scientific interests of Professor V.V. Feofilaktov were associated with fatty–aromatic azo compounds. He discovered the synthesis of  $\alpha$ -amino acids by reduction of  $\beta$ -ketocarboxylic acid hydrazones, which entered textbooks as Feofilaktov's method [373].

Valentin Vasil'evich Feofilaktov graduated from the Moscow Agricultural Institute in Petrovsko-Razumovskii (now the Russian State Agrarian University, Timiryazev Moscow Agricultural Academy), majoring in agrochemistry. While still a student, he began working in the laboratory of the famous organic scientist Academician N.Ya. Dem'yanov. After graduation from the Institute (1921), he was left at the Department of Organic Chemistry of the Agricultural Institute at the suggestion of N.Ya. Dem'yanov. From that time, his collaboration with N.Ya. Dem'yanov began and continued until his death in 1938. Simultaneously (1925–1926), Feofilaktov worked as an assistant at the department of Academician D.N. Pryanishnikov on the course "Chemistry of Plants" in the First Moscow State University.

In 1932–1934, V.V. Feofilaktov was in charge of the Department of Organic Chemistry at the Moscow Institute of Fisheries. In 1932–1936, under the contract with the All-Union Institute of Oceanography and Fisheries, he organized and headed a laboratory for the study of proteins and fats. After the transfer of the Academy of Sciences of the USSR to Moscow and foundation of the Institute of Organic Chemistry, N.Ya. Dem'yanov invited him to the laboratory he directed (1935). In June 1937 V.V. Feofilaktov was awarded the degree of Doctor of Chemical Sciences. In the spring of 1938, he moved to the Laboratory of Proteins of the Academy of Sciences of the USSR, where he worked until October 1941.

In addition to the development of the method for the synthesis of  $\alpha$ -amino acids, the main scientific achievements of V.V. Feofilaktov included the discovery and study (together with **M.S. Kozlova**) of a general reaction for the preparation of pyrazolone derivatives (tartrazine dyes). The Feofilaktov method is based on the coupling of alkyl acetoacetates with aromatic diazo compounds leading to  $\alpha$ -keto acid arylhydrazones whose subsequent reduction gives  $\alpha$ -amino acids in good yield [374]. For example, norleucine was obtained from butyl acetoacetate through intermediate  $\alpha$ -ketocaproic acid phenylhydrazone.

$$C_{4}H_{9}-CH \xrightarrow{COOCH_{3}} \xrightarrow{PhN_{2}X} C_{4}H_{9}-C-COOH \xrightarrow{KOH} C_{4}H_{9}-C-COOH \xrightarrow{HOH} COCH_{3} \xrightarrow{KOH} C_{4}H_{9}-CH-COOH \xrightarrow{Ln-HCl} C_{4}H_{9}-CH-COOH \xrightarrow{NH_{2}} C_{4}H_{9}-CH-COOH$$

In August 1943, V.V. Feofilaktov again returned to work in the Timiryazev All-Union Agricultural Academy, where he headed the Department of Organic Chemistry until 1956. The works of that period were devoted to the synthesis of various biologically active substances. As a result of the research, effective methods for the preparation of auxins (heteroauxin and indolylbutyric acid) and herbicides (2,4-dichlorophenoxyacetic and 4-chloro-2-methylphenoxyacetic acids) have been developed.

After the departure of V.V. Feofilaktov in 1943, the Department of Organic Chemistry was headed by Academician V.M. Rodionov (1878-1954), leading Soviet organic chemist, specialist in bioorganic chemistry, chemistry and technology of medicines, synthetic dyes, and fragrant substances. Vladimir Mikhailovich Rodionov studied at the Dresden Polytechnic Institute and in 1901 received a diploma of a first-degree chemical engineer. In 1906 he graduated from the Imperial Moscow Technical School with a diploma of a first-degree engineer-technologist. In the first years of his scientific career, during the period of work at the Bayer paint factory in Elberfeld-Leverkusen (1906-1909) and its Moscow branch (1909-1914), he carried out a number of outstanding studies in the field of chemistry of dyes and intermediate products. He developed the original synthesis of thioindigo from monochloroacetone and thiosalicylic acid, the synthesis of chlorine- and light-resistant dyes, and carried out

a series of studies on the chemistry of naphthalene and its derivatives. A series of works by V.M. Rodinov concerns the diazotization reaction and properties of diazo compounds, disproportionation of aldehydes, acylation and transacylation of amines, synthesis of hydroxyarylcarboxylic acids, and properties of 4-sulfobenzoic acid derivatives and other aromatic compounds.

Working for 8 years (1906–1914) at the Bayer enterprises and scientific laboratories, V.M. Rodionov became a prominent specialist in the field of dye chemistry. He organized production of the most important intermediate products such as nitrobenzene, dinitronaphthalenes, dimethylaniline, sulfanilic and naphthionic acids, phenol,  $\alpha$ - and  $\beta$ -naphthols, sulfonic acids derived therefrom, and other derivatives (Freund's acid, H- and  $\gamma$ -acids, 1,2,4-aminonaphtholesulfonic acid). Participating in the works of the Military Industrial Committee during the war of 1914– 1918, V.M. Rodionov was a consultant and expert of Aniltrest, and then of the People's Commissariat of Chemical Industry.

V.M. Rodionov has also done a lot in the pharmaceutical industry. Heading for many years the Department of Pharmaceutical Chemistry at the Moscow Higher Technical School and the Department of Chemistry of Alkaloids at the Second Moscow State University, he organized manufacture of a number of new pharmaceutical preparations and alkaloids (salicylic acid derivatives, novocaine, caffeine, theobromine, atropine, hyoscyamine, morphine, codeine, papaverine, and others). The procedure developed by V.M. Rodionov is still used to produce the most important alkaloids (codeine, cotarnine, pantopon) and purify noscapine (precursor to cotarnine).

Since 1930, V.V. Rodionov was a consultant to the Research Institute of Perfume Industry, and he directed research on the synthesis of fragrances. Under his leadership, methods have been developed for the preparation of piperonal and other aldehydes of the aromatic series, civetone, glyoxylic acid, and phenylacetaldehyde. At the same time, Vladimir Mikhailovich took an active part in organizing large-scale production of fragrant substances at factory scales, in particular of vanillin, vanillal, coumarin, etc.

Simultaneously, V.M. Rodionov was interested in other branches of chemical technology. He proposed an original and cost-effective method for the synthesis of acetic anhydride. The synthesis of chloroform from trichloroacetic acid via a continuous process is also interesting. V.M. Rodionov paid considerable attention to the Cannizzaro reaction. Taking into account that in the presence of formaldehyde benzaldehyde in alkaline solution is converted to benzyl alcohol, he developed a general method for the transformation of aldehydes to alcohols [375]. Carboxylation of phenols with carbon dioxide should also be noted. This method was proposed for the synthesis of salicylic acid from phenol (Kolbe–Schmitt) and was successfully extended by V.M. Rodionov to the transformation of  $\alpha$ - and  $\beta$ -naphthols and alkoxyphenols to the corresponding 1,2-hydroxycarboxylic acids.

Another series of problems, in which V.M. Rodionov was invariably interested, was related to alkylation (mainly methylation) reactions that are of great importance in aniline-dye and especially in pharmaceutical industries. He encountered these problems when developing a large-scale procedure for methylation of alkaloids (preparation of codeine from morphine, and narceine from narcotine) and was the first to use trimethyl(phenyl)ammonium benzenesulfonate for this purpose [376]. The Rodionov method allows selective alkylation of phenolic hydroxy, as well as amino, groups in a number of natural and synthetic biologically active substances and is still used to obtain a number of semisynthetic alkaloids.

Extensive research was carried out by V.M. Rodionov and co-workers on aldehyde acids, mainly on 4-formyl-2,3-dimethoxybenzoic (opianic) acid, a byproduct in the production of opium alkaloids. A series of works performed in this area together with his students (S.I. Kanevskaya, M.M. Shemyakin, B.M. Bogoslovskii, V.V. Levchenko, S.I. Mikhailov, and others), in addition to their theoretical significance, were oriented toward practical use of opianic acid (synthesis from opianic acid of isovanillin, dimethoxyanthranilic acids, analogs of the alkaloid damascenine, methoxylated heterocyclic compounds of the quinoline, isoquinoline, and quinazolone series, methoxylated derivatives of indigo and thioindigo, etc.) [377].

One of the most significant scientific achievements of V.M. Rodionov is the synthesis of  $\beta$ -amino acids developed by him in 1926. By carrying out the Knoevenagel reaction of aldehydes with malonic acid in the presence of alcoholic ammonia, he obtained  $\beta$ -amino acids [378]; later, it was proposed to use ammonium acetate instead of ammonia.

$$R-CHO \xrightarrow{CH_2(COOH)_2}_{CH_3COONH_4} \xrightarrow{NH_2 O}_{OH}$$



Academician V.M. Rodionov with assistant professors F. Blakno, T.K. Veselovskaya, and I.V. Machinskaya and assistants S.V. Bragin and S.F. Filatov.

V.M. Rodionov has developed one more original way of obtaining one of the most important  $\beta$ -amino acids,  $\beta$ -alanine by condensation of acrylic acid with phthalimide in the presence of trimethyl(phenyl)ammonium as catalyst [379]. Studies on the synthesis of amino acids containing an indole fragment were subsequently continued under the leadership of **N.N. Suvorov**. He synthesized  $\alpha$ -(3-indolyl)- $\beta$ -aminopropionic acid, a  $\beta$ -analog of the essential  $\alpha$ -amino acid tryptophan [380].

Apart from the synthesis of  $\beta$ -amino acids, V.M. Rodionov with a number of employees performed extensive studies (1942-1947) of their chemical properties [381, 382], which led to the development of new and improvement of previously known synthetic routes to various heterocyclic compounds such as di-, tetra-, and hexahydropyrimidines, glyoxylidones, and quinoline, isoquinoline, and quinazolone derivatives [383, 384]. He proved the mechanism of one of the most important reactions of organic chemistry, the Hoffmann reaction [385]. The path of synthesis of glyoxylidones suggested by V.M. Rodionov led him to obtain new desthiobiotin analogs, a number of which have a biotin effect. Finally, V.M. Rodionov studied the relationship between the structure of β-amino acids and their growth-stimulating effect on lower organisms (yeast) and also carried out a series of studies on the vitamin C group and pantothenic acid.

Over 30 years, V.M. Rodionov was in charge of several departments. As early as 1916, he was the first in Russia to create a department of chemistry and technology of pharmaceuticals at the Moscow Higher Technical School, which he headed for many years. In 1920, he founded the only in the USSR Department of Chemistry of Alkaloids in the Second Moscow State University. These departments brought forth the main staff of scientific and engineering workers in the field of pharmaceutical chemistry. The departments of chemical technology of coloring substances created by V.M. Rodionov at the Moscow Textile Institute (1935) and the Moscow Institute of Chemical Engineering gave rise to highly educated specialists in the technology of fibrous substances. Apart from the Department of Organic Chemistry at the Mendeleev Moscow Institute of Chemical Technology, he headed an analogous department at the Second Medical Institute and simultaneously held senior positions in some research institutes (Research Institute of Organic Intermediate Products and Dyes, All-Union Institute of Experimental Medicine) and worked as consultant and manager in the aniline-dye and pharmaceutical industry, as well as in the production of fragrances.

Being one of the leading technologists and theoreticians in the field of organic chemistry, V.M. Rodionov was elected in 1939 a corresponding member, and in 1943, full member of the Academy of Sciences of the USSR. Since 1939, V.M. Riodionov was chairman of the section of organic chemistry of the Moscow branch of the Mendeleev All-Union Chemical Society.

In 1955–1963 the department was headed by Professor V.N. Belov (1900–1963), a student of Academician P.P. Shorygin; at the same time, he was dean of the Faculty of Technology of Organic Compounds at the Mendeleev Institute of Chemical Technology (1957–1962).

After graduating from the seven classes of the Moscow Commercial College (1918), Vladimir Nikolaevich Belov volunteered for the Military Sanitary Train no. 224. Since 1921 he served in non-combatant posts in the 425th Infantry Regiment. After demobilization, he worked in the Moscow Soviet since 1923, combining his work with studies at the Moscow Industrial and Economic Institute. He completed his higher education at the Faculty of Chemistry of the Moscow Higher Technical School, specializing in the synthesis of drugs (1930). After graduation from the institute, he was sent to the Experimental Plant of the *Zhirkost'* Trust, where he worked under the supervision of Academician P.P. Shorygin. Since 1933, at the invitation of P.P. Shorygin, he passed to the Department of Organic Chemistry at the Mendeleev Institute of Chemical Technology where for many years he was in charge of the laboratory of organic chemistry.

In 1941–1944 V.N. Belov was on the fronts of the Great Patriotic War. In 1944, he was recalled from the army to work in the First Research Institute of the Ministry of Aviation Industry. In 1946 he took the post of deputy director for scientific work of the All-Union Scientific Research Institute of Synthetic and Natural Flavors. He also taught at the First Moscow Medical Institute and Lomonosov Moscow Institute of Fine Chemical Technology and headed the Department of Organic Production Facilities and Organic Chemistry at the All-Union Correspondence Polytechnic Institute.

In 1935 he defended his candidate's dissertation, and in 1946, doctoral dissertation "On some properties of dimethyl sulfate." He is the author of large publications "On attempts to close the heterocycle in (B-hydroxyethyl)aniline and on benzoyl derivatives (β-hydroxyethyl)aniline" [386] and "Chemistry and technology of fragrant substances" [387]. V.N. Belov is one of the founders of the chemistry of fragrant substances and essential oils in the USSR [388]. He created a direction in the synthesis of fragrant substances, based on the use of alkylphenols and terpenic phenols and developed the basis for the synthesis of terpenic phenols and methods for determining their structure [389]. He also discovered a number of skeletal rearrangements occurring during the alkylation of phenols with terpenes, synthesized thibetolide, santalidol, musteron, isoeugenol, cyprenal, cedrol, vetinyl acetate, etc., performed studies on the synthesis of menthol, and revealed a relationship between the structure of substances and their odor [390]. He ascertained the mechanisms of acylation of unsaturated hydrocarbons, allyl rearrangements, Kondakov's reaction, hydrobromination of undecylenic acid, etc., developed methods for the synthesis of monosubstituted acetoacetic esters, cross electrocondensation with the formation of 15-acetoxypentadecanoic acid, cyclization of  $\omega$ -hydroxy acids to macrocyclic lactones,

synthesis of macrocyclic oxalactones from 11-bromoundecanoic acid, studied the properties of opianic acid, and proposed a method for the synthesis of irone from isoprene and dimethylbutadiene. V.N. Belov developed methods of synthesis of 1-hydroxynaphthalene-2carbaldehyde, 1,2,3,4-tetrahydronaphthalene-2-one, and 3-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid by indirect electrochemical reduction of hydroxynaphthalenecarboxylic acids and compounds with a hydrogenated naphthalene ring. He published more than 100 scientific papers, including 8 USSR inventor's certificates [391] and trained about 20 candidates of sciences.

From 1964 to 1988, the Department of Organic Chemistry was headed by Prof **N.N. Suvorov**, a graduate of the Moscow State University and a student of Academician V.M. Rodionov. Scientific interests of Prof. N.N. Suvorov covered 3 main directions: indole derivatives, steroids, and benzophenanthridine alkaloids.

Nikolai Nikolaevich Suvorov was born on September 15, 1922 in Novocherkassk and was very proud of being a native of the Cossacks. In the circle of friends and colleagues, he often repeated that he was a descendant of Hetman Nalivaiko. In 1940 he became a student of the Faculty of Chemistry of the Moscow State University, and in October 1941 volunteered for the front. After demobilization from the Soviet Army in August 1943 because of pulmonary tuberculosis, N.N. Suvorov again returned to the Moscow State University and graduated therefrom with honors in July 1947; a month later, he enrolled in the postgraduate course at the Zelinskii Institute of Organic Chemistry on the specialty "Chemistry of natural compounds." In 1950 he defended his candidate's dissertation under the guidance of V.M. Rodionov.

In 1950–1952, N.N. Suvorov was an assistant at the Department of Organic Chemistry of the Mendeleev Moscow Institute of Chemical Technology. In October 1952, on the recommendation of V.M. Rodionov, he was invited to the laboratory of corticosteroids of the Ordzhonikidze All-Union Scientific Research Chemical and Pharmaceutical Institute, and only six months later (in April 1953) became its head. It was here that Suvorov began diverse research covering both corticosteroids and indole chemistry.

The productivity and significance of scientific results obtained by the thirty-year-old scientist are impressive. Indeed, virtually in a decade (from 1952 to 1962), he performed the work equivalent to two (!)

doctoral dissertations on corticosteroids and indole. However, the preference was given to the latter, and in May 1962 N.N. Suvorov defended his doctoral dissertation "Studies in the field of synthesis of biologically important indole derivatives."

In September 1963 N.N. Suvorov again returned to the Mendeleev Moscow Institute of Chemical Technology, and in January 1964 he became head of the Department of Organic Chemistry, which he headed for 25 years. At the same time, he headed the laboratory of corticosteroids in the All-Union Scientific Research Chemical and Pharmaceutical Institute. In subsequent years until his death in 1999, N.N. Suvorov continued successful pedagogical and scientific activity in the Mendeleev Russian Chemical Technological University and in the Drug Chemistry Center at the All-Union Scientific Research Chemical and Pharmaceutical Institute.

Like his teacher Academician V.M. Rodionov, N.N. Suvorov was a bright and versatile personality. The range of his scientific interests was very extensive and included research in the field of chemistry, biochemistry, and pharmacology of indole derivatives, chemistry of steroids, and benzophenanthridine alkaloids, many of which were pioneering. He developed effective methods for the synthesis of the most biologically important representatives of the indole series such analogs of gramine [392], tryptophan, and tryptamine [393]; a pilot plant for the manufacture of synthetic indole was created, and a number of new methods for the synthesis of indole derivatives were proposed [394]. The synthesis of a tetracyclic chelidonine model from ethyl bromo(phenyl)acetate and diethyl benzylmalonate, known as the Rodionov-Suvorov scheme, is the creative and scientific success of two great chemists, a teacher and a student [395].

Fruitful fundamental scientific research resulted in the introduction of a number of original drugs into medical practice. One of the first original domestic antidepressants was *indopan* [396]. V.M. Rodionov and N.N. Suvorov created the original drug *betazine* for the treatment of hyperthyroidism [397]. This work was awarded a small silver medal of the Exhibition of Economic Achievements of the USSR. Many years of joint research by synthetic chemists, radiobiologists, and pharmacologists headed by N.N. Suvorov made it possible to create a new class of radioprotectors of the indole series such as *serotonin adipate*, *mexamine*, and *indralin*. The latter was successfully used as a radioprotector of emergency action in the aftermath of the Chernobyl disaster [398]. Another radioproptector, *indometophen*, was allowed by the Pharmaceutical Committee for clinical trials as a drug for the prevention of radiation damage in prolonged irradiation [399].

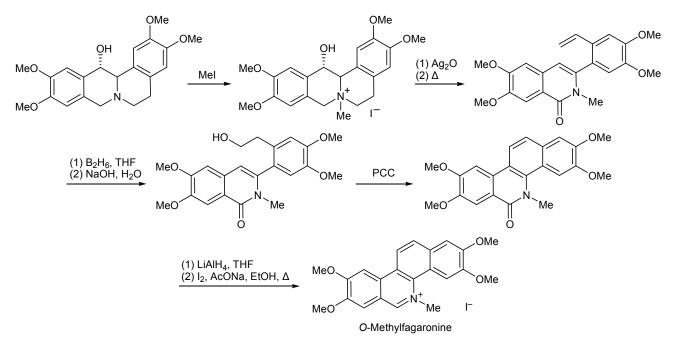
In 1965, N.N. Suvorov, V.G. Avramenko, and V.N. Shkil'kova developed a heterogeneous catalytic method for the synthesis of indole based on the Fisher cyclization of arylhydrazones [400]. A significant contribution to Russian medicine was the research conducted in the field of chemistry of steroids under the leadership of N.N. Suvorov, which also had fundamental character [401]. The results made it possible to organize large-scale manufacture of corticosteroids in the USSR (at the *Akrikhin* plant).

Under the guidance of N.N. Suvorov, B.Ya. Eryshev and V.G. Avramenko developed an industrial method for obtaining heteroauxin. Considerable attention was paid at the department to the synthesis and study of the closest heteroauxin analogs,  $\gamma$ -(indol-3yl)butyric acid and its derivatives. This acid proved to be an active plant growth stimulator whose activity was 2–2.5 times higher than that of heteroauxin [402].

A significant number of works on the synthesis of phenanthridine alkaloids and their analogs have been carried out at the department. These works were started even under the guidance of V.M. Rodionov, but only in 1991 N.S. Suvorov, N. M. Sazonova, V.I. Sladkov, and I.I. Levin succeeded in completing the synthesis of one alkaloid of this group, *O*-methylfagaronine [403]. N.N. Suvorov, R.N. Akhvlediani, V.N. Buyanov, E.P. Frolova, E.P. Baberkina, and M.E. Zhukova have synthesized a number of pyrrole analogs of fagaronine [404].

N.N. Suvorov published over 1100 scientific papers and created a large scientific school in which 10 doctors and 122 candidates of sciences were trained [405]. He developed courses on organic chemistry and its theoretical aspects, biochemistry, and chemistry of biologically active substances in the Mendeleev University of Chemical Technology of Russia. He radically revised the lecture course of organic chemistry by introducing modern concepts on the organic reaction mechanisms.

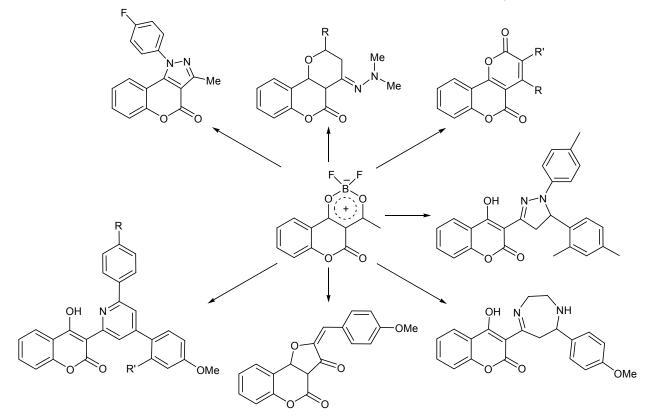
From 1988 to 2012 the department was headed by Prof. Valerii Fedorovich Traven', a student of Prof. B.I. Stepanov. V.F. Traven graduated with honors from the Mendeleev Moscow Institute of Chemical Technology. In 1967, he defended his candidate's dissertation, and in 1981, doctoral dissertation. He is



author of more than 350 scientific papers. Research interests of V.F Traven' lie in the field of synthesis and structure of organic dyes, coumarin derivatives, and hetarenocoumarins.

During that period, studies of biologically active compounds also included the study ordered by the All-Union Institute of Chemical Means for Plant Protection. V.F. Traven', N.A. Kuznetsova, and E.E. Levinson carried out work in the field of brassinosteroids as efficient plant growth regulators for agriculture [406].

The use of boron trifluoride complexes of coumarin derivatives, developed by V.F. Traven', A.V. Manaev, I.V. Voevodina, and T.A. Chibisova [407], became a fruitful direction in the synthesis of new hetarenes.



Many hetareno- and hetarylcoumarins became available on a preparative scale due to the use of 1,3,2-dioxaborinines.

On the basis of 1,3,2-dioxaborinines and 2-benzylidene-2H-furo[3,2-c]coumarin-3-one derivatives, V.F. Traven', A.V. Manaev, and N.A. Kondratova obtained effective labels for some proteins, which ensured almost 1000-fold increase in fluorescence intensity when detecting, e.g., BSA protein [408].

Being a graduate of the Department of Chemistry and Technology of Organic Dyes, Prof. V.F. Traven' created and developed a new direction for the Department of Organic Chemistry, synthesis and structural study of fused hetarenes for photonics, molecular electronics, and sensor technology. V.F. Traven' and A.Yu. Bochkov obtained a number of effective photochromic structures based on coumarinyl(thienyl)ethenes that are capable of undergoing reversible photoisomerization and are of interest for the design of optical information recording devices and new sensor elements [409]. New polymethine dyes characterized by exceptionally high light absorbance and fluorescence intensity and promising as sensitizers have been synthesized on the basis of boron complexes of 3-acetyl-4-hydroxycoumarin and dehydroacetic acid [410]. V.F. Traven' is the author of the monograph "Electronic Structure and Properties of Organic Molecules" [411] and its revised translation published in Great Britain [412].

Under the direction of V.F. Traven', the department switched to teaching organic chemistry by classes, and the program was based on modern concepts of the structure and reactivity of organic compounds, including molecular orbital representations. Professor V.F. Traven' prepared new texts of lectures on the following disciplines: "Chemistry and technology of intermediate products," "Fundamentals of quantum chemical calculations of organic molecules," "Organic chemistry" and read them in the Mendeleev University of Chemical Technology of Russia. In recent years he has prepared and read now the course "Fundamental Organic Chemistry" for students of the Higher Chemical College of the Russian Academy of Sciences. V.F. Traven' is author of the textbook "Organic Chemistry" for higher schools [413]. He prepared a practicum [414] in collaboration with A.E. Shchekotikhin, and with N.A. Pozharskaya and A.Yu. Sukhorukov, a task book on organic chemistry. Currently V.F. Traven' is head of the Higher Chemical College of the Russian Academy of Sciences and

scientific Leader of the Research Center "University of Chemical Technology of Russia-Skolkovo."

In 2013, the Department of Organic Chemistry was headed by Doctor of Chemical Sciences, Professor of the Russian Academy of Sciences Andrei Egorovich Shchekotikhin, a student of Prof. N.N. Suvorov. A.E. Shchekotikhin graduated from the Mendeleev University in 1993. During the period of 1993–1996, he studied at the post-graduate courses at the Department of Organic Chemistry and prepared a dissertation on the synthesis and biological properties of indole analogs of antitumor anthracycline antibiotics derived from naphthoindolediones [415], which was defended in 1998. He then continued to work at the Department of Organic Chemistry as head of a laboratory. In 2001, at the invitation of Prof. M.N. Preobrazhenskaya, A.E. Shchekotikhin was recruited to the Gause Research Institute of New Antibiotics of the Russian Academy of Medical Sciences, combining with the scientific and teaching activities at the Department of Organic Chemistry of the Mendeleev University of Chemical Technology of Russia.

The main direction of scientific work of this period was connected with derivatives of naphthoindolediones, as well as with the synthesis and biological properties of other heterocyclic derivatives of anthraquinone, analogs of 5,12-naphthacenequinone. Thus, original schemes for the conversion of a number of naphthoindolediones containing various pharmacophoric groups, for example, to naphthoindole analogs of gramine [416], tryptophan, and tryptamine [417] have been developed. The main results of research in this line formed the basis of the doctoral dissertation "Synthesis, chemical properties and biological activity of heterocyclic analogs of 5,12-naphthacenequinone" (consultant Prof. M.N. Preobrazhenskaya) which was defended by A.E. Shchekotikhin in 2009.

After defending his doctoral dissertation, A.E. Shchekotikhin continued his work as a professor at the Department of Organic Chemistry of the Mendeleev University of Chemical Technology of Russia, and in 2013 was elected to the position of head of the department. In 2015 he becomes deputy director of the Gause Research Institute of New Antibiotics. He successfully solved a number of complex problems related to structure determination and elucidation of mechanisms of action that inevitably arise in the study of new biologically active compounds (for example, hetarenoanthracenedione derivatives, heliomycin, oligomycin, olivomycin, glycopeptides, quinoxaline

dioxides). On the basis of hetarenoanthracenediones he developed the original chemotype of antitumor ligands for nucleic acid G-quadruplexes [418], which made it possible to discover a new mechanism of regulation of expression of genes having quadruplexes in promoter domains [419].

In 2013, the Department of Organic Chemistry switched to teaching in the framework of a two-level system of higher education (bachelor's-master's program). A.E. Shchekotikhin developed or revised in accordance with the new educational standards a number of courses currently taught to students and post-graduate students of the Mendeleev University of Chemical Technology of Russia and Gauze Research Institute of New Antibiotics Development: "Chemistry of Hydrocarbons," "Chemistry of Functional Derivatives of Hydrocarbons," "Methods of Modern Organic Synthesis," "Biochemistry," "Dynamic Biochemistry," and "Bioorganic Chemistry."

Throughout the almost century-long history, the Department of Organic Chemistry of the Mendeleev University of Chemical Technology of Russia was closely related by a system of "genealogical" and scientific ties with the leading educational and research universities in Russia, which undoubtedly played the key role in the formation of its scientific and pedagogical school. Over the years, the department has trained a galaxy of outstanding organic chemists, both known in Russia and recognized abroad. Now the Department of Organic Chemistry of the Mendeleev University of Chemical Technology of Russia remains one of the leading ones in the Mendeleev University and among similar departments of other Russian universities.

## 4.5. History of the Department of Organic Chemistry in the Peoples' Friendship University of Russia

The Department of Organic Chemistry of the Peoples' Friendship University of Russia (PFUR,



formerly Patrice Lumumba University of Peoples' Friendship) was founded in 1960 at the Faculty of Physical, Mathematical, and Natural Sciences. The founder of the department was a student of Academician I.N. Nazarov, Honored Scientist of

Russia, Doctor of Chemical Sciences, Professor Nikolai Sergeevich Prostakov.

While still a post-graduate student, N.S. Prostakov, together with academicians N.I. Nazarov and

M.F. Mashkovskii, developed the synthesis of the

participated in the creation of promedol. This drug is still extensively used in medical practice. Promedol is currently produced in India by the Rusan Pharma pharmaceutical company which is headed by Dr. Navin



Saxena (India), a student of professors N.S. Prostakov and A.V. Varlamov [420, 421].

Professor N.S. Prostakov headed the department for 29 years; in 1989 he was succeeded by his disciple, professor **Aleksei Vasil'evich Varlamov**, Honored

Worker of the Higher School of the Russian Federation A.V. Varlamov is one of the creators of the school of heterocyclic chemists of the PFUR. A.V. Varlamov headed the department for 27 years. Under his leadership, the department continued to actively develop. During this time, more than 100 candidate's and doc-



toral dissertations in chemistry were defended.

Since 2016 the department is headed by the student of A.V. Varlamov, Professor Leonid Gennad'evich

Voskresenskii, a graduate of the Department of Organic Chemistry of the Peoples' Friendship University of Russia, Doctor of Chemical Sciences, member of the International Society of Heterocyclic Compounds, Professor of the Russian Academy of Sciences, Deputy Editor-in-Chief of the Journal



*Khimiya geterotsiklicheskikh sordinenii* (Chemistry of Heterocyclic Compounds), visiting lecturer of the Ghent, Bari, and Cardiff universities.

The Department of Organic Chemistry is a graduate department which trains synthetic chemists specializing in the field of chemistry of heterocyclic compounds. Over the entire period of the existence of the post-graduate school at the Department of Organic Chemistry, 120 people, including 46 post-graduate students from countries of Africa, Asia and Latin America, have finished it. Most of all, candidates of chemical sciences were trained for India. The first candidate's dissertations were defended at the department in 1965, and the first candidates of chemical sciences were **L.A. Gaivoronskaya** (who was for a long time one of the leading lecturers at the department) and **Mani Phal-humani** (India), who became director of a textile institute in Delhi.

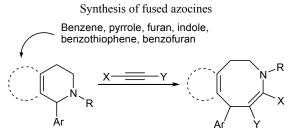
Five doctors of chemical sciences were trained at the department: Anatolii Timofeevich Soldatenkov (1984), Aleksei Vasil'evich Varlamov (1985), Valentin Petrovich Zvolinskii (1994), Vladimir Valentinovich Kuznetsov (1994), and Leonid Gennad'evich Voskresenskii (2009); the latter is now dean of the Faculty of Physics and Mathematics and Natural Sciences of the PFUR.

In the initial period, the research work at the department was related to the development of a method for the synthesis of pyridines from  $\gamma$ -piperidols via catalytic dehydrogenation and N-demethylation over a dehydrogenation catalyst. The first pyridine obtained by this method was 2,5-dimethyl-4-phenylpyridine [422, 423]. Later it was found that in the presence of the same catalyst but at a higher temperature this compound is converted to 3-methyl-2-azafluorene, the first known fused tricyclic aza heterocycle. Employees of the department (associate professors S.A. Soldatov, V.G. Pleshakov, V.P. Shalimov, A.P. Krapivko, senior lecturer O.I. Sorokin, and researchers B.N. Anisimov and A.A. Obynochnyi) developed new methods for the synthesis of azafluorenes with a specified structure. 4-Azafluorene derivatives were synthesized from 3-methyl-2-phenylpyridine (Prof. A.V. Varlamov). Professor A.T. Soldatenkov synthesized 3-azafluorene and 1-azafluorene derivatives by dehydrocyclization of 3-methyl-4-phenylpyridine and 1-methyl-2-phenylpyridine over a commercial calcium phosphate catalyst [424-426].

The alkaloid onychine (1-methyl-4-azafluorenone) was synthesized at the Department of Organic Chemistry; a few years before it was discovered in nature. Benzo[*a*]isoquinolines (associate professor L.M. Kirillova) and dihydro-10-sila-2-azaanthracenes (professor A.V. Varlamov) were obtained by catalytic dehydrocyclization of 4-benzyl- and 4-triphenyl(dimethylphenyl, diphenylmethyl)silylpyridines,. Employees and postgraduate students of the department carried out basic studies of chemical transformations of these heterocyclic systems.

The chemistry of silaazaanthracenes was studied for the first time, and their various derivatives both at the methylene group and at the pyridine ring were obtained, in particular benzopyridosilazepines, dihydrosilanaphthoindolizines, and dihydrosilazaazaaceanthrylenes [427–429].

The first Trofimov reaction in the series of aza heterocycles was studied using 1,2,5-trimethylpiperidin-4-one oxime as an example. In addition to the expected tetrahydropyrrolo[3,2-c]pyridines, pyrrolopyrimidines were isolated for the first time, and a skeletal rearrangement was revealed. Study of the transformations of tetrahydropyrrolo[3,2-c]pyridines led to the discovery of a new two-carbon ring expansion reaction of fused tetrahydropyridines and azepines with a tertiary nitrogen atom under the action of activated alkynes (professors A.V. Varlamov and L.G. Voskresenskii, associate professors T.N. Borisova and E.A. Sorokina, and senior lecturers L.N. Kulikova, A.V. Listratova, and A.A. Titov). Over a decade, this method was used to synthesize numerous azocines fused to pyrrole, thiophene, pyridine, indole, benzothiophene, benzofuran, pyrimidine, and benzene rings. The mechanism of this reaction with other fused nitrogen-containing systems is still the subject of research at the department [430-432].



X = H, COMe, COOMe; Y = COOMe.

Recently, new methods for the synthesis of 3,4-dihydropyrrolo[2,1-*a*]isoquinolines via domino reactions of 1-aroyl-substituted 3,4-dihydroisoquinolines with activated alkenes and alkynes have been developed (associate professor T.N. Borisova). Several interesting and promising research areas are associated with the synthesis of spiro aza heterocycles and fused epoxy indoles (Professor V.V. Kuznetsov, associate professor F.I. Zubkov). Tandem reactions of furfurylallylamines and heterocycles with a furfuryl fragment at the  $\alpha$ -position with respect to the nitrogen atom with  $\alpha,\beta$ -unsaturated acid anhydrides and halides formed the basis for the preparation of furoindoles and their fused derivatives with nitrogen heterocycles (associate professors F.I. Zubkov and V.P. Zaitsev) [433–437].

New directions in the scientific work of the department are domino reactions of quaternary salts and multicomponent syntheses of fused chromenoimid-

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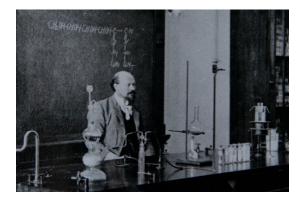
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azoles and chromenoisoquinolines (Prof. L.G. Voskresenskii, senior lecturers A.A. Festa and N.E. Golantsov) [438, 439].

Since 2012, the department organizes every two years all-Russian scientific conferences with international participation "Advances in Synthesis and Complexing." In 2017 the conference changed its status and became international. More than 300 chemists from 15 countries took part in the conference. The conferences held in 2012 and 2017 were dedicated to the 95th and 100th anniversary of Professor N.S. Prostakov. Such world-leading heterocyclic chemists as professors C. Altomare (Italy), A. Malkov (Great Britain), T. Muller (Germany), V. Gevorgyan (USA), and L. Tietze (Germany) took part in the conference.

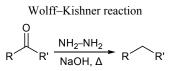
## 5. DEPARTMENT OF BIOTECHNOLOGY AND ORGANIC CHEMISTRY OF THE TOMSK NATIONAL RESEARCH POLYTECHNIC UNIVERSITY

The Department of Biotechnology and Organic Chemistry is one of the oldest departments of the Tomsk Polytechnic University. It received its modern name in 2011, having become the successor of the departments of organic chemistry and technology of organic synthesis which were unified in 1979. The Department of Organic Chemistry of the Tomsk Technological Institute was founded in 1901. It became the first scientific and educational center in the field of organic chemistry in the vast territory of Russia from the Urals to the Far East. The department was founded and headed by Professor Nikolai Matveevich Kischner, a disciple of the outstanding Russian organic chemist V.V. Markovnikov [440]. The main scientific direction since the foundation of the department was fine organic synthesis. Within the walls of the high-grade (at that time) laboratory,



N.M. Kishner reads a lecture in the small chemical lecture room of the IInd building of the Tomsk Polytechnic University

N.M. Kishner made several major discoveries, including two new reactions which were later named after him and included in all textbooks of organic chemistry. These are the Kishner reaction (synthesis of cyclopropanes by thermal decomposition of dihydropyrazoles) and Wolff–Kishner reaction (reduction of the aldehyde or ketone carbonyl group to methylene group by heating the corresponding hydrazone in the presence of strong bases; see also Section 4.1). Professor N.M. Kishner headed the department from 1901 to 1913.



An outstanding Russian chemist **Nikolai Nikolaevich Vorozhtsov** worked from 1904 to 1912 as a senior laboratory assistant in the laboratory of N.M. Kishner. N.N. Vorozhtsov is considered one of the founders of the national school of dye chemistry and is the author of



the repeatedly reprinted monograph "Fundamentals of the Synthesis of Intermediate Products and Dyes." Professor N.N. Vorozhtsov was awarded the Stalin Prize.

From 1913 to 1924 the department was headed by a student of D.I Mendeleev, Honored Worker of

Science and Technology, Professor **Yakov Ivanovich Mikhailenko**. He was one of the first in Russia to develop a course of lectures and a textbook of organic chemistry on the basis of electronic representations. During the First World War, he organized several military chemical plants in Siberia. He was twice



elected dean of the chemical faculty and for a long time was rector of the Tomsk Technological Institute.

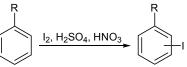
From 1924 to 1960, the department was headed by one of the founders of the Siberian School of Organic Chemists, an outstanding scientist, professor, honored worker of science of the USSR **Boris Vladimirovich Tronov**. Over this period, the department has trained more than 30 doctors and candidates



of sciences (L.P. Kulev, A.N. Novikov, L.A. Pershina, E.B. Merkushev, etc.). Having been started in the mid-1930s, works on the determination of the rate of oxidation of organic compounds became purposeful; in particular, the theory of coal oxidation was developed and factors responsible for spontaneous combustion of coals were elucidated. During the Great Patriotic War, the results of these studies have underlain the industrial method of obtaining substitutes for petroleum products. At the same time, the chemistry of organic complexes and mechanisms of organic reactions became other areas of B.V. Tronov's research.

In the early 1950s, B.V.Tronov and his student A.N. Novikov discovered a simple and convenient method for the synthesis of aromatic iodine derivatives, which was called the Tronov–Novikov method [441]. In subsequent years, a number of other reagents for effective electrophilic iodination of arenes and some heterocycles, for example, 2,4,6,8-tetraiodo-glycoluril [442] and Alk<sub>4</sub>N<sup>+</sup>ICl<sub>2</sub> [443], were developed at the department.

# Tronov-Novikov reaction





In 1960, after the departure of B.V. Tronov from Tomsk, the department was headed by his disciple, Professor **Avtonomii Nikolaevich Novikov**. He remained head of the department until 1984.

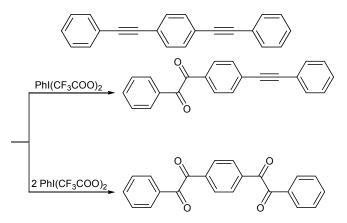


Another outstanding student of B.V. Tronov is professor, laureate of the State Prize **Leonid Petrovich Kulev**. In 1943 he organized a new department of rubber technology in the Tomsk University, which later transformed to the Department of Technology of Organic Synthesis. Being a versatile and talented scien-

tist, L.P. Kulev created in the institute new scientific directions such as chemistry and technology of biologically active compounds, dye chemistry, coke chemistry, and polymer chemistry. The last two directions were allocated to the Department of Technology of Basic Organic Synthesis. L.P. Kulev headed the Department of Technology of Organic Synthesis from 1943 to 1962.

During this period, the research carried out at the department was initially of defense insignificance and was related to identification and degassing of chemical warfare agents; subsequently, extensive and successful work was performed on the synthesis of new medicines. L.P. Kulev together with the employees created effective domestic drugs for the treatment of epilepsy (benzonal and benzobamil). In 1962, after the death of L.P. Kulev, the department was headed by his student, associate professor **Aleksei Grigor'evich Pechenkin**.

In 1979, both departments (organic chemistry and technology of organic synthesis) were combined. The head of the united Department of Organic Chemistry and Technology of Organic Synthesis was Professor A.N. Novikov. The main subject of research was synthesis and properties of iodine-containing aromatic compounds. His student, Professor E.B. Merkushev is one of the pioneers in the field of organic compounds of polyvalent iodine. In particular, he developed a convenient method for the synthesis of aryl iodoso carboxylates. He showed for the first time that [bis-(trifluoroacetoxy)- $\lambda^3$ -iodanyl]benzene in boiling chloroform or carbon tetrachloride selectively oxidizes acetylenic bonds to 1,2-dicarbonyl functionality [444]. Later on, oxidation of double and triple bonds in unsaturated compounds to 1,2-diketones under the action of DMSO in the presence of HBr, I2, or PdCl2 was also discovered at the department [445].

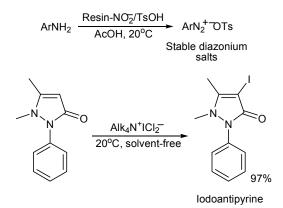


From 1984 to 2014, the Department of Organic Chemistry and Technology of Organic Synthesis was headed by **Viktor Dmitrievich Filimonov**, Honored Chemist of the Russian Federation, Honored Worker of Higher Education, Doctor of Chemical Sciences, author of more than 350 scientific works, including the monograph "Chemistry of Carbazole-Based



Monomers"; more than 20 candidate's dissertations and 5 doctoral dissertations were defended at the department under his guidance. During this period, the scientific directions historically formed of the department continued to develop; in addition, new research lines such as methods and reagents [446], in-

cluding those for "green chemistry" [447], study of mechanisms and reactivity using theoretical quantum chemical methods [448], and design of new medicines and materials for medical purposes were created. V.D. Filimonov was one of the organizers of the candidate's and doctoral dissertational council in the specialties "Organic chemistry" and "Analytical chemistry." At present, V.D. Filimonov is a professor at the Department of Biotechnology and Organic Chemistry.





From 2014 to the present time, the Department of Biotechnology and Organic Chemistry is headed by Doctor of Chemical Sciences Elena Aleksandrovna Krasnokutskaya, a graduate of the department and a student of V.D. Filimonov.

More than 60 years (since 1949), the department trains engineering personnel for pharmaceutical industry, namely chemical technologists and biotechnologists. Over 2000 specialists have been trained during this period. Currently, the department trains engineers on the following educational programs: "Biotechnology" (bachelor's and master's degrees), "Chemistry and Technology of Biologically Active Substances" (magistracy), "Organic Chemistry" (postgraduate and doctoral studies). In 2015, the educational program "Biotechnology" (bachelor's) was accredited by the Association of Engineering Education of Russia and by the EUR-ACE Framework Standards for the Accreditation of Engineering Programs. Students and postgraduates from Germany, France, the Czech Republic, China, and Vietnam were trained and interned at the department. The department implements programs of advanced training and retraining for employees of pharmaceutical enterprises in the areas of "Biotechnology" and "Chemistry and Technology of Biologically Active Substances," including those within the framework of the Presidential Program "Advanced Training of Engineering and Technical Personnel" (2014, 2014, 2016).

Nowadays, the staff of the department consists of 7 doctors of sciences (E.A. Krasnokutskaya, I.V. Mil'to, A.S. Potapov, V.Yu. Serebrov, M.E. Trusova, V.D. Filimonov, and A.I. Khlebnikov) and 9 candidates of sciences. The department has trained more than 25 doctors of sciences and more than 100 candidates of sciences.

# 6. DEPARTMENT OF ORGANIC CHEMISTRY IN THE PERM STATE UNIVERSITY

The **Perm branch of the Imperial Petrograd University** was founded in 1916. The University of Perm, which initiated higher education in the Urals, began its activity on October 1 (14), 1916. In the first year, 32 departments were established at the university, including the Department of Chemistry. In 1917 the Perm branch of the Petrograd University was transformed into the **Perm University** consisting of four faculties: historical–philological, physico-mathematical, law, and medical [449].

In January 1918, Yulii Sigizmundovich Zal'kind came from Petrograd and founded the Department of Organic Chemistry whose staff was

represented by only 2 people, Yu.S. Zal'kind and the assistant G.A. Arbuzov who came with him. On February 23, 1918, Yu.S. Zal'kind read the introductory lecture "Modern Problems of Organic Chemistry." Later he lectured, and G.A. Arbuzov conducted seminars.



Gradual arrangement and equipment of the Department of Organic Chemistry began, for which the resources of local pharmacies, drug stores, and various Perm laboratories were used. In addition, the staff of the department traveled to Moscow, Petrograd, and other cities of the country to purchase various equipment, reagents, and glassware. At the suggestion of the



Perm University. The chemical building is located on the left (late 1910s).

university commission, Y.S. Zal'kind began to prepare the course of his lectures on organic chemistry for publication, but because of the Civil War his book "Lectures on Organic Chemistry. Part 1. Open-Chain Organic Compounds" was published only in the autumn of 1920.

From July 1919 to September 1920 the department, like the whole university, did not work due to the evacuation to Tomsk on the orders of Kolchak. After the return of the university to Perm, the Department of Organic Chemistry appeared in a very difficult situation. During the evacuation almost all equipment and other facilities were lost, and the work of the department had to be restored from scratch [450].

In December 1920 **Tat'yana Ivanovna Temnikova** was admitted to the department; at that time she was a student of the chemical department of the Faculty of Physics and Mathematics. The main load of the material and technical support of the department fell on her. In addition, T.I. Temnikova led the practical work of students. Despite the small number of employees (only three people) and the large training load for teaching students of four faculties, the department also carried out scientific work, in particular, G.A. Arbuzov studied chemical properties of acetylenic glycols. He also attracted T.I. Temnikova to these studies, and she studied the action of potassium hydroxide on  $\gamma$ -glycols of the acetylene series.

In early 1921, Yu.S. Zal'kind left the Perm University because of his election as a professor at the Second Petrograd Polytechnic Institute. Subsequently, he worked as head of the Department of Organic Chemistry of the Herzen State Pedagogical Institute (1929– 1948), and since 1934, also headed the Department of Organic Chemistry of the Leningrad Institute of Technology. He was editor of the Journal of General Chemistry and author of a number of articles and textbooks.

The department of organic chemistry was then headed by G.A. Arbuzov. However, in August 1922 he moved to Moscow, and Professor D.V. Alekseev became part-time head of the department. Finally, in May 1923, the department was headed by Professor

Andrei Ivanovich Lun'yak (also as part-time head). While working in Perm, A.I. Lun'yak was dean of the agricultural and forestry (1918–1919), physico-mathematical (1920–1921), and medical faculties (1921–1922) and head of the scientific and educational part (1922–1924). Despite the short period of leader-



ship of the Department of Organic Chemistry, A.I. Lun'yak succeeded in repairing and equipping the laboratory of organic chemistry, and the equipment and glassware were purchased abroad. In 1924, A.I. Lun'yak moved to Kazan, where he became a professor and then rector of the Kazan University.

Because of frequent change of the chairmen of the department (by 1928 there were six heads of the department replaced, most of whom were part-time workers), neither full-fledged scientific work nor formation of a single scientific direction was possible. In addition, the academic load of the department in this period reached a large scale, since the department had to teach organic chemistry at all faculties of the Perm



State University. The situation at the department began to gradually stabilize only in 1928, when the department was headed by professor of the Kazan University **Dmitrii Mil'tiadovich Marko**.

Immediately upon his arrival in Perm, D.M. Marko started extensive work on organizing and equipping the laboratory of organic chemistry. In particular, he purchased new laboratory equipment, mainly imported. There were valuable optical instruments, electric furnaces for elemental analysis, vacuum pumps, etc. In the spring of 1929, D.M. Marko performed the first analyses of the Verkhne-Chusovskava oil discovered near Perm. He organized an oil department at the laboratory of organic chemistry, the task of which was to service the Ural oil exploration. The name of D.M. Marko in Perm University is primarily connected with significant improvement of the educational process at the Department of Organic Chemistry. Thanks to him, the general course of organic chemistry was expanded, and new courses were introduced: "Theoretical Foundations of Organic Chemistry," "Stereochemistry," "Methods for Determination of the Structure of Organic Compounds," "Organic Analysis," and "Chemical Technology of Organic Production." Scientific research work began to revive at the department.

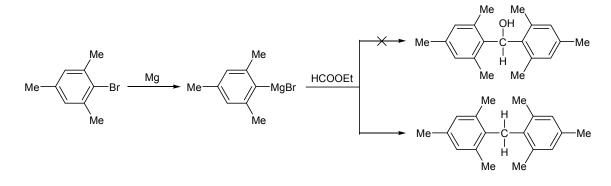
Due to rapid development of chemical industry in the Urals in 1929, it was decided to transform the Chemical and Pharmaceutical Department of the Medical Faculty of the Perm State University into the Faculty of Chemistry. The first dean of the Faculty of Chemistry was Nikolai Ivanovich Kromer. In 1929 the staff of the faculty consisted of two professors, one assistant professor, one senior assistant, and four junior assistants. Five postgraduate students were trained. **Tat'yana Ivanovna Temnikova** took an active part as an assistant in the work of the department during this period (subsequently she became the famous Soviet organic chemist; see also Section 3). In December 1931, she left the university and went to Leningrad. Subsequently, T.I. Temnikova headed the department of the structure of organic compounds of the Leningrad State University, organized the first in the country department of physical organic chemistry, and wrote the textbook "The Course of Theoretical Foundations of Organic Chemistry" and a number of other books.

In the summer of 1930, the laboratory of organic chemistry, together with other chemical laboratories of the Faculty of Chemistry, was transferred to the relevant department of the Perm Institute of Chemical Technology, and an insignificant part of its equipment was given to the educational pedagogical institute. On June 1, 1930, Professor D.M. Marko was transferred to the post of head of the Department of Organic Chemistry of the Perm Institute of Chemical Technology.

The first dean of the Faculty of Chemistry (revived in 1933), was a graduate of the Kazan University, **Ivan Ivanovich Lapkin**, who came to Perm from Grozny in 1930. The research work of the department in the early 1930s was mainly related to the Ural oil. However, this subject did not receive further development at the department.



The most relevant topics of scientific research carried out at the department in the mid-1930s were associated with secondary and tertiary alcohols of the aromatic and furan series, synthesis and structure of naphthenic acids, iodination of aromatic compounds, essential oils, brown coals from the Komi–Permyak District, and improvement of the gasoline quality. Since the second half of the 1930s, the department has been trying to find a new scientific direction that would unite the efforts of the entire team and determine its scientific face. In 1940, I.I. Lapkin in coauthorship with the graduates of the Faculty of Chemistry V.S. Shklyaev (later doctor of chemical



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

sciences, professor, rector of the Perm Pharmaceutical Institute, head of the laboratory of the Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences) and. T.I. Shklyaeva published an article on organomagnesium compounds (specifically, on steric effects in the Grignard reactions) in the Russian Journal of General Chemistry. It was shown that the reaction of mesitylmagnesium bromide with ethyl formate gives dimesitylmethane instead of the expected dimesitylcarbinol. This publication initiated a new scientific direction of the department, studies in the field of chemistry of organoelement compounds.

After the Great Patriotic War, the number of students enrolling in the Faculty of Chemistry increased, and lecturers from other universities in Perm were attracted to the teaching process. In particular, Professor Nikolai Semenovich Kozlov, later Academician of the Academy of Sciences of the BSSR, Director of the Institute of Physical Organic Chemistry of the Academy of Sciences of the BSSR (1967-1972). head of the Laboratory of Organic Catalysis of the Institute of Physical Organic Chemistry of the Academy of Sciences of the BSSR (since 1973) came to the department. N.S. Kozlov was the author of 7 monographs, 810 scientific articles, and 200 inventor's certificates for new methods of synthesis of organic compounds, highly efficient reforming catalysts, and biologically active compounds; 54 doctoral and candidate's dissertations were carried out under his guidance [451].

In the postwar years, the scientific theme of the department was finally determined as the chemistry of

organoelement compounds. Under the leadership of I.I. Lapkin, L.V. Lyubimov, A.I. Golovkov, and O.M. Lapkina began to work in this direction. The results of the research in this line led I.I. Lapkin to defend doctoral dissertation "Steric Inhibition in Organomagnesium Reactions" at the Kazan University in 1948. In 1951, D.M. Marko, after retiring, transferred the management of the Department of Organic Chemistry to I.I. Lapkin.

In the 1950s, the work of the department developed in several directions. Much was achieved in the synthesis of esters, so that some difficultly accessible compounds became readily accessible. A method for controlling organometallic reactions by adding a third component was developed. The relation between the "geometry" and chemical reactivity was studied, and it was shown that less active groups are involved in certain reactions more easily due to their smaller molecular volume.

In the mid-1950s, I.I. Lapkin initiated study of the chemistry of haloalcoholates. The subjects of the research were thermal stability of metal haloalcoholates and their chemical transformations. Knowledge of the thermal and chemical behaviors of these compounds made it possible to predict the reaction course under different conditions and, what is the most important, to control them.

In 1958, post-graduate courses were organized at the department. Since the early 1960s, research has begun in the field of organosilicon compounds, and then of organotin compounds. During this period, the chemistry of ethers and esters was also extensively



Teaching staff of the Department of Organic Chemistry (mid-1960s). Standing (from left to right): Z.D. Belykh, N.V. Bogoslovskii, I.S. Rogozhnikova, V.A. Dumler, Yu.V. Ionov, G.A. Yuzhakova, E.V. Dormidontova, N.V. Efstafeeva. Sitting (from left to right): L.D. Orlova, R.G. Mukhina, I.S. Berdinskii, I.I. Lapkin, V.P. Zhivopistsev, M.N. Rybakova, M.I. Belanovich.

studied. Since 1965, syntheses with organozinc compounds have been systematically developed, and studies initiated by scientists of the Kazan Chemical School were continued. In particular, a new class of organozinc compounds, halozinc ketones, was discovered.

I.I. Lapkin worked at the Perm State University for more than 60 years (1930–1993). For 9 years he was vice-rector for scientific work (1958–1967), for 13 years (1933–1936 and 1948–1958) headed the Department of Chemistry, and for 40 years (1951– 1991) headed the Department of Organic Chemistry. Three doctoral and 50 candidate's dissertations were defended under his leadership. I.I. Lapkin is author and co-author of about 500 articles, two monographs, and more than two hundred inventor's certificates.

A prominent student in the history of the Department of Organic Chemistry of the Perm University was a graduate of the Faculty of Chemistry (1941) Ivan Ivanovich Berdinskii. In April 1970 he defended his doctoral dissertation "Arylhydrazides of disubstituted glycolic acids" and then (1970-1972) worked as professor at the Department of Organic Chemistry of the Perm State University. In 1973, I.I. Berdinskii headed and until 1987 supervised the Department of Chemistry of Natural and Biologically Active Compounds created by him. To this end, he developed new training programs and new lecture courses and modernized student's practicum. During his work at the Faculty of Chemistry, he prepared 16 candidates of chemical sciences, including Ya.M. Vilenchik, N.N. Machulenko, O.P. Pilipenko, N.A. Asanova, L.N. Krasnova, E.Yu. Posyagina, L.S. Nikulina, G.S. Posyagin, and others. He is author of 241 articles, 62 USSR inventor's certificates, and the monograph "Pharmacology and Chemistry of Hydrazine Derivatives" (1976, together with V.E. Kolla).

In 1991, the Departments of Organic Chemistry was merged with the Department of Chemistry of



Natural and Biologically Active Compounds. The joint department was headed by Doctor of Chemical Sciences, Professor **Yurii** Sergeevich Andreichikov. In 1986 he defended his doctoral dissertation "Synthesis and chemical transformations of 5-aryl-2,3-dihydrofuran-2,3-

diones." Yu.S. Andreichikov introduced a new research line, the chem-istry of five-membered dioxo heterocycles. Studies in this field were continued by

S.N. Shurov, D.D. Nekrasov, V.V. Zalesov, and A.N. Maslivets [452]. Yu.S. Andreichikov was the creator and recognized leader of the school of heterocyclic chemists in the Western Urals and co-author of the monograph "Chemistry of Five-membered 2,3-Dioxo Heterocycles" (1994). Among his students there are 47 candidates of chemical or pharmaceutical sciences and 11 doctors of chemical sciences (A.N. Maslivets, V.V. Zalesov, D.D. Nekrasov, S.N. Shurov, I.V. Mashevskaya, etc.).

In the 1990s, new special courses were developed at the department: "Chemistry of heterocyclic compounds," "Modern problems of organic chemistry" (Yu.S. Andreichikov), "Quantum chemical methods for calculating organic molecules" (S.N. Shurov), and "Chemistry of five-membered dioxo heterocycles" (A.N. Maslivets). In addition, traditional research work of the department (chemistry of organoelement compounds) was continued to develop by associate professors Yu.P. Dormidontov and V.V. Shchepin and senior lecturer N.F. Kirillov.

In 1993, the faculty switched to a two-tier training system. Special courses "Solvents and solvent effects in organic chemistry," "Quantum chemical methods for calculating molecules of heterocyclic and organoelement compounds," "Quantum chemical modeling of organic reactions," "Fundamentals of computer chemistry" (S.N. Shurov), "Chemistry of polycarbonyl compounds," and "Methodology of synthesis of complex biologically active compounds" (A.N. Maslivets) have been developed for the magistracy opened at the department.

In February 1998, after the death of Yu.S. Andreichikov, the Department of Organic Chemistry was headed by Professor **Vasilii Viktrovich Shchepin** whose field of scientific interests was the synthesis of organic compounds using organozinc, organomagnesium, and organosilicon intermediates [463].

In 2001, the Department of Natural and Biologically Active Compounds was organized once again at the Faculty of Chemistry in connection with the arrival in Perm of Corresponding Member of the Russian Academy of Sciences **A.G. Tolstikov**, who also headed the Institute of Technical Chemistry.

In 2007, **S.N. Shurov**, a student of Yu.S. Andreichikov, was elected the head of the Department of Organic Chemistry. In 2003 he defended his doctoral dissertation "Study of the reaction of 5-substituted 2,3-dihydrofuran-2,3-diones with compounds containing activated C=X bonds." In 2006, **I.V. Mashevskaya** 





S.N. Shurov

I.V. Mashevskaya

defended her doctoral dissertation, and in 2007 she became a professor in the Department of Organic Chemistry. Since 2013 she was dean of the Faculty of Chemistry of the Perm State National Research University [454].

Since June 2017, the Department of Organic Chemistry is headed by Prof. A.N. Maslivets. His



research interests include methods of synthesis of acyclic and heterocyclic compounds on the basis of dioxo heterocycles and polycarbonyl compounds, chemistry of acyl heterocumulenes, de- and recyclization reactions, and cycloadditions. A.N. Maslivets is the most quoted scientist of the university. Currently,

6 doctors of sciences (A.N. Maslivets, I.V. Mashevskaya, S.N. Shurov, G.G. Abashev, N.E. Shchepina, and Yu.V. Shklyaev) and 6 candidates of sciences work at the Department of Organic Chemistry. The staff of the department performs research work in the following areas:

(1) Development of methods for directed synthesis of complex biologically active molecules on the basis of transformations of dioxo heterocycles and polycarbonyl compounds (A.N. Maslivets, I.V. Mashevskaya, S.N. Shurov);

(2) Development of methods for directed synthesis of complex acyclic and heterocyclic molecules on the basis of Reformatskii's reaction (N.F. Kirillov, E.A. Nikiforova);

(3) Development of methods for the synthesis of functionalized polymers and monomers, including those possessing superconducting properties (G.G. Abashev, E.V. Shklyaeva);

(4) Study of the structure and reactivity of organic compounds by quantum chemical methods (S.N. Shurov, A.N. Vasyanin).

In January 2018, the Department of Organic Chemistry of the Perm State National Research University will celebrate its 100th anniversary.

### 7. HISTORY OF ORGANIC CHEMISTRY IN IVANOVO

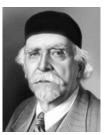
# 7.1. Organic Chemistry in Ivanovo until 1930

The university course of organic chemistry in the Ivanovo-Voznesensk Polytechnic Institute (IVPI) was read for the first time in the 1918/1919 academic year by the outstanding Russian chemist, Academician **Vladimir Nikolaevich Ipat'ev** (1867–1952), with the assistance of **Ivan Ivanovich Zaslavskii** (1889–1973). Academician **N.D. Zelinskii** also took part in reading the course.





I.I. Zaslavskii



V.N. Ipat'ev

N.D. Zelinskii

The Ivanovo-Voznesensk Polytechnic Institute was the first higher school organized in Soviet Russia (the decree of the Council of People's Commissars was signed by V.I. Lenin on August 10, 1918). It was created largely on the basis of the Riga Polytechnic Institute (RPI) evacuated during the First World War in Moscow, where the educational process was conducted in classrooms and laboratories of various higher schools. After the Brest-Litovsk Peace Treaty, Germany demanded the return of the RPI with all property to Riga, but most students and a part of professors refused to move. As a result, on the initiative of the former deputy of the Ivanovo-Voznesensk Duma Ivan Ivanovich Vlasov (1880-1943), a lawyer graduated from the Moscow State University, it was decided to follow the proposal of Mikhail Vasil'evich Frunze (1885–1925), who was the first governor of the newly created Ivanovo-Voznesensk province, to move the RPI to Ivanovo.

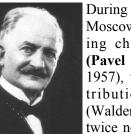
Just over 70 days (!) have passed since the signing of the decree before the beginning of classes (October 22, 1918; for more details on the foundation of the Ivanovo-Voznesensk Polytechnic Institute, see [455]). **Mikhail Nikolaevich Berlov** (1867– 1935) became the first rector of the institute.



1370

The RPI was built by the type of higher technical schools in Germany and Switzerland, which were aimed at producing specialists capable of solving everyday engineering tasks. Therefore, the applied aspect of scientific research in the RPI has received much attention. The experience of the RPI, which was a private higher education institution (!) with a state's share in financing of no higher than 25%, was used by the Ministry of Education of the Empire for the creation of Polytechnic Institutes in Tomsk (1896), Kiev and Warsaw (1898), St. Petersburg (1899), and Novocherkassk (1907).

Among the chemists working in the RPI, it is especially necessary to note **Wilhelm Friedrich Ostwald** (1853–1932), Nobel Prize winner of 1909 for his work in the field of catalysis and the founder of the famous school of physical organic chemistry. N.D. Zelinskii (see above) was among the students of W. Ostwald; however, it was in Leipzig.



During the evacuation of the RPI to Moscow, its rector was an outstanding chemist, Academician **Paul** (Pavel Ivanovich) Walden (1863– 1957), who made a significant contribution to organic chemistry (Walden inversion). P. Walden was twice nominated for the Nobel Prize

(in 1913 and 1914); he was in charge of the Laboratory of Physical Chemistry of the Academy of Sciences, founded back in 1748 by M.V. Lomonosov.

Ivan Ivanovich Zaslavskii (1889–1973) was a student of P. Walden. In 1916, he graduated with honors from the Riga Polytechnic Institute, and in the 1918/1919 academic year he had happened to help Academician V.I. Ipat'ev in reading the course of organic chemistry. Laboratory works were conducted by the senior assistant of the Department of Technical and Organic Chemistry Mikhail Ivanovich Sladkov, who later became the first head of the Department of Organic Chemistry of the IVPI.

Taking advantage of the geographical proximity from Moscow, the administration of the IVPI and the authorities of Ivanovo-Voznesensk organized lecturing of outstanding scientists in a simple but very effective way: a "professorial" soft car was running between the cities, and the lecturers lived therein while working in the IVPI.

This was the start of the development of organic chemistry in Ivanovo-Voznesensk. In 1929–1930, the IVPI was divided into 4 independent higher schools.

On the basis of the Faculty of Chemistry of the IVPI, the Ivanovo Institute of Chemistry and Technology was founded (subsequently the Academy, and now the Ivanovo State University of Chemistry and Technology).

#### 7.2. History of Organic Chemistry in the Ivanovo State University of Chemistry and Technology

The Department of Organic Chemistry of the Ivanovo State University of Chemistry and Technology is of the same age as the IVPI. Until 1930, the department was located on the first floor of the socalled "Kuvaevskii Corps," where it had four rooms with a total area of  $180 \text{ m}^2$ , including a student preparative laboratory for 16 workplaces and two offices. In those years the laboratory had neither exhaust ventilation nor gas. Students worked on Primus stoves (mostly their own). Nevertheless, scientific research was carried out at the department under these difficult conditions. Thus, in 1926 three works on the chemistry of pyrrole were published in German journals (N.A Naryshkin co-authored with T.N. Godnev). Tikhon Nikolaevich Godnev received the title of professor in the IVPI; in 1927 he moved to Belarus where in 1940 he was elected a full member of the Academy of Sciences of the BSSR. He was rightfully recognized as the founder of the Soviet scientific school on the biosynthesis of chlorophyll [456].

The first head of the department was Mikhail Ivanovich Sladkov (1896-1943), who was elected in 1920 as associate professor of the department. In 1925 M.I. Sladkov, along with other lecturers of the IVPI (N.N. Vorozhtsov and N.P. Peskov), was invited to the position of professor at the Mendeleev Moscow Institute of Chemical Technology (now Mendeleev University of Chemical Technology of Russia) for "strengthening readable courses" [457]. He was also the scientific leader of Glavanil (later Research Institute of Organic Intermediate Products and Dyes) and the executive secretary of the editorial board of Zhurnal Khimicheskoi Promyshlennosti (Journal of the Chemical Industry). In 1937 he was repressed, thrice sentenced to be shot (shot in 1943), and posthumously rehabilitated. In 1922 his son Aleksei Mikhailovich Sladkov was born In Ivanovo; he discovered carbyne, the third allotrope of carbon [458].

In 1925, **Evgenii Alekseevich Shilov** was appointed to read the course of organic chemistry and manage the organic laboratory of the Faculty of Chemistry of the IVPI; he had worked at the Institute for 28 years,



including 22 years at the Department of Organic Chemistry [459]. He passed from a junior assistant to a professor, doctor of chemical sciences, and corresponding and then full member of the Academy of Sciences of the Ukrainian SSR. E.A. Shilov stood at the beginnings

of the foundation of the Department of Organic Chemistry of the Ivanovo Institute of Chemistry and Technology, and he initiated systematic research work in the department, which made a significant contribution to the world science.

Scientific interests of E.A. Shilov were very wide. At the beginning of his scientific career in the IVPI in the 1920s, he studied terpenes [460], reactions of silver compounds with haloalkanes [461], and organomercury compounds [462] and developed analytical equipment (e.g., improved pipettes and burettes) [463]. In the 1950–1960s, he established the mechanism of some catalytic reactions modeling the action of enzymes and discovered precursors of carotene, fats, and rubber in the biosynthesis of green plants using radioactive isotopes [459].

However, E.A. Shilov achieved the real world fame due to his works on the mechanisms of organic heterolytic and catalytic reactions, which he started in the 1930s at the Department of Organic Chemistry of the Ivanovo Institute of Chemistry and Technology. While studying together with the staff of the department (G.V. Kupinskaya, S.M. Solodushenkov, N.P. Kanyaev) the hydrolysis of halogens [464-466] and the kinetics of their reactions with unsaturated compounds in aqueous solution, E.A. Shilov found out mechanisms of halogenation of C=C bonds in ethylene [467-469] and other olefins [470, 471], as well as of the chlorination of phenol [472] and other aromatic compounds [473]. The results of his studies enabled him to develop the theory of addition of electrophilic and nucleophilic agents to unsaturated compounds, reveal the role of solvents and solvate complexes in addition reactions, advance a hypothesis on the formation of  $\pi$  complexes by electrophilic reagents with multiple bonds of unsaturated compounds (long before their discovery by experimental methods), and introduce the concept of the formation of cyclic transition complexes (states) [474, 475]. The development of the cyclic transition state concept later led him to substantiate specific effect of bifunctional catalysts in organic reactions [476, 477]. In the 1950s, E.A. Shilov studied acetylene derivatives [478-481], discovered

nucleophilic addition of hydrogen halides to a triple bond, studied the effect of nucleophilicity of anions on the stereochemistry and regioselectivity of the addition, and revealed trimerization and polymerization of activated acetylenic compounds by the action of nucleophiles. He also studied stereochemistry and mechanism of reduction of acetylenic compounds with hydrogen in statu nascendi [482]. The active participation of E.A. Shilov in the development of the Russian chemical nomenclature should be noted [483, 484]. Working at the Institute of Information Technologies in the 1930s, E.A. Shilov together with his students S.I. Burmistrov, N.P. Kanyaev, A.I. Kobenin, S.I. Solodushenkov, G.V. Kupinskaya, and A.N. Kurakin developed theoretical basis for the solution of important national economic problems of that time, such as synthesis of rubber [485] and chlorine bleaching of cotton fabrics [486].

During the Great Patriotic War, the department switched to defense studies. Procedures for the synthesis of sulfathiazole and intermediate products for its preparation (chloroacetone, thiourea, and aminomethylthiazole) were developed, and medicines for the needs of the front were produced on a pilot plant at the department.

In 1945, E.A. Shilov was elected a member of the Academy of Sciences of the Ukrainian SSR, and in 1947 he moved to Kiev. The department was briefly headed by his student, associate professor N.P. Kanyaev, who studied mechanisms of halogenation of double bonds in aqueous solution [466–468, 470, 471, 474, 487–489]. In 1948, the head of the department was Doctor of Chemical Sciences, Professor Aleksandr Aleksandrovich Spryskov

(1904–1979) [490]. After graduating from the Faculty of Chemistry of the IVPI in 1929, he worked as a process engineer at the Rubezhnoe Chemical Factory, in 1932 he became a research fellow at the Institute of Chemical Technology, and, after defending his dissertation, from 1938 to 1948 he headed the



Department of Organic Chemistry of the Ivanovo State Medical Institute. It was at this time that he began intensive research on the sulfonation of aromatic compounds [491].

A.A. Spryskov paid much attention to the development of the department, whose staff increased from 20 people in 1967 to 34 in 1973, including 16 lecturers

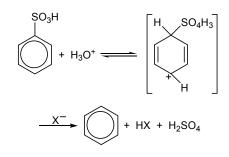


A.A. Spryskov reads a lecture on organic chemistry. Lecture assistant O.S. Ivanova (1952).

(in 1947 there were three). Teaching of organic chemistry was also improved. A large number of visual aids for the lecture course were prepared, and techniques of demonstration experiments for lectures were perfected.

The department was equipped with the most modern equipment for those times (gas-liquid chromatographs, instruments for organic microanalysis, UV spectrophotometer, thermostats, etc.), and in 1957 a radiochemical laboratory was organized at the department. All this allowed the staff of the department to perform under the leadership of A.A. Spryskov a series of fundamental works to elucidate details of the mechanism of electrophilic substitution in aromatic compounds, first of all, of sulfonation and protodesulfonation of arenes. The role of the works of A.A. Spryskov's school is best told by the memoirs of one of his students, Boris Grigor'evich Gnedin: "In the 60-70s, there were practically no book and no any review concerned in one or another way with the topic of sulfonation and desulfonation, where works of Aleksandr Aleksandrovich and his students were not mentioned ... A.A. Spryskov was always interested in not only (and not so much) "kitchen," but also the mechanism, i.e., essence of the processes under study. And this ultimately led him to discover the phenomenon of accumulation of thermodynamically most stable products in reaction mixtures when carrying out organic reactions... This principle was discovered by A.A. Spryskov by studying the formation and transformations of isomeric monosulfonic acids of the naphthalene series [492, 493] and was then extended to sulfonation of other aromatic compounds, ... reversible Friedel-Crafts acylation, high-temperature isomerization of di- and polyhalogenated (aromatic compounds) [494], and a number of other processes."

The priority of this discovery was confirmed by a number of authors [495]. A.A. Spryskov's works on the mechanism of desulfonation of aromatic sulfonic acids in aqueous solutions of strong acids (hydrolysis of sulfonic acids) were recognized as fundamentally important [496].



Not only fundamental research was carried out under the guidance of A.A. Spryskov. For example, in the early 1950s the sulfonation of copper phthalocyanine was studied at the request of the Zavolzhskii Chemical Plant [497], and the results of this study formed the basis for the technology for the manufacture of C.I. Direct Blue 86. Phthalocyanines became one of the main subjects of study at the Department of Organic Chemistry after retirement of A.A. Spryskov in 1973 (see below).

A.A. Spryskov is author of more than 250 publications [490] and several dozen inventions; he supervised 19 candidate's dissertations. Five of his students continued research begun under his direction and later defended their doctoral dissertations in the field of reactivity of aromatic compounds. V.A. Kozlov continued his work at the Institute and became the head of the Department of Varnishes and Paints. Yu.G. Erykalov founded the Department of Organic Chemistry at the classical Ivanovo State University, where E.N. Krylov and S.N. Ivanov also moved to work (see Section 9.3). O.I. Kachurin worked in Donetsk at the Institute of Physical Organic and Coal Chemistry of the National Academy of Sciences of Ukraine.

From 1973 to 1995, the Department of Organic Chemistry was headed by Doctor of Chemical Sci-

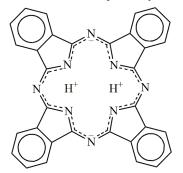
ences Professor **Boris Dmitrievich Berezin**, Honored Scientist of the RSFSR, Laureate of the State Prize of the USSR, Academician of the Russian Academy of Natural Sciences, an outstanding scientist [498].

In 1952, B.D. Berezin graduated with honors from the Ivanovo Institute of Chemistry and Technology

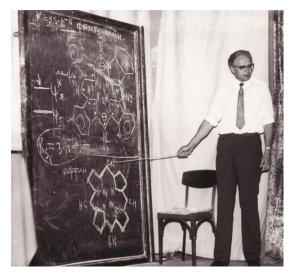


and entered postgraduate courses under the guidance of Professor K.B. Yatsimirskii, future academician of the Academy of Sciences of the Ukrainian SSR. In 1955 he defended his candidate's dissertation "Studies in the field of mercurimetry" and began to develop a radically new area, physicochemical properties of phthalocyanine complexes. B.D. Berezin conducted systematic studies of phthalocyanine complexes with most *d*-metals in proton-donor solvents and was the first to apply an original approach to the study of the stability of metal phthalocyanines on the basis of kinetic characteristics of their dissociation and the spectral strength criterion. Subsequently, the kinetic methods for determination of mechanisms of reactions involving macroheterocycles have become widespread in the works of both B.D. Berezin and other researchers. All physicochemical experiments were carried out in sulfuric acid, a solvent unusual for coordination compounds, which (as confirmed by the studies of B.D. Berezin) has the properties of an ideal ionizing solvent. Having studied the state and transformations of 25 phthalocyanine complexes in sulfuric acid, B.D. Berezin substantiated the division of metal phthalocyanines into labile and stable ones, depending on the nature of the coordination bond. B.D. Berezin proposed a new structural formula phthalocyanine (socalled delocalized model) with internally ionized NH bonds on the basis of its acid-base properties.





In 1966 he defended his doctoral dissertation on this subject in Kiev, in 1967 he became a professor in the Department of Analytical Chemistry, and in 1973, head of the Department of Organic Chemistry. The results of his doctoral and subsequent studies, where the mechanism of complexation of porphyrin type ligands with metal ions was established, formed the basis of his monograph on porphyrins and phthalocyanines, which was published in 1978 and was soon translated into English [499].



Professor B.D. Berezin reads the lecture "On the structure of phthalocyanine" (1975).

In 1980, the first scientific institution of the Academy of Sciences of the USSR, the Department of Non-aqueous Solutions Chemistry, was founded in Ivanovo and was reorganized in 1981 into the Institute of Non-aqueous Solutions Chemistry, where B.D. Berezin began to direct the research line "Coordination chemistry of porphyrins."

Under the leadership of B.D. Berezin, a scientific school was formed from the staff of the Institute of Non-aqueous Solutions Chemistry of the Academy of Sciences of the USSR and the Department of Organic Chemistry of the Ivanovo Institute of Chemistry and Technology; this school occupies now a leading position in the coordination chemistry of porphyrins and phthalocyanines. The results of studies were summarized in reviews and collective monographs prepared on the initiative of B.D. Berezin and published under the editorship of Academician N.S. Enikolopyan [500–502].

In 1987 B.D. Berezin, together with other scientists working in the field of solution chemistry, was awarded the State Prize of the USSR in the field of science and technology for the series of works "Development of the theoretical foundations of the chemistry of non-aqueous solutions and their practical use" published in 1962–1985. In 1995, the Ivanovo branch of the Russian Academy of Natural Sciences was opened thanks to the organizational work of B.D. Berezin.

B.D. Berezin devoted much time to improving the teaching of chemistry. In 1983, together with the Corresponding Member of the Russian Academy

of Sciences G.A. Krestov, B.D. Berezin published the monograph "Basic Concepts of Modern Chemistry" [503], and in 1999, "Basic Laws of Modern Chemistry" [504]. B.D. Berezin in co-authorship with his son D.B. Berezin wrote the textbook "The Course of Modern Organic Chemistry" [505], which was published in 2003 and later reprinted many times.

Under the direction of B.D. Berezin, more than 60 candidates of sciences were trained only at the Ivanovo State University of Chemistry and Technology, and 12 of which subsequently defended their doctoral dissertations. Currently, corresponding member of the Russian Academy of Sciences **O.I. Koifman**, full member of the Russian Academy of Natural Sciences **O.A. Golubchikov**, and doctors of sciences and professors **O.G. Khelevina**, **V.G. Andrianov**, **P.A. Stuzhin**, **D.B. Berezin**, **A.S. Semeikin**, and **O.A. Petrov** continue to develop and expand B.D. Berezin's scientific direction at the Ivanovo State University of Chemistry and Technology and the Department of Organic Chemistry.

In 1995, B.D. Berezin completely moved to work at the Institute of Non-aqueous Solutions Chemistry of the Russian Academy of Sciences, and the Department of Organic Chemistry of the Ivanovo State University of Chemistry and Technology was headed by his student, Professor **Oleg Aleksandrovich Golubchikov**.



Together with B.D. Berezin, O.A. Golubchikov carried out a series of studies on the complexation of porphyrins with transition metal salts in various solvents [506], the results of which were summarized in the joint monograph "Coordination Chemistry of Solvate Complexes of

Transition Metal Salts" [507]. O.A. Golubchikov's scientific interests are connected with porphyrins with a strained and distorted macrocycle [508]. Being the head of the department, he contributed in every possible way to continuation of the development of the porphyrin themes by the employees. O.A. Golubchikov was the inspirer and organizer of the Schools of Young Scientists in Porphyrin Chemistry and the editor of the series of monographs "Advances in Porphyrin Chemistry" [509]. Among his students there are more than 20 candidates and 2 doctors of chemical sciences.

In 1995–2015 O.A. Golubchikov headed the Department of Organic Chemistry of the Ivanovo State University of Chemistry and Technology. Since 2015,

he is the main research fellow of the department and is actively engaged in research related to practical applications of porphyrin complexes for the design of new catalytic materials [510] and galvanic coatings [511], etc. In 2015–2016 the department was headed by a student of B.D. Berezin and O.I. Koifman, Professor S.A. Syrbu, who then moved to the Institute of Solution Chemistry of the Russian Academy of Sciences.

At present, there are 5 professors and 2 chief researchers at the Department of Organic Chemistry of the Ivanovo State University of Chemistry and Technology; they are all students of B.D. Berezin.

Professor Olga Grigor'evna Khelevina (acting head of the department), Honored Scientist of the Russian Federation, is engaged in modification of tetraazaporphyrins via electrophilic and nucleophilic substitution [512], as well as in their complexing [513] and basic properties [514]. Professor V.G. Andrianov, Honored Worker of Higher Professional Education, is an expert in the field of acid-base interactions of porphyrins [515]; for many years he was dean of the Faculty of Organic Chemistry and Technology of the ISUCT. His student, Professor D.B. Berezin, continues the ideas of his father B.D. Berezin and studies the complexation of "nonclassical" porphyrins and their analogs [516, 517], as well as the possibility of using porphyrins in antibacterial photodynamic therapy. Professor O.A. Petrov studies slow proton-transfer reactions in H-complexes of porphyrazines [518]. Original approaches to the synthesis of modified mesoaryl-substituted porphyrins [519] have been developed by the main researcher Professor A.S. Semeikin, who heads the laboratory of porphyrin synthesis. Professor P.A. Stuzhin was the first to obtain new heterocyclic analogs of phthalocyanine [520-522]; he studies perfluorinated porphyrazines [523] and iron azaporphyrinates [524] and is a co-organizer of the symposium on porphyrazines at the International Conferences on Porphyrins and Phthalocyanines (ICPP4-ICPP10); he also and leads joint projects with the La Sapienza University of Rome. Professor O.G. Khelevina is deputy chief editor of the "Russian Chemical Journal," and Professor P.A. Stuzhin, of the "Macroheterocycles" journal. Despite the strong reduction in the teaching staff in recent years and significant increase in the classroom and other academic load, the department remains one of the leading in the Ivanovo State University of Chemistry and Technology in terms of the level and volume of scientific research.

# 7.3. History of Organic Chemistry in the Ivanovo State University

At the end of 1973, it was decided to set up the Ivanovo State University on the basis of the Ivanovo Pedagogical Institute. The Faculty of Biology and Chemistry was among the new faculties. The next stage in the development of chemistry began in Ivanovo, now in the Ivanovo State University (ISU). The Ivanovo Institute of Chemistry and Technology rendered a huge support to the foundation of the faculty and organization of the educational process and scientific research therein. Young and promising doctors of sciences (V.I. Klopov, Yu.G. Erykalov, L.V. Kuritsvn) were sent to the university together with their students and disciples. The Department of Organic and Biological Chemistry of the Ivanovo State University began its work in October 1976. Yurii Georgievich Erykalov (1930-2008), Doctor of Chemical Sciences, Professor, Chevalier of the Order of Peoples' Friendship, Honorary Worker of the Higher School of the Russian Federation, was the founder and first head of the department (1976–1996).

Yu.G. Erykalov, together with A.A. Spryskov and subsequently independently or with his students, conducted a fundamental study of high-temperature isomerization of di- and polyhaloaromaric compounds, the results of which were summarized in his doctoral dissertation "Study of isomeric transformations of polyhalobenzenes in the presence of some conjugated acids" [525].

A.A. Spryskov's disciples, candidates of sciences E.N. Krylov, N.I. Rudakova, V.P. Leshchev, and S.N. Ivanov went to the Ivanovo State University (ISU) together with Yu.G. Erykalov. It is difficult to overestimate the role of Professor Yu.G. Erykalov, who was vice-rector on scientific work of the Ivanovo State University from 1977 to 1990, in the development of the university to a large scientific center. At that time, postgraduate study was organized, specialized councils were opened, and contractual research work began to develop.

Since 1996, the department (and later the unified department, which became known as the Department of Organic and Physical Chemistry) was headed by Doctor of Chemical Sciences, Professor **Mikhail Vasil'evich Klyuev** (born in 1952), a graduate of the Ivanovo Institute of Chemistry and Technology of 1975. He finished post-graduate courses at the Institute of Chemical Physics of the Academy of Sciences of

the USSR under the guidance of Professor **Mikhail** L'vovich Khidekel' (1932-2001) and doctorate at the Faculty of Chemistry of the Moscow State University (his scientific consultant was head of the Department of Petroleum Chemistry and Organic Catalysis, Professor Eduard Avetisovich Karakhanov). In 1991 M.V. Klyuev defended his doctoral dissertation "Catalytic synthesis of amines by hydrogenation and hydroamination." M.V. Klyuev and his students (22 candidates and 2 doctors of sciences) performed an integral study of the hydrogenation/amination of carbonyl compounds with amines and their precursors. Recently, catalysts based on metal containing carbon nanomaterials have been studied [526–531].

The department was one of the pioneers in the Russian Federation in using quantum chemical calculations to explain the reactivity of organic compounds. Works on the use of quantum chemical calculations to explain the reactivity of various substrates in hydrogenation and hydrogenation/amination [532–537] and in virtual screening of potential biologically active molecules [538, 539] have been published. Much attention was paid to the synthesis of drugs via hydrogenation/amination, and hydrogenation/acylation [540–545].

The department (jointly with the ISUCT) organized seven scientific schools–conferences of young scientists "Quantum Chemical Calculations: Structure and Reactivity of Organic and Inorganic Molecules," which are held alternately in both universities every two years.

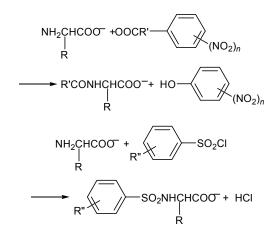
Professor **Nina Ivanovna Giricheva** (born in 1947) has been working at the united Department of Organic and Physical Chemistry since 2012; previously, for 9 years she headed the Department of Physical Chemistry. N.I. Giricheva is one of the founders of the Zonal Laboratory of Molecular Parameters in Ivanovo. The laboratory currently occupies one of the first places in the world in the field of electron diffraction studies of the structure of free molecules [546–550].

A new important stage in the development of chemistry in the ISU began in February 2005, when the University and the Institute of Chemical Physics Problems of the Russian Academy of Sciences created the scientific educational association "Chemical Physics." In 2007, this association was included as a structural unit in the Research Institute of Nanomaterials at the Ivanovo State University.

In 2008, 2009, 2011, 2013, 2015, and 2017 six schools-conferences of young scientists "Organic and

Hybrid Nanomaterials" were held by the ISU on the basis of the sports and recreation camp *Rubskoe* Lake under financial support by the Ministry of Education and Science of the Russian Federation and by the Russian Foundation for Basic Research. Lectures delivered at these conferences have been published in the form of collective monographs [551–555], which are used in teaching not only in the ISU, but also in many other universities and scientific institutions.

In 2016 the department was headed by Professor **Tat'yana Petrovna Kustova** (born in 1967), a graduate of the Faculty of Biology and Chemistry, a student of Doctor of Chemical Sciences Professor **Lev Viktorovich Kuritsyn** (born in 1932). The latter was at the origins of the Faculty of Biology and Chemistry of the ISU and was the first head of the Department of Physical Chemistry [556–561]. A particular place in the research work carried out at the department is given to the synthesis of amides and sulfonamides derived from such biologically significant compounds as  $\alpha$ -amino acids and dipeptides.



Recently, researchers' efforts have been focused not only on the experimental study of the acylation kinetics but also on the analysis of solvation effects in acyl transfer reactions and simulation of their mechanisms by quantum chemical calculations of the corresponding potential energy surfaces (associate professor L.B. Kochetova). It has been shown that these reactions follow a common concerted bimolecular nucleophilic substitution mechanism. The kinetic school of Professor L.V. Kuritsyn gave rise to 12 candidate's and 3 doctoral dissertations.

The first graduation of chemistry specialists from the Faculty of Biology and Chemistry of the Ivanovo State University was in 1979. Since then, more than 1200 students have successfully graduated from the



Department of Organic and Physical Chemistry (June 2017).

chemical department of the faculty. Among them are doctors of sciences S.A. Syrbu, M.G. Abdullaev, T.P. Kustova, N.V. Belova, and I.V. Terekhova and more than 70 candidates of sciences.

# 8. DEPARTMENT OF ORGANIC CHEMISTRY OF THE FACULTY OF CHEMISTRY OF THE LOBACHEVSKII STATE UNIVERSITY OF NIZHNY NOVGOROD

The Department of Organic Chemistry was established in 1918 at the Faculty of Chemistry and Physics of the State University of Nizhny Novgorod under the leadership of Ivan Ivanovich Ostromyslenskii, formerly a professor at the Warsaw Polytechnic Institute [562-564]. I.I. Ostromyslenskii (1880-1939) was a prominent organic chemist who made a significant contribution to the history of domestic chemical science. In 1908-1910, he worked on coordination compounds in collaboration with A. Bergman. In 1910 he studied isomerism of coordination compounds. In the same year, I.I. Ostromyslenskii used the relation found by Chugaev to recognize optically active forms of crystals on the basis of their optical properties. I.I. Ostromyslenskii received special prominence for his research on the synthesis of rubber. He discovered three isomeric modifications of polymerized vinyl bromide, which were readily convertible into each other. The isomeric modifications discovered by I.I. Ostromyslenskii were identical to the simplest Harries' butadiene rubber bromide. Unfortunately, I.I. Ostromyslenski left Nizhny Novgorod as early as by the end of 1918.

After his departure, from 1918 to 1935 the Department of Organic Chemistry was headed by A.M. Butlerov's student, doctor of chemistry **Ivan Ivanovich Bevad** (1857–1937). Simultaneously, in 1919 he



headed the research institute founded at the university. I.I. Bevad was one of the first organic chemists in Nizhny Novgorod. He arrived in this city on the Volga with the evacuated Warsaw Polytechnic Institute (later Nizhny Novgorod Polytechnic Institute) and worked in the Nizhny

Novgorod City People's University, State University of Nizhny Novgorod, Gorky Institute of Chemical Technology, and Gorky Industrial Institute.

I.I. Bevad's memoirs were stated by his granddaughter M.L. Pirogova in a note about her grandfather: "In 1876 I graduated from the grammar school and entered the St. Petersburg University, where the natural branch of the Faculty of Physics and Mathematics was famous for its outstanding scientific powers. They were represented by D.I. Mendeleev, A.M. Butlerov. A.A. Famintsyn, A.N. Beketov, I.M. Sechenov, and others. Before the university, I was not familiar with chemistry at all, and I got acquainted a little with botany and zoology in addition to the gymnasium course.

At the university in the first year I saw and heard D.I Mendeleev for the first time; his lectures on inorganic chemistry, artless in form and full of deep internal content presentation, immediately aroused my interest in this subject. He attracted so many listeners to his lectures that not only all the benches, all the passages between them were occupied by them, but they were also placed in the doors leading to the corridor.

Something unexplored, full of fascinating interest, was inspired by these lectures. We waited impatiently for the days when these lectures were read. Despite the early hour (9 a.m.), the auditorium was always crowded with listeners. From the very first acquaintance with chemistry, all my sympathies were drawn thereto. The first steps in studying this completely new field for me were difficult, and it was only after intensive work during the first two years that I managed to master the subject so much that I was able to take it more consciously and thoughtfully when studying it further.

In the second year, during the lecture on organic chemistry, I happened to get acquainted with another bright star of the Faculty of Physics and Mathematics, A.M. Butlerov, who, thanks to the oratorical talent and a special system of course presentation, despite the absence of external lecture luster (then organic chemistry was read almost without demonstrations), attracted a full audience to his lectures. We listened with delight to smooth like ivory-cut speech of Butlerov, who stood at the height of glory and was able to fascinate anyone who dealt with him.

In the third year, each student chose a specialty. I was particularly interested in chemistry in its practical applications and agrochemistry, and I was carried away by the letters of Liebig and Engelhardt about agriculture. I read the works of Darwin and Wallace, being especially interested in the then fashionable question of the origin of man, struggle for existence, and natural selection. I chose an agronomic specialty. Agronomy was then read by A.V. Sovetov; lectures were read in a family environment in an agronomic office; dozen specialists were placed around the table, behind which the lecturer himself was placed with his invariable notebook and books, in which he showed us sketches and drawings, sending them round in the hands of listeners. The family atmosphere of lectures made them especially attractive; I gladly visited them; the lecturer himself, who at one time acquired a scientific name as a propagandist of grass seeding, was not a brilliant oratorical talent, but he knew how to attract listeners and interest them with his artless speech, simplicity and accessibility.

In addition, I listened to a soil science lecture on the chernozem of private-docent V.V. Dokuchaev, who had just returned from a scientific trip, the result of which was the appearance of his famous work "About Chernozem." My studies on agronomy were not limited to listening to these lectures, at the same time I was studying in the laboratory of organic chemistry under the guidance of A.M. Butlerov and his assistant M.D. L'vov; I enrolled there in the fourth year; except me there were two more of my classmates, five people who had already completed the course, and two people from the third year.

Classes were conducted by L'vov who spent in the laboratory all day until 4–5 p.m. and also went there in the evening. Butlerov went to the laboratory almost every day, walked around all working, questioned them about the work, made instructions, and gave advices. The relationship between pupils and teachers was the friendliest; the even temper of Butlerov and his extraordinary delicacy in communications were especially attractive; We never heard from him a rude or at least stern word for our inevitable mistakes; thanks to this no one hid their mistakes and was not afraid to confess to them. Provincial chemists who came to Petersburg often looked in at the laboratory: here I first saw G.G. Gustavson, V.V. Markovnikov,

a scientific purpose, where I got acquainted with the experience of the teaching of chemistry in universities and higher technical and agronomic schools in Western Europe and with the equipment of newest laboratories. I attended lectures of outstanding professors and worked under their leadership; So, in the summer of 1889 I studied at the University of Göttingen under the leadership of Victor Meyer, and in

A.N. Popov, etc. D.I. Mendeleev often passed through

the rooms in which we worked, while going to his

laboratory from his apartment or back. Sometimes,

when he met with Butlerov here in a tiny weighting

room, which simultaneously served as both library and

office, there were fierce debates about the "theory of structure," whose adherent, one of the creators, and

propagandist of which was Butlerov, and the enemy

was Mendeleev, or about the then fashionable question

of "spiritualism," whose zealous adherent was But-

lerov, while Mendeleev's attitude to it was critical. It

was interesting to observe this dispute between two

great chemists; we listened with outstretched breath to

the ferocious growl of Mendeleev, who does not know

how to keep in his rage, attacking his opponent, and in

return to the cold-blooded, without slightest increase in

his voice, Butlerov's delicate objection; at times it

seemed that the argument would end in a fight as he

took such sharp forms, but the door swung open, and

these two celebrities went therefrom arm in arm, while

In the spring of 1880, I passed the final exams and

graduated with a candidate's degree. In the autumn of

the same year, I entered the Petrovskii Academy (near

Moscow) as a student at the agricultural department,

assuming to specially engage in agronomic chemistry,

but soon again returned to Butlerov's laboratory in

Petersburg and continued to study there until April

1881, when, on the recommendation of Butlerov and

L'vov, entered the University of Warsaw to prof.

A.N. Popov as a laboratory assistant at the Department

of Inorganic and Analytical Chemistry. In 1892,

I passed master's examination at the St. Petersburg

University and defended master's thesis under the title

"Synthesis of mononitro derivatives of saturated

hydrocarbons" at the University of Warsaw ... In 1900

I defended my doctoral dissertation "On the reaction of

nitrous esters and nitroparaffins with alkylzincs" at the

St. Petersburg University; in 1901 I was appointed

an ordinary professor in the Department of General

Chemistry and in 1902 transferred to the Department

of Organic Chemistry.

were already talking peacefully and laughing.

the winter semester, in Munich under the leadership of Adolph Bayer; in the winter and summer semesters of the 1892/1893 academic year I studied bacteriology in Berlin under the guidance of Hunter; in the summers of 1896 and 1899 I was on a business trip to inspect the newest laboratories in Germany, Austria, Italy, Switzerland and France."

In 1904, I.I. Bevad moved from the University of Warsaw to the Polytechnic Institute at the Department of Organic Chemistry, which remained vacant after the death of Professor E.E. Wagner, an outstanding chemist with a world-wide reputation, who held this post since 1896. From the poor environment at the university, I.I. Bevad moved to the luxury of a newly built university in Warsaw, the construction of which spared no expense.

From 1905 to 1907 he was elected three times dean of the chemical department of the Warsaw Polytechnic Institute, and in 1910 he was promoted to a honored professor. As the First World War began, in 1915 the Polytechnic Institute was evacuated and in 1916 transferred to Nizhny Novgorod, where it was renamed University of Nizhny Novgorod, then to the Chemical Technological Institute, then to the Gorky Industrial Institute, and again to the Nizhny Novgorod Polytechnic Institute; in 1918 the institute was closed in connection with the foundation of the University of Nizhny Novgorod, and I.I. Bevad remained a professor in it until 1930, when six institutes emerged from the university.

Studies of I.I. Bevad entered the history of domestic chemical science [565, 566]. Bevad's classical syntheses of secondary and tertiary nitro compounds of the paraffin series are well known. In his doctoral dissertation I.I. Bevad studied reactions of nitrous esters and nitroparaffins with cycloalkanes. He was the author of the first in Russia "Brief Guide to Chemical Agricultural Analysis" and rightfully can be considered one of the founders of domestic agrochemistry. In subsequent years, I.I. Bevad repeatedly headed the Faculty of Chemistry of the University of Nizhny Novgorod as a dean.

At that time, large construction was developing in Nizhny Novgorod. The auto giant and new radio engineering and machine-building plants were built. The country required a large number of specialists with a narrower but deep specialization. The faculties of the State University of Nizhny Novgorod were reorganized into the corresponding institutes. The chemical technological and mechanical machine-building institutes thus appeared and were soon merged into the Industrial Institute (now the State Technical University of Nizhny Novgorod). The Construction Engineering, Agricultural, Medical, and Pedagogical institutes were also founded.

However, it soon became clear that it is impossible to develop the latest technologies and the corresponding technological equipment without fundamental science and specialists with broad scientific horizons and deep theoretical knowledge, which could be trained at universities. Therefore, in 1931, by the government's decision on the proposal of the Nizhny Novgorod authorities, the university was restored in Nizhny Novgorod, initially on the basis of only the Faculty of Physics and Mathematics. The faculties of physics and mathematics of the Moscow and Leningrad universities included the natural, chemical, and physical-mathematical departments. Following this tradition, in 1931 the University of Nizhny Novgorod included only the faculties of biology and physics and mathematics, but already in 1932, the chemical faculty was opened.

The year of 1932 was the final year of the First Five-Year Plan. The first auto giant was put into operation, the Krasnoe Sormovo plant was expanded, and the chemical industry grew. The industry of Gorky (Nizhny Novgorod was given the name Gorky in 1933) needed its own scientific chemical center. The Faculty of Chemistry of the Gorky State University became such center. Initially (in 1932 and 1933), the course of organic chemistry for biologists was read by the wellknown but already very ill I.I. Bevad. In 1934, the closest associate of Academician A.E. Favorskii, a student of V.N. Ipat'ev, a Leningrad specialist in petroleum chemistry and motor fuels, senior researcher of the Academy of Sciences of the USSR Aleksandr Dmitrievich Petrov, was invited to the faculty.



A.D. Petrov also managed to quickly organize a laboratory of organic chemistry, generate a creative atmosphere around himself, and attract young talented students to work. Since 1935, he headed the department of organic chemistry, without stopping scientific and organizational activities at the institutes

of the Academy of Sciences in Leningrad and Moscow. A.D. Petrov (1895–1964) headed the department from 1935 to 1946 (see also Section 3); he was an outstanding organic chemist, corresponding member of the Academy of Sciences of the USSR, State Prize winner for his work on the chemistry of hydrocarbon fuels, and author of more than 600 publications, including 14 monographs [567–569].

Being a student of Academician A.E. Favorsky, A.D. Petrov began his scientific career in Leningrad in the laboratory of Academician V.N. Ipat'ev and headed it after the departure of this scientist abroad in 1931. Since 1934 A.D. Petrov's laboratory became a part of the Institute of Organic Chemistry of the Academy of Sciences of the USSR, which was founded in the same year. In 1931, a year after the departure of V.N. Ipat'ev, A.D. Petrov was appointed as head of the Laboratory of High Pressures (later it became known as the Laboratory of Pyrogenic Processes, later the Laboratory of Hydrocarbons). In 1934 the Laboratory of Pyrogenic Processes moved to Moscow. In Moscow, A.D. Petrov began working at the Institute of Organic Chemistry of the Academy of Sciences of the USSR, which was created on the basis of Ipat'ev's Laboratory of High Pressures and N.D. Zelinskii's and (in part) A.E. Favorskii's laboratories. In 1935 he became doctor of chemical sciences, and in 1936, professor.

In 1935, A.D. Petrov headed the Department of Organic Chemistry at the University of Gorky. Every month he went for a week in Gorky for lecturing. He carried with him reagents for scientific work, including diethyl ether for Grignard reactions, which was far from safe. His well-known work on the synthesis of individual hydrocarbons as models of fuels and oils was carried out simultaneously in the Gorky University and in the Institute of Organic Chemistry.

In the 1930s, repressions began that affected the friendly Ipat'ev collective. G.A. Razuvaev was arrested first, he was imprisoned for more than 10 years and worked for a while in a closed scientific institution. Then Ipat'ey's son Vladimir Vladimirovich was subjected to verbal condemnation. N.A. Orlov was lucky less than others; as a descendant of noble tsarist generals, he was exiled to Saratov, where he lectured in organic chemistry at the university. At that time, an explosion occurred at the Saratov oil refinery. N.A. Orlov publicly stated: "Well, what kind of explosion is this, if I took up the job, the explosion would be real." The next night he had a search. Several cans of picric acid were found, which was needed for scientific work. N.A. Orlov, his wife, and son were shot. N.A. Orlov was the largest scientist, one of the best coal chemists in Russia.

In the prewar years, A.D. Petrov wrote several monographs: "Advances in the Chemistry of Aliphatic

ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS

Hydrocarbons" (1936), "Essays on the Chemistry of Motor Fuels and Lubricant Oils" (1941), etc. They described the results of large studies on the synthesis and determination of properties of model hydrocarbons, carried out at the Gorky University and in the Institute of Organic Chemistry.

Having started, the Great Patriotic War radically changed the life of the whole country, and the Gorky University did not stay aside. Many teachers and students of the University went to the front; those remaining in the rear were forced to subordinate their scientific interests to the needs of the front and the defense industry. The documents on the work of the Department of Organic Chemistry on the synthesis of urotropine for the Pharmacy Department, of phenolphthalein for special workshop of the mining enterprise, of diethylaniline for special workshop of the Industrial Institute, of dipicrylamine for the defense plant, and of ethyl acrylate for the maxillary hospital, as well as on the analysis of captured fuel, have been preserved. A method for the synthesis of white and red sulfanilamide was developed, a composition for impregnation of gas masks, rubber compounds from waste produced by the Dzerzhinsk Osoaviakhim plant, and recipes for low-hardening aviation oils and lubricating oils have been developed.

In 1946, A.D. Petrov was elected corresponding member of the Academy of Sciences of the USSR. In 1947, he was awarded the Stalin Prize for research in the fields of synthesis of motor fuel and lubricating oil hydrocarbons and catalytic hydrodimerization of acetylene; in the same year he received S.V. Lebedev's award for research in the field of catalytic synthesis of isobutylene. Employees of the Gorky University (Yu.A. Ol'dekop, E.V. Mitrofanova, etc.) and of the Institute of Organic Chemistry participated in this work.

In 1946 A.D. Petrov was replaced by G.A. Razuvaev. Presenting G.A. Razuvaev to the people of Gorky, A.D. Petrov said: "I leave to you a diamond of the first water instead of myself." His students were Academician O.M. Nefedov, corresponding members of the Academy of Sciences of the USSR V.A. Ponomarenko, G.I. Nikishin and E.A. Chernyshev, and doctors of sciences V.F. Mironov, I.E. Dolgii, V.M. Vdovin, and Yu.N. Ogibin. His students in Gorky were Yu.A. Ol'dekop, E.P. Kaplan, E.I. Fedotova, E.V. Mitrofanova, P.S. Sanin, I.G. Sumin, V.I. Kogtev, D.N. Andreev, L.D. Karlik, and others. A large number of A.P. Petrov's students worked in

the Academies of Sciences of the Union Republics. Among them academicians of the Academy of Sciences of Georgia I.M. Gverdtsiteli, R.M. Lagidze, and others, as well as academicians of the Academies of Sciences of Azerbaijan, Armenia, Latvia, Tajikistan, and others.

Since 1946, after the appointment of **G.A. Razuvaev** as acting head of the Department of Organic Chemistry, a scientific school in the field of chemistry of organometallic compounds began to extensively develop at the Faculty of Chemistry of the Gorky State University. A.D. Petrov



retained the leadership and lecturing in the specialization "petroleum chemistry."

In 1947, studies of the mechanisms of liquid-phase radical reactions involving peroxides and organometallic compounds were initiated at the university under the leadership of G.A. Razuvaev. These studies also gave rise to the development of related fields such as polymer chemistry and thermodynamics of polymers and organometallic compounds [570, 571]. Based on these studies, in 1966 G.A. Razuvaev organized the first in Gorky Academic Scientific Institution, the Laboratory of Polymer Stabilization of the Academy of Sciences of the USSR, which was transformed in 1969 into the Institute of Chemistry of the Academy of Sciences. He became director of the institute but until the last days of his life he kept in touch with the Faculty of Chemistry, working as a professor of the Department of Organic Chemistry.

The school of Academician G.A. Razuvaev trained such well-known academic chemists as Full Member of the Russian Academy of Sciences G.A. Abakumov, corresponding members of the Russian Academy of Sciences G.A. Domrachev and V.K. Cherkasov, professors N.S. Vyazankin, G.G. Petukhov [572], V.A. Dodonov, V.N. Latyaeva, and many others.

**Grigorii Alekseevich Razuvaev** (1895–1989) headed the department from 1946 to 1971 (see also Section 3). He studied at the Faculty of Physics and Mathematics of the Moscow University, specializing in chemistry. Lectures on organic chemistry were read by N.D. Zelinskii, and on inorganic, by I.A. Kablukov. In order not to encroach on the family budget, G.A. Razuvaev was engaged in tutoring, and he bought books for the earned money. Among these books, there was P. Walden's book "Free Radicals" accidentally encountered in the student years, which became his reference book and played a major role in making up of his personality. Along with his studies, G.A. Razuvaev began to work in the laboratory at the Zelinskii's department, but because of the revolution that began in February, he could not continue studying and, after completing two courses, went to his mother in Ukraine. He then decided to continue his education at the university and reached Petrograd. While studying at the university, G.A. Razuvaev worked in the Commission for Studying Natural Productive Forces of the country at the Russian Academy of Sciences; he examined minerals from interesting but completely disordered collections, and then worked at a private plant producing solid carbon dioxide. The diploma work "Dissociation of hexamethylethane" on the chemistry of free radicals was carried out very quickly under the guidance of Academician A.E. Favorskii. Academician V.N. Ipat'ev, one of the largest chemists of the twentieth century, whom Razuvaev regarded as his main teacher [573, 574], was also a student of A.E. Favorskii.

After graduation from the university, G.A. Razuvaev worked in the laboratory of the Academy of Sciences, and then in the Military Chemical Department which was created by V.N. Ipat'ev to develop chemical protection equipment in the army. At the invitation of V.N. Ipat'ev, in 1927 he began to work in V.N. Ipat'ev's Laboratory of High Pressures, where he was head of a department. Simultaneously, G.A. Razuvaev headed the laboratory of organic chemistry in the Academy of Sciences and began to head the department at the Leningrad Institute of Technology, where he read the course of chemistry of toxic substances.

While working at the Laboratory of High Pressures, G.A. Razuvaev studied the free radical derived from dihydrophenarsazine. He also dealt with applied problems related to toxic agents. He managed to understand the reasons for the leakage of diphosgene from old artillery shells in the warehouses. Simultaneously with the work, G.A. Razuvaev read the course of chemistry of toxic substances in the Military Medical Academy and the course of organic chemistry at the Leningrad University. He was the author of, apparently, the first in Soviet Russia monograph on the chemistry of toxic agents.

Since 1926, V.N. Ipat'ev concentrated his forces on his new offspring, the State Institute of High Pressures. The institute quickly achieved considerable success in improving the technology of fertilizer production; the advances were so significant that the firm Bayerische Stickstoff Gesellschaft appealed to the Soviet Union to jointly develop a new method for the production of phosphoric acid. V.N. Ipat'ev began to lead the work in the German group of Karl Freitag and often go there. G.A. Razuvaev often had to substitute him for reading lectures. Gradually, the course of organic chemistry and the special course of the Artillery Academy were completely transferred to him. In 1929, V.N. Ipat'ev received an award of the German Chemical Society (5000 DEM) and went to Germany, and then on preferential terms to Chicago, where he received a laboratory and worked there until his death in 1952. V.N. Ipat'ev is considered one of the creators of modern petrochemistry in the United States.

In May 1929, G.A. Razuvaev (then deputy director of the Institute of High Pressures), under the patronage of V.N. Ipat'ev, was sent for an internship at the Bavarian Academy of Sciences to the laboratory of Heinrich Wieland at the University of Munich. Acquaintance with the work of the renowned chemical school of the Nobel laureate was extremely useful for G.A. Razuvaev. He studied the formation of free radicals in the decomposition of organic peroxides; the results of these works were published in 1931-1932. In Munich, H. Wieland had a young international team of trainee scientists from different countries, including Russia, England, Japan, Spain, Ecuador, etc. With some of them, G.A. Razuvaev maintained friendly relations until the last days of his life. At the end of his business trip, he continued his research on the chemistry of organometallic compounds.

In 1930, G.A. Razuvaev returned to Leningrad. Since 1932 he was in charge of the Department of Toxic Agents and Explosives at the Institute of Technology. In 1934 he was arrested on the false denunciation of a colleague in Article 58 for "counterrevolutionary activity, assistance to the European bourgeoisie, sabotage, and groupings" and sentenced to death, which was replaced by 10 years of camps. It was removed to the North and released only in 1942. The final release occurred in 1946, and in 1955 he was rehabilitated. Being imprisoned, G.A. Razuvaev worked in the timber fellings, mining shale, in the Vorkuta camps at the mine, sorted the coal, and then analyzed it in a laboratory. A year and a half he worked as a teacher-educator in a colony of juvenile offenders. When the decree was issued on the use of imprisoned specialists in their specialty, G.A. Razuvaev began to work as a production manager in the Vodny village located 25 km from Chib'yu (a tributary of the Ukhta River) to extract radium from water.

Together with Professor F.A. Toropov (also a prisoner), he wrote the monograph "Methods for Preparation of Radium by Crystallization and Enrichment to Pure Radium." F.A. Toropov and G.A. Razuvaev succeeded in improving the degree of extraction of radium from water to 97%.

The lack of a scientific degree created additional difficulties for G.A. Razuvaev. Although before the arrest he was both professor and head of the department, he was not even a candidate of sciences, since the academic degrees appeared in the country after his arrest. In 1945, G.A. Razuvaev (not yet released!) was sent by head of the Water Fishery Dorofeev to Moscow with finished products; ampules containing radium were transported in lead containers only by a courier with guards. In Moscow, G.A. Razuvaev visited Academician A.N. Nesmeyanov, who decided that G.A. Razuvaev had to defend his candidate's dissertation "Meriquinoid derivatives of the phenarsazine series" according to the author's abstract written according to imprints of the accidentally preserved publications. G.A. Razuvaev thus became (without a passport!) a candidate of sciences. A few months later, in early 1946, he received a passport and permission to leave without the right to live in capitals and large cities. In the same year (1946) he defended his doctoral dissertation "Free radicals in reactions of organometallic compounds."

In 1946, on the initiative of A.D. Petrov, G.A. Razuvaev was sent to Gorky to head the Department of Organic Chemistry at the Gorky University. He headed the department until 1971 and remained a professor of the department until the end of his life. He read the general course of organic chemistry and a special course on the structure of organic compounds. He had a loud expressive voice, and his words reached every listener. He had no orientation to an "average" student and was convinced that the acquisition of knowledge requires continuous work with lectures and educational literature. His special course was considered one of the most difficult. G.A. Razuvaev was a very demanding and principled examiner, and the preferential grades he gave both students and post-graduate students and candidates were "excellent" and "unsatisfactory."

From 1940–1950, G.A. Razuvaev regularly went (once a week) to Dzerzhinsk and supervise the work of some Dzerzhinsk chemists at the Research Institute of Polymer Chemistry and Technology (Polymer Research Institute), then known as the Dzerzhinsk Branch of P.O. Box 702. The life and the work in Gorky were the time of creation of a scientific school and recognition of its leader, G.A. Razuvaev. His students were Yu.A. Ol'-dekop, N.A. Maier, G.G. Petukhov, N.S. Vyazankin, V.A. Dodonov, G.A. Domrachev, G.A. Abakumov, A.N. Egorochkin, and many others.

In 1958, G.A. Razuvaev was awarded the first in the USSR Lenin Prize in Chemistry for his studies on the chemistry of free radicals. In 1958 he became corresponding member of the Academy of Sciences of the USSR, and in 1961, full member; in 1985 he was elected Honorary Citizen of Gorky. He believed especially important to combine fundamental and applied research. The results of his studies lead to industrial implementation of effective initiators and catalysts for polymerization of vinyl monomers. Under his leadership, methods were developed for obtaining filamentary single crystals and laminated films of germanium and other metals for semiconductor engineering and electronics. G.A. Razuvaev is a coauthor of the unique monograph "Organometallic Compounds in Electronics" [575]. He was the first chairman of the Commission for the Use of Organometallic Compounds for Inorganic Coatings and Materials of the Scientific Council for Organoelement Chemistry of the Academy of Sciences of the USSR and organizer of numerous meetings and seminars on this problem.

G.A. Razuvaev discovered reactions of metal derivatives as new methods of synthesis of organoelement compounds, which are used now by chemists of Russia and abroad. For example, together with Corresponding Member of the Belarusian Academy of Sciences Professor Yu.A. Ol'dekop, he developed a new method for the synthesis of alkyl- and arylmercury derivatives by thermal decarboxylation of mercury carboxylates in the presence of a catalytic amount of diacyl peroxides as radical initiators [576].

 $(RCOO)_2Hg \longrightarrow (RCOO)HgR + CO_2$ 

Together with Professor M.N. Bochkarev (head of a laboratory of the Institute of Organometallic Chemistry of the Russian Academy of Sciences), the metalorganic hydride method for synthesizing organometallic compounds by reaction of alkyl metal derivatives with some organoelement hydrides was discovered, as a result of which a hydrocarbon is released [577].

Et₂Hg + 2Et₃GeH → Et₃GeHgGeEt₃ + 2EtH

In 1971, G.A. Razuvaev moved to the post of director of the Institute of Chemistry of the Academy

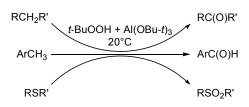
of Sciences of the USSR created by him and transferred the department of organic chemistry of the Gorky State University to his student **Victor Alekseevich Dodonov**. By that time candidate of chemical sciences V.A. Dodonov has already been experienced in working at the Research Institute of Chemistry at the Gorky State University in the laboratory of doctor of chemical sciences G.G. Petukhov. Being a post-graduate student, he passed a one-year internship at the Oxford University in the leading laboratory of Professor William A. Waters on the recommendation of G.A. Razuvaev.

Interest in peroxides became decisive for V.A. Dodonov for many years to come. He synthesized new classes of organic and organoelement peroxides (candidate's dissertations of associate professors T.I. Zinov'eva, T.I. Starostina, S.N. Zaburdyaeva, and V.V. Chesnokov). Complexes and radicals formed during the reaction of peroxides with organoelement compounds exhibit unique ability to initiate polymerization, as was noted by V.A. Dodonov in his joint works with Academician G.A. Razuvaev and Professor A.V. Ryabov and was studied with post-graduate students Yu.A. Ivanova, Z.V. Orlova, D.F. Grishin, Yu.V. Zharov, A.I. Dregich, I.N. Aksenova, L.L. Semenycheva, Yu.L. Kuznetsova, Zh.V. Garusova, A.I. Vilkov, and R.V. Verkhovykh. As a result of these works, unique glue compositions were created that were able to glue polyethylene, polypropylene, and Teflon, which were considered "non-adhesive" until now, at room temperature without preliminary preparation of the surface, and new composite materials from these polymers and metals were thus obtained. A new technology for accelerated adhesive assembly of polymer pipelines for sewage systems was utilized in the construction industry (at the Minyugstroi enterprises). For a number of years, the Dow Chemical Company funded students and graduate students working in this direction. A new technology of assembling cars was launched at European car factories, where polymer bumpers on the conveyor are glued to the steel body. The simplicity of the method was due to the use of an air-stable complex of an organoboron compound with an amine. On mixing it with methacrylic acid free organoborane was released and oxidized with air to generate alkyl radicals promoting the curing process of

 $Et_{3}B \cdot NR_{3} + CH_{2}=C(Me)CO_{2}H$   $\longrightarrow Et_{3}B + CH_{2}=C(Me)CO_{2}NR_{3}H$   $Et_{3}B + O_{2} \longrightarrow Et' + EtO' + products$ 

the adhesive composition; in addition, alkoxy radicals were generated and involved in grafting macrochains to the elastomer surface to be bonded [578].

Another important area of research developed by V.A. Dodonov was the study of oxidation of organic substances with peroxides in the presence of metal compounds (Al, Ti, V). It was found that under mild conditions at room temperature it is possible to introduce oxygen-containing functional groups into the carbon skeleton of organic molecules of various classes, including inert hydrocarbons [579, 580].



One more research line pursued at the Department of Organic Chemistry under the leadership of V.A. Dodonov was organic synthesis with the use of arylantimony and arylbismuth compounds under catalysis by copper and palladium complexes. These organometallic reagents allow selective action at 20–  $50^{\circ}$ C on certain functional groups of organic molecules, for example, OH, NH, and C=C [581, 582]. Analogous studies were simultaneously conducted by Nobel laureate Sir Derek H.R. Barton; therefore, the discovered transformations were called Barton– Dodonov condensation [583].

$$\begin{array}{c} \text{Barton-Dodonov condensations} \\ \text{ROH} & \xrightarrow{\text{Ph}_3\text{Bi}(\text{OAc})_2 + 0.01 \text{ Cu}(\text{OAc})_2, 20^\circ\text{C}} \\ \text{R}_2\text{NH} & \xrightarrow{\text{Ph}_3\text{Bi}(\text{OAc})_2 + 0.01 \text{ Cu}(\text{OAc})_2, 20^\circ\text{C}} \\ \text{RCH=CH}_2 & \xrightarrow{\text{Ph}_3\text{Bi}(\text{OAc})_2 + 0.01 \text{ Pd}(\text{OAc})_2, 20^\circ\text{C}} \\ \end{array} \\ \begin{array}{c} \text{RCH=CHPh} \end{array}$$

Currently, the department is headed by Doctor of Chemical Sciences Aleksei Yur'evich Fedorov. He

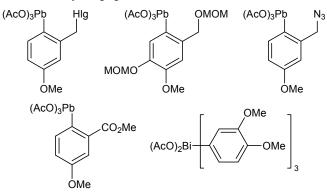
graduated from the Faculty of Chemistry of the Gorky (Nizhny Novgorod) State University in 1993, and defended his candidate's dissertation in 1996 under the guidance of Professor V.A. Dodonov. From 1999 to 2015 A.Yu. Fedorov passed the way from an assistant to head of the department. In 2008 he defended his



doctoral dissertation devoted to the development of arylation methods and their application in the synthesis of biologically active compounds (scientific consultant Academician I.P. Beletskaya). The fields of scientific interest of A.Yu. Fedorov include organic synthesis, homogeneous catalysis, synthesis of natural compounds and their analogs exhibiting antitumor activity, and design photoactive bioconjugates. The scientific work conducted by A.Yu. Fedorov is focused on the design, synthesis, and properties of biologically active

pounds and their analogs exhibiting antitumor activity, and design photoactive bioconjugates. The scientific work conducted by A.Yu. Fedorov is focused on the design, synthesis, and properties of biologically active compounds, in particular, those exhibiting antitumor activity. A.Yu. Fedorov and his co-workers developed new polyfunctional arylating agents generated *in situ* from organobismuth and organolead compounds; these agents made it possible to synthesize various heterocyclic derivatives via cascade reactions [584–588].

Arylating agents based on lead and bismuth



A new, actively developing direction of department's research work is the creation of multivalent photoactive antitumor conjugates based on derivatives of natural chlorophyll *a* and synthetic porphyrins [589], as well as new antitumor agents based on natural coumarins [590], combretastatins [591], and colchicine alkaloids [592–594].

## 9. ORGANIC CHEMISTRY IN UNIVERSITIES OF YAROSLAVL

The history of the higher school in Yaroslavl dates back to 1803, when the **Demidov Yaroslavl College of Higher Sciences** funded by P.G. Demidov was opened. The school occupied the next position directly after two central universities. In addition to humanitarian subjects, mathematics, physics, chemistry, and technology were taught here. The first pro-rector was Professor of Chemistry, Natural History, and Technology K.I. Yanish. In 1834 the school was transformed into the Demidov Law Lyceum [595–597].

In 1919, the Yaroslavl State University was founded on the basis of the Demidov Lyceum; there were five chemical departments, including the Department of Organic Chemistry headed by Professor A.I. Gorskii). The University was closed in 1924, and its pedagogical faculty became an independent university, Yaroslavl Pedagogical Institute of Public Education, where the course of organic chemistry was read by N.V. Belinskii. In 1927, the Department of Inorganic and Organic Chemistry was formed in the Yaroslavl Pedagogical Institute; the head of the department was Professor A.V. Znamenskii [598].

The real development of organic chemistry in Yaroslavl has started after the construction of the Yaroslavl Synthetic Rubber Plant SK-1 [599, 600]. The purpose of the plant construction was replacement of imported natural rubber by synthetic produced by S.V. Lebedev's method from alcohol [601]. Rubber was needed for the manufacture of tires, so that the plant was built near the Yaroslavl rubber and asbestos plant. S.V. Lebedev (1874–1934) also took part in the construction of SK-1.

The emergence of a large chemical industry in Yaroslavl required primarily participation of prominent industrial organic chemists and, secondly, training of qualified engineers, especially chemical technologists. M.I. Farberov and B.A. Dolgoplosk should be mentioned first among the scientists worked in this field.

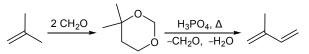
In 1944, the Yaroslavl Technological Institute of Rubber Industry was formed, in 1953–1973 it was the Yaroslavl Technological Institute, in 1973–1994, the Yaroslavl Polytechnic Institute, and since 1994, the Yaroslavl State Technical University [602, 603]. The above mentioned scientists headed the chemical departments opened in 1944 in the new university: the Department of Technology of Basic Organic Synthesis was headed by M.I. Farberov, and the Department of Organic Chemistry, by B.A. Dolgoplosk.

Mark Iosifovich Farberov (1899–1986), Doctor of Engineering, Professor, Honorary Chemist of the USSR Ministry of Chemical Industry, and Honorary Petrochemist of the USSR, in 1927 graduated from the Faculty of Chemistry of the Moscow Higher Technical School, where he studied with such outstand-



ing chemists as A.E. Chichibabin, A.N. Nesmeyanov, and V.N. Ipat'ev. In 1927–1938 he worked as the chief chemist of the Yaroslavl rubber and asbestos plant, then in Moscow as head of a department at the Research Institute of Rubber Industry. He was repressed in 1938. While imprisoned, he laid the theoretical foundations for a new method for obtaining diene hydrocarbons. After rehabilitation in 1964, together with M.S. Nemtsov, he developed and put into operation the dioxane process for the synthesis of isoprene. This production in the USSR began 10–12 years earlier than abroad [600].

Dioxane synthesis of isoprene



Doctor of Chemical Sciences Professor **M.I. Farberov** was the head of scientific laboratories at the plant P.O. Box 135. Since 1947, he lectured at the Yaroslavl Technological Institute of Rubber Industry. He founded the Yaroslavl scientific school of industrial organic chemists [604, 605].

**M.S. Nemtsov** is one of the inventors of isoprene rubber, laureate of the Lenin Prize. Together with P.G. Sergeev, R.Yu. Udris, and B.D. Kruzhalov, he discovered the method of joint production of phenol and acetone (the cumene method). This discovery was made in Yaroslavl at the plant P.O. Box 135 (now joint stock company *Yarsintez* Scientific Research Institute).

Academician of the Academy of Sciences of the USSR Boris Aleksandrovich Dolgoplosk (1905–



1994) graduated from the Faculty of Chemistry of the Moscow State University in 1931. In 1932–1946 he worked at synthetic rubber plants. While working at the Yaroslavl Synthetic Rubber Plant, he improved Lebedev's catalyst for the synthesis of butadiene from alcohol, so that the yield of butadiene increased by 25%; the catalyst was introduced in

all plants that produced butadiene from alcohol. In 1944–1946 he lectured at the Yaroslavl Technological Institute (since 1945, as a professor). Since 1946 he worked at the All-Union Research Institute of Synthetic Rubber and simultaneously (since 1948) at the Institute of Macromolecular Compounds of the Academy of Sciences of the USSR. He created the basis for the synthesis of rubber by emulsion polymerization. He discovered redox initiation of radical processes. In 1957, he developed a technology for the manufacture of stereoregular polybutadiene [606–608].

B.A. Dolgoplosk [609, 610], headed the Department of Organic Chemistry and organized educational process and scientific research with the involvement of students. In the year of the foundation of the department two teachers and one laboratory assistant worked therein and about 150 students were trained. The first student's scientific circle was organized at the department, which was later led by professors Yu.S. Musabekov and M.I. Farberov. In the circle, the future professors B.F. Ustavshchikov and S.I. Kryukov and associate professor K.A. Machtina, began their journey into science.

In 1946, the department was headed by Professor **Yusuf Suleimanovich Musabekov** (1910–1970), who graduated from the Lenin Azerbaijan

Pedagogical Institute in 1927. In 1939 he was drafted into the army, where he began his career as a private soldier and graduated as an engineer-captain of chemical forces. His works on the history of chemistry made him internationally recognized [602, 603, 611–613]. The



second direction of Yu.S. Musabekov's research was radical processes in organic reactions.

Y.S. Musabekov invited a number of young scientists to the department, who then defended their candidate's dissertations and worked as associate professors: R.M. Basaev, L.V. Koshkin, V.V. Voronenkov, N.N. Basaeva, S.K. Kramerova, I.S. Kopashchikova, and G.S. Kazakova.

In 1972, Professor G.S. Mironov became head of the Department of Organic Chemistry; he replaced associate professor A.G. Belorossova on this post. A new stage of development of the department began with his arrival.

German Sevirovich Mironov (1935–2008) graduated from the Yaroslavl Technological Institute in 1958 and worked at the Voronezh branch of *Gidrokauchuk*. In 1963 he defended his candidate's dissertation, and in 1971, doctoral dissertation. In 1972, he was awarded the title of professor. In 1972–1983 G.S. Mironov worked as vice-rector



on scientific work of the Yaroslavl Polytechnic Institute, from 1972 to 1993, as head of the Department of Organic Chemistry, and in 1983–2005, as rector of the Demidov Yaroslavl State University. He



Department of Organic Chemistry of the Yaroslavl Technological Institute.

is author of 4 monographs, more than 500 scientific articles, and about 200 inventor's certificates [602, 603]. His students defended 10 doctoral and more than 40 candidate's dissertations.

Having headed the Department of Organic Chemistry of the Yaroslavl Technological Institute, G.S. Mironov invited V.A. Ustinov and Yu.A. Moskvichev, who soon defended their candidate's dissertations at the department and became associate professors, and later, doctors of sciences and professors. The educational process was improved: in the course of organic chemistry, reaction mechanisms were considered at the present level [614]. At the Department of Basic Organic Synthesis, G.S. Mironov developed methods for the large-scale synthesis of vinyl ketones on the basis of the Mannich reaction, and the synthesis of methyl vinyl ketone was implemented on the industrial scale [615-617]. G.S. Mironov later created a new scientific direction in the Yaroslavl Technological Institute, development of methods for the synthesis of monomers for heat-resistant polymeric materials based on polyfunctional polynuclear aromatic compounds.

The Department of Organic Chemistry, headed by G.S. Mironov, became a real forge of cadres for the Yaroslavl Higher School: employees of the department worked at different times or are now working in the majority of Yaroslavl universities. For instance, two more rectors, Yu.A. Moskvichev (Yaroslavl State Technical University) and A.I. Rusakov (Yaroslavl State University), as well as heads of departments V.V Plakhtinskii, E.M. Alov, I.G. Abramov, A.V. Tarasov, A.V. Kolobov (Yaroslavl Polytechnic Institute–Yaroslavl State Technical University), V.A. Ustinov [618–620], V.V. Kopeikin, V.Yu. Orlov (Yaroslavl State University), M.V. Dorogov (Ushinskii Yaroslavl State Pedagogical University), and M.M. Kuznetsov (Yaroslavl State Medical University), came from the walls of the department.

V.A. Ustinov in 1984 became vice-rector for scientific work of the Yaroslavl State University. Thanks to his organizational skills, V.A. Ustinov together with G.S. Mironov achieved a significant expansion of the problem research laboratory for the synthesis of initial monomers and intermediate products and of the branch laboratory of the USSR Ministry of Chemical Industry.

From 1986 to 2007 Yurii Aleksandrovich Moskvichev was rector of the Yaroslavl Polytechnic Institute– Yaroslavl State Technical University. He headed the department of chemical technology of organic substances. Yu.A. Moskvichev's students defended more than 10 candidate's and 2 doctoral dissertations (E.M. Alov and A.V. Tarasov). Yu.A. Moskvichev directed research on methods of synthesis of sulfurcontaining derivatives of polynuclear aromatic systems, for example, of diphenyl sulfide and diphenyl sulfone [621–623].

The development of scientific research was favored by the presence at the department of the problem research laboratory for the synthesis of initial monomers and intermediate products. In addition, the Department of Organic Chemistry conducted work in the branch laboratory of the Ministry of Chemical Industry of the USSR in cooperation with the Research Institute of Plastics [624] and *Khimvolokno* scientific industrial association [625].

E.R. Kofanov studied methods of synthesis of monomers for heat-resistant polymers of the benzophenone series (tetraamine, aminodicarboxylic acids, etc.) [624, 626], nitration of biphenylcarboxylic acids, and synthesis biologically active heterocyclic compounds [627, 628]. His colleagues defended six candidate's and one doctoral dissertation (A.V. Kolobov). V.V. Plahtinskii defended his doctoral dissertation in 1991, and in 1993 he received the title of professor. His students defended 7 candidate's and 2 doctoral dissertations (M.V. Dorogov and I.G. Abramov) [629-632]. O.A. Yasinskii and A.I. Rusakov were the first in the Yaroslavl Polytechnic Institute to use quantum chemical methods in their scientific research [633-635]. V.V. Voronenkov defended his doctoral dissertation in 1989 on conformational and stereoelectronic effects on the course of organic radical reactions [636, 637]. Professor T.A. Obukhova studied oxidation of alkylbenzenes and hydrogenation of the aromatic ring to afford alkylcyclohexanecarboxylic acids [638-640]. The results of these researches were implemented in industry to produce LCD materials.



**Evgenii Mikhailovich Alov** was elected in 1998 to the post of the head of the Department of Organic Chemistry, and he held this position until 2012. E.M. Alov developed research in the field of synthesis of sulfur-containing monomers for aromatic polycondensation polymers [623, 641–643].

I.G. Abramov (since 2005, head of the Department of General and Physical Chemistry) conducts research in the field of aromatic nucleophilic substitution in phthalonitriles under phase-transfer conditions. The reaction stages have been determined, and methods for the synthesis of dicarbonitriles fused to 5-, 6-, and 7-membered heterocycles have been developed [644, 645]. M.V. Dorogov studied aromatic nucleophilic substitution of the nitro group and sought for methods of synthesis of monomers for heat-resistant polymers [632, 646]. In 2000 he moved to the Ushinskii Yaroslavl State Pedagogical University, where he headed the Department of Organic Chemistry.

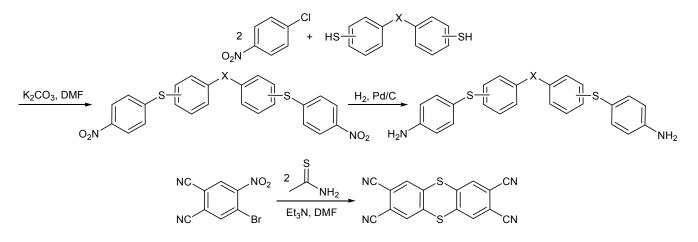
A great contribution to the development of the Department of Organic Chemistry was also made by associate professors A.F. Betnev, G.G. Krasovskaya, K.L. Ovchinnikov, and V.V. Sosnina, as well as by M.S. Belyshev and A.S. Danilov. A great work carried out by head of the laboratory R.P. Usatyuk on reequipment of the department and organization of the educational process and scientific research should also be noted.

Since 2012 the Department of Organic Chemistry of the Yaroslavl State Technical University is headed by Associate Professor, Doctor of Chemical Sciences **Aleksei Vladislavovich Kolobov**. His scientific interest is related to methods of synthesis of vicinal dicarboxylic



acids and their derivatives, including heterocyclic and macrocyclic compounds possessing biological activity [647–649].

Today there are 3 doctors and 6 candidates of sciences at the Department of Organic and Analytical Chemistry (united in 2015). The interdepartmental laboratory of physicochemical research, opened at the initiative of the department, is equipped with analytical instruments of the research level. In connection with the organization of pharmaceutical cluster enterprises in the Yaroslavl region since 2014, the department has started to prepare bachelors in chemical technology in the specialty "Development, production, and quality



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017



Department of Organic and Analytical Chemistry of the Yaroslavl State Technical University.

control of chemical and pharmaceutical preparations and products of fine organic synthesis."

Lectures on organic chemistry are read at the department to all students-technologists; also, students of the specialty "Chemistry" are lectured on special courses. The laboratory practicum allows students to get practical skills in the chemical laboratory; it is conducted individually and ends with the implementation of sophisticated synthesis. Currently, the department trains more than 350 students. Two scientific and educational centers "Organic Chemistry" of the Yaroslavl State Technical University with a steroid laboratory of the Zelinskii Institute of Organic Chemistry of the Russian Academy of Sciences [650] and the laboratory for the synthesis of highly temperatureresistant polymers of the Institute of Macromolecular Compounds of the Russian Academy of Sciences [651] were organized and are operating. In total, for the period from 1981 to 2014, 13 doctoral and about 50 candidate's dissertations were prepared and defended by employees of the Department of Organic Chemistry.

Studies in the field of organic chemistry are conducted at a number of chemical departments of the Institute, often in conjunction with the Department of Organic Chemistry. Thus, theoretical and applied aspects of the synthesis of functional aromatic, alicyclic, and polycyclic systems for the preparation of polymers, liquid crystals, and biologically active substances have been developed at the Department of General and Physical Chemistry under the leadership of Professor G.N. Koshel' [652, 653]. Professor A.V. Tarasov at the Department of Chemical Technology of Organic Compounds studies the synthesis of various sulfocarboxylic acid derivatives [654–656]. Works of Professor N.P. Gerasimova in the field of organic chemistry should also be noted [623, 657]. Close relations were established with the Ushinskii Yaroslavl State Pedagogical University, when the Department of Organic Chemistry therein was headed by M.V. Dorogov (2000).

In 2001, the research laboratory "Organic Chemistry" was founded on the basis of the department. The main research line of the laboratory was development of methods for the synthesis of new organic compounds possessing predetermined biological activity and forming the basis for the design of modern medicines [658–660]. The laboratory was supported by the Chemical Diversity Research Institute (Moscow).

In 2007, the scientific educational center "Innovative Research" was created on the basis of the department and the Institute of Chemogenomics Problems at the Yaroslavl State Pedagogical University. The department trains specialists for *R-Pharm* and *Farmoslavl* companies (Russia), Takeda Nycomed (Japan), and Teva (Israel), localized in the Yaroslavl pharmaceutical cluster. Since 2016 the research work of the department has moved to the Center for Transfer of Pharmaceutical Industry Technologies. After merging of the Department of Organic Chemistry with the Department of Inorganic Chemistry, the Department of Chemistry and Theory and Methods of Teaching Chemistry was formed, which was headed in 2016 by A.V. Kolobov.

The organic chemists of the Yaroslavl State Technical University successfully cooperate with many scientific centers: Ufa Petroleum Institute [661], Ivanovo State University of Chemistry and Technology [662–664], Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences [665, 666], Zelinskii Institute of Organic Chemistry of the Russian Academy of Sciences [667, 668], Skryabin Moscow State Academy of Veterinary Medicine and Biotechnology [650], Voronezh State University [669], Favorskii Irkutsk Institute of Chemistry of the Siberian Branch of the Russian Academy of Sciences [670], Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences [671], Demidov Yaroslavl State University [672, 673], as well as North-West University (South Africa) [674].

In 1984, a branch of the Yaroslavl school of organic chemists was formed at the **Yaroslavl State University**. Its founder was rector of the Yaroslavl State University G.S. Mironov. The Department of General and Bioorganic Chemistry (headed by V.N. Aleksinskaya) was founded as a structural sub-division of the Faculty of Biology.

In 1988 the department was headed by V.V. Kopeikin. The main directions of its activity were related to the synthesis of monomers for polyheteroarylenes (diamines) and intermediate products for color photography (amines containing various functional groups). Various methods of reduction of nitro compounds have been studied, in particular catalytic hydrogenation [675], electrochemical reduction (mediated by carriers), and reduction with transition metal salts. Particular attention was paid to the regioselectivity problems in reactions involving competition of several reaction centers. Another research area covered reactions with rupture of C–C bond and formation of a new

bond. The effect of substituents in benzene rings on the direction of transformation of the dichloroethylene bridging group in reactions with alkali metal nitrites was studied [676].

Since 1999, the department is headed by Vladimir Yur'evich Orlov, who works in the field of nucleo-

philic substitution of hydrogen in nitroarenes and substituted benzonitriles. Data on the reaction mechanism and a variety of new structures were obtained [677, 678]. The results of these studies were implemented as technologies for the preparation of new monomers materials for color photography.



In 2006 and 2007 the educational process significantly expanded in terms of both volume and nomenclature of disciplines in view of the emergence of the new specialty "Applied Informatics in Chemistry" and training of bachelors in the specialty "Chemistry." This greatly extended the possibilities for the development of a community of organic chemists in the Yaroslavl State University. At that time, there were 5 professors, 5 associate professors, and 3 senior lecturers at the department.

In 2009, due to development of chemical education in the Yaroslavl State University and increase in the number of structural subdivisions, the department was named the **Department of Organic and Biological Chemistry**. At present, the department is a structural subdivision of the Faculty of Biology and Ecology, and it provides training in chemical specialties (organic chemistry, biochemistry, nanochemistry, etc.) bachelor's program "Chemistry" (medicinal and pharmaceutical chemistry), master's program



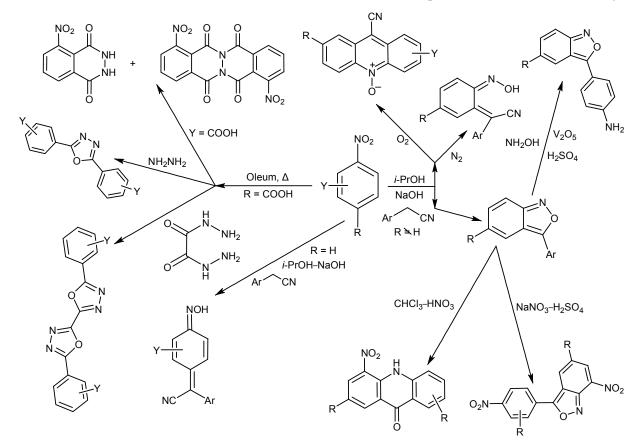
Department of Organic and Biological Chemistry of the Yaroslavl State University.

"Chemistry" (physical organic and pharmaceutical chemistry), bachelor's programs "Biology" and "Ecology and Nature Management," and master's program "Ecology and Nature Management" (environmental monitoring). Six post-graduate students are being trained in the specialty "Organic Chemistry."

As a part of the Yaroslavl school of organic chemists, the Department of Organic and Biological Chemistry has stable scientific relations with the Institute of Organic Chemistry of the Russian Academy of Sciences, Institute of Organoelement Compounds of the Russian Academy of Sciences, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Tula State Pedagogical University, Vladimir State University, Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences, Yaroslavl State Technical University, etc. [679, 680]. Molecular design of organic structures and reactions, targeted search, synthesis and testing of carbo- and heterocyclic systems, chemistry of carbon-containing nanoparticles, computer modeling of molecular and supramolecular organic entities and their transformations, modern methods for analysis of organic substances, and environmental chemistry are the priority directions of scientific research.

The research work of Prof. V.Yu. Orlov's group is focused on nucleophilic substitution of hydrogen, catalytic systems for nucleophilic aromatic substitution in heterophase systems, hydrogenation reactions in flow reactors, formation of organic periphery of carbon nanotubes, computer modeling of molecular and supramolecular objects. As a result of the studies, data were obtained on the mechanism of nucleophilic substitution of hydrogen in substituted nitroarenes with carbanions derived from arylacetonitriles [681].

Catalytic systems that substantially accelerate heterophase nucleophilic aromatic substitution of halogens in nitrohalobenzenes have been proposed [682]. Algorithms for optimizing the hydrogenation of polyfunctional heterocyclic systems under conditions of competition between different reaction centers have been approved. Reactions of covalent and noncovalent modification of carbon nanotubes by bulky functional groups were successfully carried out, which greatly expanded the possibilities of their use (in particular, for the creation of composite materials, which was piloted in industrial conditions). The use of computer modeling allowed extensive information to be obtained on the structure and behavior of a wide range of molecular, supramolecular, and nanoscale objects.



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

The research group directed by associate professor R.S. Begunov developed a new method for the synthesis of fused imidazole derivatives with a bridgehead nitrogen atom via reductive cyclization of N-[2-nitro (het)aryl]pyridinium chlorides, a new reductive isomerization/recyclization of N-[2-nitro(het)aryl]-5,6-R-benzimidazoles was discovered, key intermediates were established, reaction mechanism was proposed, the reactivity of substituted pyrido[1,2-*a*]benzimidazoles in electrophilic substitution was studied, and high regioselectivity of the reaction was explained; more than 300 previously unknown polyaza heterocycles were synthesized, and their structure was studied; intercalation of pyrido[1,2-*a*]benzimidazoles with DNA was revealed [683, 684].

It should be specially noted that young researchers, students and undergraduates, are widely involved in scientific research. In recent years, they have received more than 300 awards, including the Lomonosov Medal of the Russian Academy of Sciences and gold medals of Scientific and Technical Creativity of Youth and All-Russia Exhibition Center. In addition, young scientists are widely involved in competitions for grants, which further motivates students and expands the community of organic chemists.

## 10. DEPARTMENT OF ORGANIC AND BIOORGANIC CHEMISTRY IN THE CHERNYSHEVSKII SARATOV STATE UNIVERSITY

The founder of the department and its leader from 1922 to 1947 was Vladimir Vasil'evich Chelintsev



(1877–1947), a scientist of world renown, corresponding member of the Academy of Sciences of the USSR, a member of the French, American, and London chemical societies [685]. It was during this period that the foundations of the scientific and pedagogical school of

the department were laid.

In 1900, V.V. Chelintsev graduated from Moscow University, where he was left for 2 years at the Department of Chemistry to prepare for the professorship. His first scientific supervisor was Professor N.D. Zelinskii. In 1905 V.V. Chelintsev was at the universities of Germany, France, and Switzerland to get acquainted with the educational and scientific work; he visited the laboratories of E. Fischer, J. Van't Hoff, V. Grignard, A. Lichte, and other famous chemists. His first independent research devoted to the study of Grignard reaction mechanism was later summarized in the thesis "Individual organomagnesium compounds and their transformations into oxonium and ammonium complexes" (1908). These studies were evaluated by leading organic chemists (N.D. Zelinskii, A.E. Favorskii) as classical; Nobel Prize laureate V. Grignard presented his portrait with an autograph to V.V. Chelintsev. After defending the thesis, private docent V.V. Chelintsev was appointed to the position of extraordinary professor in the Department of Chemistry of the Nicolas Imperial University of Saratov (1910). He took an active part in organizing the laboratory of organic chemistry, equipping it with necessary imported equipment and reagents, and creating a library of chemical literature; he wrote: "... I am happy ... that scientific research has already begun in our laboratories."

Along with fundamental research under the guidance of V.V. Chelintsev, work was carried out in the field of petrochemistry, catalysis, chemical technology, analytical chemistry, history of chemistry, and the chemistry of oil shale. V.V. Chelintsev traveled to the Urals and Western Siberia, visited famous Ural plants and mines, brought for the University of Saratov a collection of minerals, and participated in expeditions to search for minerals such as oil, gas, peat, shale, and salt deposits on the lake Elton.

In 1911, the entire university board which opposed the reactionary policy of the Minister of Education was dismissed at the Moscow State University. As a sign of protest, 100 professors and teachers resigned, including N.D. Zelinskii, the teacher of V.V. Chelintsev. With the purpose of preserving the continuity of the scientific school, N.D. Zelinskii insisted that Professor V.V. Chelintsev be appointed to the position of head of his laboratory of organic and analytical chemistry, and V.V. Chelintsev was approved as an acting extraordinary professor of the Moscow (see Section 4). In 1917, the dismissed professors were returned to their previous posts, and V.V. Chelintsev transferred his powers to N.D. Zelinskii and in 1918 returned to his native city, where he was appointed as professor of the Saratov University in the united department of organic, inorganic, and physical chemistry at the Faculty of Physics and Mathematics.

Having headed the Department of Organic Chemistry and the Laboratory of Quantitative Analysis, V.V. Chelintsev continued the research started at the Moscow University and devoted to high-valence oxygen-, sulfur-, and nitrogen-containing compounds and methods of synthesis of heterocyclic compounds. In 1920, V.V. Chelintsev initiated foundation of the Saratov Chemical Society, which he headed until 1930 and since 1945, after its reorganization to the Saratov Branch of the Mendeleev All-Russia Chemical Society. In 1922 he was elected a member of the Bureau of the Mendeleev Congresses.

V.V. Chelintsev was "the founder of the Saratov Chemical School, which he headed for 30 years," wrote Academician A.E. Arbuzov in his book "A Brief Outline of the Development of Organic Chemistry in Russia." The department staff carried out research in the field of onium complexes; heats of formation of the main groups of organic compounds were determined, and tables of thermochemical data were compiled. On the basis of thermochemical studies, the formulas of complex oxonium compounds described by A. Bayer and V. Villiger were corrected. The results of studies of onium compounds were summarized in the monographs "Studies of Higher Valencies in Oxygen, Sulfur, and Nitrogen Compounds" [686] and "Organic Catalysts" [687].

A long period in the scientific activity of V.V. Chelintsev was associated with the chemistry of pyrrole compounds. When studying the condensation of pyrrole with acetone, ethyl methyl ketone, and methyl hexyl ketone, he found that these reactions lead to the formation of systems comprising four pyrrole rings, which are the structural basis of the natural complexes chlorophyll and hemoglobin. In 1918, V.V. Chelintsev's monograph "Study of Pyrrole Compounds" was published.

Since 1930, systematic studies of furan chemistry have been started. Particular attention was paid to furfural, an accessible representative of the furan series obtainable from agricultural raw materials and waste from the timber processing and hydrolysis industries. The aldolysis reaction was discovered, i.e., the ability of formaldehyde (or acetaldehyde) to displace furfural, and of furfural, to displace benzaldehyde from the ylidene compounds. The condensation of furfural with carbonyl compounds leading to the formation of colored substances formed the basis for methods for determining small amounts of furfural, acetone, formaldehyde, and acetaldehyde. A technological scheme was developed for the production of furfural from the husks of sunflower seeds and a workshop for its production was opened at the Saratov butter factory.

In the 1930s, investigations were carried out at the department in the fields of petrochemistry and catalysis, characteristics of oils of Second Baku, and

methods of cracking and desulfurization of oils. V.V. Chelintsev participated in the development of gas-phase and oxidative cracking; he was a member of the commission of the USSR Academy of Sciences for studying Volga, Kama, and Bashkir oils.

V.V. Chelintsev believed that "a deep real assessment of scientific knowledge cannot be made ... without history, without knowledge of the progress of discovery." He wrote that the history of science is an important means of educating students and young scientists and justified the priority of discoveries of Russian chemists. The role of Russian scientists, such as M.V. Lomonosov, D.I. Mendeleev, A.M. Butlerov, N.N. Zinin, M.G. Kucherov, A.A. Voskresenskii, V.V. Markovnikov, N.E. Lyaskovskii, and A.P. Borodin, in the development of organic chemistry was highlighted in a number of publications of V.V. Chelintsev. He published the books "Organic Chemistry in Biographies of Its Main Figures" (where 20 portraits were presented) and "The First Russian Chemists and Foundation of the First Russian Chemical Schools." In the last years of his life, V.V. Chelintsev enthusiastically read a course of lectures on the history of chemistry for students. V.V. Chelintsev was a brilliant teacher, he wrote and published two textbooks "Organic Chemistry for Universities" with the review of N.D. Zelinskii, a textbook for technical schools, published 17 monographs and brochures, and 600 scientific and popular articles and reports. Among students of V.V.Chelintsev, professors E.K. Nikitin, S.I. Spiridonova, G.V. Medoks, B.V. Tronov, M.N. Tilichenko, V.I. Kuznetsov, V.I. Esafov, and others should be noted.

In 1947, **Mikhail Nikitovich Tilichenko** was elected head of the department. He came to the depart-

ment pulpit immediately after demobilization from the army, where he was in the Polish Army. He was awarded the Polish Order of the Silver Cross for his military service. A new scientific direction was created with his participation, chemistry of 1,5-dicarbonyl compounds and carbo- and heterocyclic compounds



based thereon. In the difficult post-war period, 3 candidate dissertations were defended (V.G. Kharchenko, V.A. Popova, and N.K. Astakhova) under his guidance in a short time.

M.N. Tilichenko discovered a new reaction, diketone condensation, that is cross-linking of two ketone molecules by one aldehyde molecule; it was shown that 1,5-diketones extremely easily undergo carbo- and heterocyclization to give new series of sixmembered mono-, bi-, and tricyclic  $\beta$ -hydroxy ketones and six-membered O-, N-, S-, and Se-containing (poly)heterocyclic compounds [688].

A student of M.N. Tilichenko was Professor Nicolae Bărbulescu; during the internship at the department he studied the condensation of acetaldehyde with cyclohexanone and, after his return to Romania, cooperated with his teacher.

In 1959, M.N. Tilichenko together with his students left for Vladivostok, where he headed the Department of Organic Chemistry of the Far Eastern State University. He created a school of organic chemists in the Far East of Russia, the outstanding representatives of which were graduates of the department Academician of the Russian Academy of Sciences Vladimir Ivanovich Vysotskii and Professor Vladimir Abramovich Kaminskii.

Aleksandr Aleksandrovich Ponomarev defended his candidate's dissertation "Synthesis of alkyl-sub-



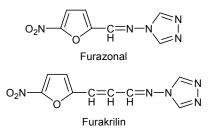
stituted mono- and divinyl ketones" on June 21, 1941. On June 23, he was drafted into the army, and all the years of the Great Patriotic War he was in the active army (until September 1945) in the rank of captain of special units, as head of the chemical laboratory. In 1952 he

was seconded to the doctorate at the Department of Organic Chemistry of the Lomonosov Moscow State University (1952–1954). Its scientific adviser at the Moscow State University was Corresponding Member of the Academy of Sciences of the USSR A.P. Terent'ev. In 1954 A.A. Ponomarev defended his doctoral dissertation "Study in the field of furan aldehydes, ketones, and their derivatives," and in 1955 he headed the Department of Organic Chemistry of the Saratov State University.

In 1957, under A.A. Ponomarev, one of the first in the country problem laboratories of hydrogenation and catalysis was created. On its basis, laboratories for organic microanalysis, physical research methods, catalytic synthesis, and high-pressure catalytic processes were founded. To conduct the research, A.A. Ponomarev achieved the construction of a special building, chemical pavilion, on the territory of the campus, where the autoclave room was placed, and a flow reactor was installed to carry out catalytic processes under pressure. The creation of the laboratory favored introduction of the special course "Organic Synthesis and Catalysis" and a large training practicum for it.

Under the guidance of A.A. Ponomarev, studies in the field of furan compounds, five-membered nitrogencontaining heterocycles, and heterocyclic spiro compounds were performed. Methods of heterogeneous catalysis, dehydrogenation, dehydration, and hydroamination at ordinary and elevated pressure were widely used. The catalytic properties of platinum, palladium, nickel, and copper/chromium catalysts were studied. New types of catalysts were obtained on the basis of ruthenium and rhodium and were used for the catalytic hydrogenation of heterocyclic and aromatic compounds, including those of practical value [689, 690]. Together with Academician A.A. Balandin, the author of the multiplet theory of catalysis. regularities of hydrogenation and hydrogenolysis of  $\alpha,\beta$ -unsaturated ketones and aldehydes of the furan series on skeletal nickel catalyst were established and theoretically substantiated. Lecturers of the department and employees of the problem laboratory Z.V. Til', A.S. Chegolya, A.V. Finkelstein, N.S. Smirnova, A.D. Shebaldova, V.N. Kravtsova V.V. Zelenkova, L.V. Vlasova, N.S. Monakhova, Z.N. Kuzmina, and many others took an active part in these studies.

The applied aspect of the research carried out during that period was reflected in screening of biologically active substances, which was facilitated by the organization of interinstitution laboratory of the Saratov State University and Saratov Medical Institute (K.I. Bender, G.M. Shub, L.K. Kulikova). New antimicrobial nitrofuran drugs *furazonal* and *furakrilin* (M.D. Lipanova) and antitussive drug bitiodin (N.I. Martem'yanova) were created. The first (1959, 1962) All-Union conferences on the chemistry of furan compounds were organized and held at the Saratov State University.



A.A. Ponomarev's monograph "Syntheses and Reactions of Furan Compounds" [691] became the reference book of chemists working in the field of furans.

tionSynthesis and stereochemical studies in the seriesof 1,2-dihydropyrrolizine and pyrrolizidine" at theClMoscow State University.AiAfter the death of Professor A.A. Ponomarev, theSedepartment was headed by Zinaida Vasil'evnathTil' (1968–1971). At that time, the scientific adviser ofwthe department was professor, doctor of chemicalresciences M.L. Khidekel' (Chernogolovka) whoarpinitiated new studies on metal complexes and theirpinitiated

Professor J.A. Elvidge, he used the NMR method for stereochemical studies of pyrrolizidines as examples. Upon his return from England, he studied the stereochemistry of pyrrolizidine, its homologues, and pyrrolizidine alcohols. He and his co-authors determined the fundamental thermodynamic parameter for the conformational analysis of pyrrolizidines, the enthalpy of *cis*-*trans* isomerization of the parent base. During the study of intramolecular hydrogen bonds in pyrrolizidine alcohols, a general GLC method for determination of the energy of intramolecular hydrogen bonds was developed. In 1989, he defended his doctoral dissertation "Synthesis and stereochemical studies in the series of 1,2-dihydropyrrolizine and pyrrolizidine" at the

application in catalysis. Complexes of transition

metals, including cobalt, palladium, and platinum, with

demonstrated (A.D. Shebaldova). In 1970 the work

"Catalytic Disproportionation of Unsaturated Hydrocarbons" was published (M.L. Khidekel', A.D. She-

baldova, M.V. Kolechits; Moscow).

professor, and from 1963 to 1971, the dean of the Faculty of Chemistry. With her assistance, a branch of the Faculty of Chemistry of the Saratov State University was founded in the Shihany village in Saratov oblast. V.A. Sedavkina developed conditions for the hydrolytic opening of the furan ring in order to obtain  $\gamma$ -ketocarboxylic acids and their esters, which were used to synthesize various heterocycles. Until the end of her life (2000), V.A. Sedavkina worked as a professor of the department.

A.A. Ponomarev's student I.M. Skvortsov in 1967

was sent to a 10-month internship in England at the

University of Surrey in London. Under the guidance of

date's dissertations were defended. His students were V.A. Sedavkina, A.P. Kriven'ko, M.V. Noritsina, I.M. Skvortsov, and A.S. Chegolya; they later became doctors of sciences. **Valentina Aleksandrovna Sedavkina** since 1956 was an assistant of the department, then an assistant

Under the guidance of A.A. Ponomarev, 17 candi-

ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS

For 21 years (1971–1992), the department was headed by Valentina Grigor'evna Kharchenko,

a student of M.N. Tilichenko. Scientific researches at the department headed by her and at the Department of Organic Chemistry of the Saratov Research Institute of Chemistry of the Saratov State University were conducted in the field of chemistry of carbonyl and heterocyclic compounds. Nucleophilic and electro-



philic reactions of saturated and unsaturated arylaliphatic, seven-membered, and bicyclic 1,5-diketones have been extensively studied, competitive mechanisms for the formation of pyrylium, and thio- and selenopyrylium salts have been revealed, and the ability of pyrans to undergo recyclization to thio- and selenopyrans by the action of nucleophiles has been demonstrated. It was found that acidophilic alkyl-, aryl-, and functionally substituted furans in strongly acidic media recyclize to the corresponding thio- and selenophenes [692–694].

These studies were carried out with participation of the employees of the department and its graduates, in particular A.F. Blinokhvatov (later vice-president of the Russian Academy of Natural Sciences, rector of the Penza Agricultural Institute), S.K. Klimenko (professor of the Saratov Agrarian University), and B.I. Drevko (corresponding member of the Russian Academy of Natural Sciences, head of the department of chemistry of the Saratov Military Institute of Radiation, Chemical, and Biological Protection.

In 1989, a branch of the Department of Organic Chemistry was established at the Saratov branch of the All-Union Scientific Research Institute of Genetics and Selection of Industrial Microorganisms. The head of the branch during its organization and development was Sergei Petrovich Voronin. In 1991, the branch was reorganized in order to attract the scientific potential and facilities of the Institute of Biochemistry and Physiology of Plants and Microorganisms of the Russian Academy of Sciences to the educational process (director Professor V.V. Ignatov, head of the branch Doctor of Chemical Sciences Professor S.Yu. Shchegolev).

During this period, five interinstitutional and All-Russian conferences "Carbonyl Compounds in the Synthesis of Heterocycles" (1977, 1982, 1985, 1989, 19920) were held on the research topics developed at the department.

From 1992 to 2008 the department was headed by Adel' Pavlovna Kriven'ko. New approaches to the



conversion of furans into five-membered aza heterocycles and of 1,5-diketones, cyclic  $\beta$ -hydroxy ketones, pyrylium and pyridinium salts into six-membered nitrogen-containing compounds of the (cyclano)piperidine series have been developed, and studies have been carried out in the

field of their stereochemistry, conformational behavior, and mechanisms of formation.

Successful experience of the department and its branch at the Institute of Biochemistry and Physiology of Plants and Microorganisms of the Russian Academy of Sciences in training the personnel of the bioorganic profile predetermined renaming of the Department of Organic Chemistry to the Department of Organic and Bioorganic Chemistry.

In 1945, the Research Institute of Chemistry was founded at the Saratov State. The largest subdivision of the Saratov State University was the united Department and Section of Organic Chemistry whose staff amounted up to 80 people. In the 1990s, the educational scientific complex was transformed into an educational scientific and production complex, which included the Department of Organic Chemistry, the Section of Organic Chemistry, and the branch of the department at the Institute of Biochemistry and Physiology of Plants and Microorganisms of the Russian Academy of Sciences. The Department of Organic Chemistry of the Research Institute of Chemistry included 3 laboratories, chemistry of heterocyclic compounds, catalytic synthesis, and fine organic synthesis. In 1994, a laboratory for testing food and agricultural products was founded at the department and was accredited in the system of the State Standard of the Russian Federation (head of the laboratory senior researcher, candidate of chemical sciences G.V. Bespalov). Scientific conferences of various ranks were held on the basis of the department [695-697].



Since 2008, the department is headed by **Ol'ga Vasil'evna Fedotova**. She carried out research in the field of complex spiro heterocycles and fused heteroatom-bridged N-, O-, S-, and Se-containing compounds. Under her scientific guidance, 14 candidate's dissertations and one doctoral dissertation (N.V. Pchelintseva) were defended. Since 2009, O.V. Fedotova is dean of the Faculty of Chemistry reorganized into the Institute of Chemistry of the Saratov State University.

The scientific and educational center "Biocatalysis," headed by S.P. Voronin was created at the department, and the spectral laboratory (Professor I.N. Klochkova, associate professor A.A. Anis'kov) received further development. Great work on the computerization of the department is conducted by Professor V.V. Sorokin. Academician of the Russian Academy of Natural Sciences Professor A.Yu. Egorova is a scientific consultant of the journal "Promyshlennost' of the Volga region." The laboratory of organic chemistry of the Chemical Technologies Section of the Institute of Chemistry of the Saratov State University, the laboratory of the department at the Institute of Biochemistry and Physiology of Plants and Microorganisms of the Russian Academy of Sciences (director Doctor of Chemical Sciences Professor S.Yu. Shchegolev), and the laboratories of spectral analysis, elemental analysis, and new substances and materials work according to a common plan [698, 699]. An ecological and chemical lyceum was created. There are 14 lecturers at the department, including 8 doctors of sciences and professors.

The department trains bachelors in chemistry and pedagogical education, masters (including representatives from Iraq) in chemistry, and post-graduate students in organic chemistry.

The department has always had close contacts with universities and leading institutes in Russia, first of all, with the Moscow State University, where its employees and lecturers defended their doctoral and candidate's dissertations, held internships, carried out joint scientific research, and published in co-authorship (Institute of Organic Chemistry of the Academy of Sciences of the USSR, Moscow Institute of Fine Chemical Technology, Institute of Organoelement Compounds of the Russian Academy of Sciences, St. Petersburg, Far East, Voronezh, Samara, and Astrakhan Universities, Perm Pharmaceutical Academy).

During the years of its existence the department has trained more than 1000 students. Its graduates include academicians, corresponding members of the Russian Academy of Natural Sciences, honored scientists of the Russian Federation, over 30 doctors and over 90 candidates of science, 2 rectors, directors of factories and laboratories, laureate of the State Prize of Russia, Hero of Socialist Labor.

# 11. DEPARTMENT OF ORGANIC AND BIOMOLECULAR CHEMISTRY OF THE URAL FEDERAL UNIVERSITY (YEKATERINBURG)

The history of the Department of Organic and Biomolecular Chemistry of the Yeltsin Ural Federal University goes back to the beginning of the last century, when the Urals State University was founded in the Urals in October 1920. One of the structural divisions of the University was the Ural Polytechnic Institute which combined the mechanical, chemical, and forestry engineering faculties. Chemist Aleksandr Makovetskii became director of the Polytechnic Institute which was the largest part of the new university. On May 15, 1925, according to the resolution of the Council of People's Commissars of the RSFSR, the Ural State University was renamed the Ural Polytechnic Institute (UPI), where the history of the Department of Organic Chemistry has started.<sup>36</sup> Sergei Gordeevich Karmanov, a representative of Zelinskii's scientific school, was appointed the first head of the department, and the first research work was related to organomagnesium compounds.

In 1926, Isaak Yakovlevich Postovskii was invited to the post of head of the department. I.Ya. Postovskii



was educated in Germany, at the Munich Higher Technical School where he worked in the laboratory of Nobel Prize winner Hans Fischer. The name of I.Ya. Postovskii is associated with the formation of a scientific school of organic chemists in Sverdlovsk (now Yekaterin-

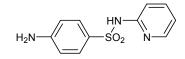
burg). Deep erudition and broad scientific interests enabled him to make a significant contribution to various fields of organic chemistry. During this period, the research works at the department were aimed at solving problems of the developing industry in the Urals, in particular the composition of oil extracted in the Chusovaya river basin and the nature of coals and products of their semi-coking were studied.

Being in Sverdlovsk in 1939, Academician N.D. Zelinskii visited the Department of Organic Chemistry and assessed it as one of the best in the Soviet Union. During these years, a whole series of pioneering works in the field of organic chemistry, such as the synthesis of perylene (L.N. Golodyrev),

rubicene (V.I. Khmelevsky), azacholanthrene, and other compounds of the acridine series (B.N. Lundin) were accomplished under the guidance of I.Ya. Postovskii.

### 11.1. Sulfonamides and Other Antibacterial Drugs

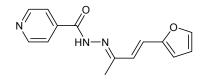
Professor I.Ya. Postovsky instilled in the employees an interest in physiologically active substances. After the discovery of streptocide (1936), a new direction began to develop at the department, connected with the synthesis and properties of sulfanylamides. Methods for the synthesis of a large series of compounds of this series have been developed, and their structure and pharmacological action have been studied. One of these, sulfapyridine [2-(4-aminobenzenesulfonylamino)pyridine] initiated the era of antibacterial sulfonamide preparations in the USSR. Later, *sulfazole* (1940) and *sulfathiazole* (1941) were tested.



Sulfidine-the first Russian antibacterial drug.

It was shown that sulfanylamide drugs are efficient in the treatment of pneumonia and a wide range of infections and are relatively low toxic. With the efforts of the staff of the Department of Organic Chemistry, the production of these medicines was organized at the Sverdlovsk Chemical and Pharmaceutical Plant, which saved the lives of many thousands of wounded during the Great Patriotic War. Works on the creation of new medicines and technologies for their manufacture (*sulfidine*, etc.) were awarded the State Stalin Prize (I.Ya. Postovskii, 1946).

In the postwar 1950s, research on new antituberculous compounds was initiated at the department under the guidance of Professor I.Ya. Postovskii. The research was carried out jointly with the Sverdlovsk Research Institute of Tuberculosis of the Ministry of Health of the RSFSR (now the Ural Research Institute of Phthisiopulmonology of the Ministry of Health of



Antituberculous drug Larusan

<sup>&</sup>lt;sup>36</sup> This section does not include the history of the Department of Technology of Organic Synthesis of the Ural Federal University.

the Russian Federation). As a result of these works, the anti-tuberculosis drug *Larusan* (*laru* is the *Ural* read from right to left) was created, which retained its importance to the present day.

# 11.2. Participation in the Nuclear Project. Organofluorine Chemistry

Fundamental knowledge, a broad mental outlook, and the ability of scientific foresight allowed I.Ya. Postovskii to make a significant contribution to the development of chemistry of organofluorine compounds. One of the problems related to the creation of nuclear weapons in the country was the development of industrial separation of uranium isotopes. Special lubricants based on perfluorinated hydrocarbons were required for ultracentrifuges to enrich natural uranium with <sup>238</sup>U, which operated at high velocities in very strongly oxidizing media (uranium hexafluoride). In 1948 I.Ya. Postovskii and his student B.N. Lundin led the work on a special government task with the goal of creating the famous UPI lubricant. Their contribution to the program for the development of nuclear weapons was marked by the Order of Lenin (1951) and by the closed State Stalin Prize (1952). Professor B.N. Lundin continued the development of fluorinecontaining lubricants (UPI lubricant and its analogs are produced at the present time).

Later, under the guidance of I.Ya. Postovskii and V.Ya. Kazakov, the chemistry of fluorine- and oxygencontaining compounds developed successfully at the department and in the laboratory of the Institute of Chemistry of the Ural Branch of the Academy of Sciences of the USSR. These works resulted in the creation of an original class of organofluorine compounds, perfluorinated polyesters that are copolymers of hexafluoropropylene and oxygen obtained by a photochemical method. These compounds are widely used as lubricants and surfactants to this day. Professors S.V. Sokolov and I.Ya. Postovskii developed a new research direction related to fluorine- and nitrogen-containing organic compounds. The obtained results formed the basis for the development of chemistry and technology of organofluorine compounds and polymers in the Lebedev All-Union Research Institute of Rubber in Leningrad, where S.V. Sokolov came to work.

Simultaneously, studies in the field of chemistry of free radicals of the hydrazine series were successfully developed under the guidance of Professor R.O. Matevosyan. **Rafael' Oganesovich Matevosyan**  is a worthy graduate of the Ural school of organic chemists. Later (mid-1970s) he moved to Yerevan, where he founded the Armenian Branch of the Institute of Chemical Reagents and Ultrapure Substances, which in 1981 became the lead agency in the *SoyuzReactiv* system of production of organic reagents.

The 1950s could become tragic for the development of chemistry in the Urals. At that time, Professor I.Ya. Postovskii was accused of idealism and devotion to foreigners (the "theory of electronic resonance") and forgetting the work of Russian scientists. Only in the 1960s, when Pauling became a Nobel laureate, I.Ya. Postovskii was forgiven for "idealism."

### 11.3. Heterocyclic Chemistry

The sixties of the last century were marked by the rapid development of chemistry of heterocyclic compounds in Russia and in the world (primarily in the USA). At that time hundreds of various derivatives of heterocyclic compounds were synthesized at the department, and physical methods such as IR and UV spectroscopy, polarography, dipole moments, mass spectrometry, and ESR were extensively used to study their physicochemical properties. I.Ya. Postovskii with co-workers (N.P. Bednyagina, N.N. Vereshchagina, I.N. Goncharova, V.A. Ershov) and colleagues from the All-Union Research Chemical and Pharmaceutical Institute (Yu.N. Sheinker) carried out pioneering studies on azido-tetrazole rearrangements in the azole and azine series.

In these same years, the chemistry of heterocyclic formazans was initiated. The impetus was given by the observation of Professor N.P. Bednyagina that alcoholic solutions of 1-alkyl-2-hydrazinobenzimidazoles acquire an intense violet color on exposure to air and purple crystals gradually separate from the solution. They were identified as 1,5-bis(1-alkylbenzimidazole-2-yl)-3-substituted formazans with the help of I.Ya. Postovskii, who previously dealt with arylformazans. Thus, the self-oxidation of hetarylhydrazines was discovered, which made it possible to synthesize a large number of symmetrical and unsymmetrical hetarylformazans and their complexes with metals. The obtained compounds are widely used as analytical reagents, test systems, electrochemical sensors, catalysts, and components of optical recording media and specialty dyes.

In 1968 the first All-Union Conference on physicochemical properties of heterocyclic compounds was held in Sverdlovsk. ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS

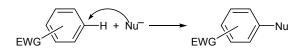
# 11.4. Nucleophilic Substitution of Hydrogen—A New Methodology for Organic Synthesis

In the 1970s, Oleg Nikolaevich Chupakhin, who succeeded in 1976 I.Ya. Postovskii as head of the



department, and his graduate students (V.A. Trofimov, V.G. Kirichenko, V.L. Rusinov, E.O. Sidorov, T.L. Pilicheva, V.N. Charushin, V.I. Shilov, A.I. Matern, S.K. Kotovskaya) carried out an extensive series of pioneering systematic studies of the reactions of nucleo-

philic aromatic substitution of hydrogen and their application scope and determined the structure of intermediates, mechanism, and kinetic patterns, which formed the basis of the  $S_N^H$  methodology. The results of these studies were summarized for the first time in the world practice in a review article by O.N. Chupakhin and I.Ya. Postovskii published in 1976 in the journal *Uspekhi Khimii* (Russian Chemical Reviews) [700].



At that time, textbooks on organic chemistry affirmed that "substitution of hydrogen in the aromatic ring is unlikely" [701]. In the following decades, the situation changed radically; hundreds of published reports, tens review articles, and two monographs [702–713] made this area, according to the figurative expression of Professor F. Terrier, "... the fascinating subject ..." [714] and one of the most attractive topics for authoritative chemical publications. Research groups from Poland, Belgium, Germany, Spain, Japan, USA, and several scientific centers of Russia (Moscow, Rostov, Novosibirsk, St. Petersburg, Yekaterinburg, Stavropol, Kazan) made a significant contribution to the development of direct nucleophilic C-H functionalization, thereby demonstrating the importance of this topic and its international recognition, which is reflected in the collective monograph [647]. In addition, Chapter 13 in the modern version of March's textbook on organic chemistry [715], devoted to aromatic nucleophilic substitution, contains the subsection "Hydrogen as a leaving group."

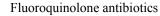
The works of professors G.V. Zyryanov, E.N. Ulomskii, V.L. Rusinov, V.N. Charushin, and D.N. Kozhevnikov, associate professors M.V. Varaksin, S.L. Deev, I.A. Utepova, and I.S. Kovalev, and research workers A.A. Musikhin, I.A. Khalymbadzha, D.S. Kopchuk, P.O. Serebrennikova, and R.F. Fatykhov) showed that  $S_N^H$  reactions have a huge fundamental and practical significance as they allow modification of various nitro and aza aromatic compounds and their benzo-fused analogs, as well as quinones, azinones, porphyrins, azulenes, and other aromatic substrates via nucleophilic substitution of hydrogen and formation of new carbon–carbon and carbon– heteroatom bonds. The  $S_N^H$  methodology includes a large number of reactions such as nucleophilic alkylation, alkenylation, alkynylation, arylation, amination, aminoarylation, hydroxylation, alkoxylation, cyanation, cyanomethylation, halogenation, and sulfurization, and also cymantrenylation, carboranylation, ferrocenylation, etc.

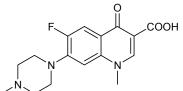
The accumulated data on the  $S_N^H$  reactions show that it is time for understanding and, possibly, changing the logic of organic synthesis. In fact, halogen atoms in an aromatic ring and other leaving groups that are usually easily replaced by nucleophiles can be considered as substituents protecting the corresponding carbon atom and thereby directing nucleophilic attack on the C–H bond. American chemists Daniel Morton and Huw Davies consider this area so important for the future that they invited organic chemists to create a Center dealing with selective C–H functionalization [716].

#### 11.5. Synthesis of Medicines

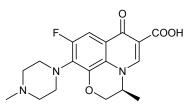
**Fluoroquinolones.** One of the outstanding achievements of chemical science in the twentieth century is undoubtedly the creation of a new generation of effective antibacterial drugs based on fluoroquinolone derivatives. The department had considerable experience in working with heterocyclic and organofluorine compounds and took part in the development of this subject.

Employees of the department (O.N. Chupakhin, V.N. Charushin, G.N. Lipunova, G.A. Mokrushina, S.K. Kotovskaya, E.V. Nosova, Z.M. Baskakova, G.M. Petrova, O.M. Chasovskikh, E.V. Tsoi, N.M. Perova, M.G. Ponizovskii), in cooperation with the Postovskii Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences, Zelinskii Institute of Organic Chemistry of the Russian Academy of Sciences (Academician O.M. Nefedov, senior researcher N.V. Volchkov), Institute of Organic Chemistry of the Ufa Scientific Center of the Russian Academy of Sciences (Academician G.A. Tolstikov, V.A. Grusev) and Volgograd branch of the Boreskov Institute of Catalysis of the Siberian Branch of the





Pefloxacin-one of the first fluoroquinolones



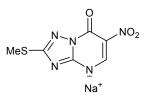
Enantiomerically pure Levofloxacin

Russian Academy of Sciences (Academician V.N. Parmon) and close collaboration with biologists of the Institute of Antibiotics (Academician of the Russian Academy of Medical Sciences S.M. Navashin, Professor I.P. Fomin), Institute of Microbiology of the 48th Central Research Institute of the Ministry of Defense of the Russian Federation (Professor P.G. Vasil'ev, E.V. Pimenov), performed a wide range of scientific, research, technological, and experimental design works on the synthesis of pefloxacin, levofloxacin, and other antibacterial drugs of the fluoroquinolone series, as well as of their heteroanalogs in the series of bi-, tri-, and polycyclic fluorine-containing heterocycles [717-722]. The developed technologies for the synthesis of pefloxacin and other fluoroquinolones have been tested at the pilot plant of the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences in Volgograd.

**Triazavirin and other azoloazines.** Nitrogencontaining heterocycles have always been in the field of attention of researchers of the Department of Organic and Biomolecular Chemistry, taking into account that many substances of this series are analogs of vital DNA and RNA bases.

Azoles, azines, azoloazines and their nitro derivatives were initially considered as the basis for creating energetic compounds with critically high nitrogen content. The cycle of works in this field was awarded in 1990 by the Council of Ministers of the USSR (O.N. Chupakhin, V.L. Rusinov, Yu.A. Azev, T.L. Pilicheva), and later (2005) the study of azolefused nitro azines was awarded the Zelinskii scientific prize (O.N. Chupakhin, V.L. Rusinov, G.L. Rusinov). As a result of a systematic study of compounds of the azoloazine series [723–728] and extensive interdisciplinary studies performed jointly with the Institute of Influenza of the Ministry of Health of the Russian Federation in St. Petersburg (Academician O.I. Kiselev, A.V. Vasin, E.G. Deeva), Virology Center of the Ministry of Defense of the Russian Federation in Sergiev Posad (Corresponding Member of the Russian Academy of Science S.V. Borisevich), Institute of Military Medicine in St. Petersburg (S.V. Chepur, A.V. Stepanov), and Volgograd State Medical University (Academician A.A. Spasov), new original families of biologically active compounds were created.

The first antiviral drug of this series, *triazavirin* (2-methylsulfanyl-6-nitro[1,2,4]triazolo[5,1-*c*][1,2,4]-triazin-7-one sodium salt dihydrate), completed clinical trials as an anti-influenza drug and was included on August 28, 2014, in the register of medicines of the Russian Federation (no. LP-002604). The *Medsintez* plant and the Ural Center for Biopharmaceutical Technologies organized industrial production of the drug and its distribution (from 2015) through the pharmacy network.



Triazavirin-antiviral drug with a broad spectrum of action.

Another antiviral drug, *triazid* (5-methyl-6-nitro-[1,2,4]triazolo[1,5-*a*]pyrimidin-7-one argininium salt), is under clinical trials. The works on creation of antiviral drugs of the azoloazine series were awarded the Tatishchev and de Hennin Prize in the field of science, engineering, and medicine in 2008, as well as the International Prix Galien Russia 2016 as the best research in Russia in the field of pharmaceutics (academicians O.N. Chupakhin and V.N. Charushin, Corresponding Member of the Russian Academy of Sciences V.L. Rusinov).

The department and its founder, Academician I.Ya. Postovskii, after whom a street of Yekaterinburg and the Institute of Organic Synthesis were named, had a great influence on the emergence of the Ural chemical institutes of the Academy of Sciences of the USSR, Eastern Coal Chemical Institute, and UNIKhIM Institute, and on the formation of pharmaceutical and chemical science and industry in Sverdlovsk oblast.



General Secretary of the International Prix Galien Russia F. Boucheseiche (France), Corresponding Member of the Russian Academy of Sciences V.L. Rusinov, General Director of *Medsintez Plant* Ltd. A.A. Petrov, and academicians O.N. Chupakhin and V.N.Charushin at the ceremony awarding the prize for the best scientific research in the field of pharmaceutics.



Lecturers of the First Youth School-Conference on Organic Chemistry.



On the initiative of the department in Yekaterinburg in 1998 (the year of the 100th anniversary of the birth of I.Ya. Postovskii), the first Youth Conference on Organic Chemistry was held, the emblem of which withstood the test of time and

became a symbol of the Russian youth scientific schools held in its leading scientific centers.

For a long time the Department of Organic Chemistry of the Ural Polytechnic Institute–Ural State Technical University belonged to so-called "nongraduate" ones and provided general training in fundamental organic chemistry for students not only of chemical technological, but also other faculties such as silicate technology, metallurgical, physical engineering, etc. Since 2008 the department trains masters in chemical technology (integrated chemical and physical research and expert evaluation of organic materials), and since 2011, master's program in chemistry (medicinal chemistry) has been implemented.

Since September 1, 2016, the department is headed by Academician Valerii Nikolaevich Charushin,

a student of Academician O.N. Chupakhin. Simultaneously, he is director of the Postovskii Institute of Organic Synthesis, thus preserving the direct and figurative meanings of the traditions of the "academic" department which conducts fundamental research in close cooperation with the academic community.



The Ural Scientific School of Organic Chemists is well known in Russia and abroad. During the development of the department its employees were awarded two Stalin Prizes, two Prizes of the Council of Ministers of the USSR, and two State Prizes of the Russian Federation. Thus, the State Prize of the Russian Federation in 2011 in the field of science and technology was awarded for a major contribution to the development of organic synthesis and innovative technologies for the production of medicines and materials, including those for special purposes (O.N. Chupakhin, V.N. Charushin), and in 2015, the prize of the President of the Russian Federation in the field of science and innovation for young scientists was awarded to D.N. Kopchuk for the development of new luminescence and functional materials for molecular devices for various purposes.

## 12. DEPARTMENT OF ORGANIC CHEMISTRY OF THE SAMARA STATE TECHNICAL UNIVERSITY

The chemical industry in the Samara province, as well as in other regions of the USSR, remote from the centers of chemical science, was represented by the very primitive (from the technological point of view) enterprises producing sulfur, matches, potassium chlorate and sulfuric acid, and fertilizers. There were no educational establishments in which personnel for the chemical industry were trained.

In February 1930, it was decided to create in the shortest possible time a chemical technology institute in the Samara Region. The Department of Organic Chemistry was organized under the guidance of Professor **Nikolai Ivanovich Putokhin** as a part of the



Mid Volga Chemical Technological Institute.

In 1916, **N.I. Putokhin** graduated from the Moscow University with a degree in chemistry. In 1917 he graduated from the Moscow Agricultural Institute (later Timiryazev Agricultural Academy) with a degree

in organic and agronomic chemistry. There he drew the attention of Academician N.Ya. Dem'yanov, who after the training of N.Ya. Putokhin interceded "leaving him for preparation to scientific and educational activities" at the Department of Organic Chemistry. From 1921 to November 1927 he worked at the Department of Organic Chemistry under the leadership of Academician N.Ya. Dem'yanov and was engaged in the development of new ways of synthesis of amino acids. N.I. Putokhin's studies of proline and tryptophan [729–731] aroused great interest of the chemical community. In the opinion of Academician N.Ya. Dem'yanov "... this cycle of research has been carried out very skillfully and successfully ... the discovery of a new original and elegant method of proline synthesis is especially important ...". The work on the synthesis of proline was highly appreciated as the Butlerov Prize of the Russian Physicochemical Society in 1925.

In 1927, N.I. Putokhin was elected a professor at the Department of Inorganic and Organic Chemistry of the Samara Agricultural Institute, where he worked until December 1941. Working there, he actively engaged in the creation of the Department of Organic Chemistry (as well as an organic chemistry laboratory) at the Samara Institute of Chemistry and Technology. The department was opened in 1930, and N.I. Putokhin became its head.

During this period, N.I. Putokhin performed a number of new isomeric transformations of nitrogen heterocycles and demonstrated the ability of isatin, pyrrole, and indole derivatives to expand the ring [732–737]. Another series of studies led to the creation of a new method for the synthesis of fatty diamines and hydroxy amines by introducing a number of improvements into the Gabriel synthesis. N.I. Putokhin synthesized ethylenediamine in the presence of K<sub>2</sub>CO<sub>3</sub>, so that potassium phthalimide *in statu nascendi* reacted with ethylene bromide. The yield of ethylenediamine reached 55–60% [738, 739]. Other amines were obtained with almost theoretical yield.

One direction of N.I. Putokhin's scientific activity was connected with the development of new methods for the preparation of amines containing pyrrole and indole rings. These studies included reduction of the pyrrole and indole rings, development of a method for the synthesis of proline by catalytic reduction of pyrrolecarboxylic acid, and study of a number of proline derivatives. A number of works were related to reactions of formaldehyde with pyrrolidine and piperidine. Derivatives of isatin and phthalimide were studied, and isomerization of ethylenediisatin to quinoline was discovered.

Because of disagreements with some party activists, in 1933 N.I. Putokhin was forced to temporarily leave the department, and the acting head became associate professor **A.S. Nekrasov**, who studied Friedel–Crafts reactions. In 1934 N.I. Putokhin was awarded the degree of Doctor of Chemical Sciences without public defense, and from 1936 he again began to head the Department of Organic Chemistry.

During the Great Patriotic War, the staff of the Department of Organic Chemistry worked in the interests of the defense industry for the enterprises of the Kuibyshev oblast; in particular, they developed new ways of utilizing waste from the oil shale and oil industry. In the postwar years, N.I. Putokhin founded the Department of Chemistry at the Kuibyshev Aviation Institute.

N.I. Putokhin studied methods for the preparation of bromophthalimide and its application in organic synthesis, in particular for bromination of various substrates [740], isolation of pure amino acids from the hydrolysis products of proteins, and oxidation of amino acids. Together with his colleague D.E. Churkin, N.I. Putokhin performed research on the pyrolysis of aromatic hydrocarbons with the goal of establishing the mechanism of high-temperature chemical transformation of hydrocarbons. He proposed a mechanism for the Hoffmann rearrangement, according to which [741] halogen in haloamino compounds is linked to oxygen [742]. The chemistry of thiophene became one of the main research lines. Ring expansion isomerization of 2-aminomethylthiophene and 2-thienylcarbinol was discovered [743]. Much effort of the staff of the department in these years was aimed at studying electrophilic substitution in the thiophene series [744].

Despite the extreme instability of amines of the thiophene series, the Putokhin school not only developed methods for their synthesis (including 2.4-diaminothiophene) [745] and isolation as double tin salts but also disproved the established opinion that diazotization of aminothiophenes is impossible. Diazotization of aminothiophenes under ordinary conditions leads to electrophilic substitution in the thiophene ring, self-condensation, and subsequent polymerization. However, diazotization of their salts with tin(IV) chloride gives diazonium salts and their derivatives with high yields, and even bis-diazonium salts can be obtained [746]. Work in the field of diazotization of 2-thiophenamine opened the way to new azo dyes of the thiophene series [747]. N.I. Putokhin developed a convenient method for the nitration of thiophene substrates using copper(II) nitrate trihydrate in a mixture of acetic acid and acetic anhydride; in this case, the yield of 2-nitrothiophene was 85% [748]. This method was extended to substituted thiophenes, arvland hetarylthiophenes, and 2,2'-bithiophene. Sulfochlorination of thiophene and a number of its derivatives with chlorosulfonic acid gave the corresponding sulfochlorides which were converted to thiophene analogs of sulfonamide medicines [749]. Properties of carbonyl derivatives of the thiophene series were studied [750].

N.I. Putokhin paid much attention to the methodical work; in 1956 he published a textbook on organic chemistry, which withstood three reprints and was translated into Vietnamese.

Scientific research in the field of thiophene chemistry was continued by N.I. Putohin's students. This new and very promising area of organic chemistry has received considerable development in the works of many of its students, including **L.A. Kazitsyna**, who later became professor of the Faculty of Chemistry of the Moscow State University [751].

From 1966 to 1977, the department was headed by N.I. Putokhin's student **Andrei Evgen'evich Lipkin** 

(1932–1987). Simultaneously, from 1965 to 1971, A.E. Lipkin was dean of the Faculty of Chemical Technology; during these years he was engaged in research on the chemistry of hetarylthiophenes. His students later formed the backbone of the scientific and pedagogical staff of



the department. They developed methods for the synthesis of 4-thienyl- and bithienylthiazoles and their derivatives, and bromination of the thiophene ring was studied [752]. Under the leadership of A.E, Lipkin, the regioselectivity and reactivity of electrophilic substitution in 2,2'-bithiophene [753] and its substituted derivatives, as well as in quinoline derivatives, were studied in detail [754]. A large number of functionally substituted heterocycles has been synthesized [755–757]. Compounds with pronounced biological activity (antimicrobial drug *nibitin*) [758], a new class of organic luminophores, laser dyes, and highly selective analytical reagents were obtained.

Since 1977, the Department of Organic Chemistry was headed by Nikolai Vasil'evich Stulin (1937-

2000). N.V. Stulin was an excellent teacher and favorite of students. Colleagues noted his exceptional energy, initiative, the ability to mobilize the team, resourcefulness, sociability, and at the same time adherence to principles. His main motto "You are a patriot of the department" was the main credo of



the team, and N.V. Stulin himself was the soul of the department.



In 1980, **Igor' Konstantinovich Moiseev**, a well-known specialist in the field of chemistry of nitro compounds, was elected head of the department, and he headed the department for 24 years (until 2004). I.K. Moiseyev was born in 1932; in 1955 he graduated from the Faculty of Engineering and Technology of

the Kuibyshev Industrial Institute. In 1960, he entered the postgraduate school of the Kazan Institute of Chemical Technology. After defending his candidate's dissertation under the guidance of Professor I.E. Moisak, he worked as an assistant professor at the Kuibyshev Polytechnic Institute, and was then invited to work at the Dzerzhinsk Research Institute of Chemical Technology.

Since the mid-1960s, research in the field of organic synthesis of cage hydrocarbons has been started in a number of leading institutions in the country. Under the guidance of corresponding member of the Academy of Sciences of the USSR S.S. Novikov, a research team of the Zelinskii Institute of Organic Chemistry began studying new compounds of the adamantane series. I.K. Moiseev actively joined these studies. In 1978 I.K. Moisevev defended his doctoral dissertation and was appointed as head of the laboratory of energetic materials, and in the summer of 1980 he moved to Kuibyshev. Here he became later a dean of the Faculty of Chemical Technology. I.K. Moiseev worked on the development of methods for the synthesis of adamantane derivatives containing  $NO_2$ ,  $ONO_2$ , and  $NHNO_2$  groups, which made it possible to obtain an explosive more potent than TNT and resistant to bullet shot [759].

In Kuibyshev, I.K. Moiseev directed the work in the field of chemistry of cage polycyclic compounds, methods of C–H bond activation in electrophilic media, chemical behavior of adamantane and related compounds in reactions with nitrogen-containing electrophiles and oxidants [760], development of new methods for the preparation of adamantane derivatives, and directed synthesis of biologically active compounds with a broad spectrum of activity [761] (doctoral dissertation of Yu.N. Klimochkin, 1999).

At that time, principles of functionalization of cage compounds were established, and preparative methods for the synthesis of a wide series of compounds with practically valuable properties for the needs of medicine, polymer chemistry, electrochemistry, and agriculture were developed. The technologies for the manufacture of rimantadine and midantane were implemented at the Olaine plant in Latvia [762].

Another research line related to development of methods for the synthesis of ketones containing an adamantyl substituent was dictated not only by chemical problems but also by the possibility of obtaining biologically active compounds. Methods for the synthesis of adamantyl bromomethyl ketones,  $\alpha$ - and  $\beta$ -unsaturated ketones, etc. have been developed (doctoral dissertation of N.V. Makarov, 2001). Their chemical properties have been studied, and ways of



Chemical building of the Samara State Technical University (the former building of the Peasants' Land Bank built in 1911 by Alexander von Gauguin).

synthesizing heterocyclic compounds based thereon have been determined [763]. Studies were also carried out in the field of saturated heterocycles of the adamantane series (oxiranes, iminooxathiolanes), which formed the basis of the doctoral dissertation of A.K. Shiryaev (2005) [764]. The results of the studies carried out at the department for more than 25 years were summarized in the monograph "Advances in the Chemistry of Adamantane" [765].

Further development of the Department of Organic Chemistry is connected with Yurii Nikolaevich Klimochkin, who headed the department since 2004.



Yu.N. Klimochkin (born in 1959) graduated in 1981 from the Faculty of Chemical Technology of the Kuibyshev Polytechnic Institute, and then finished postgraduate courses and doctoral studies on the specialty organic chemistry. In 1999, Yu.N. Klimochkin was appointed to the position of as vice-rector for

scientific work of the Samara State Technical University, which he held until 2009.

Since 2005, the Department of Organic Chemistry graduates specialists in "Fundamental and Applied Chemistry" and bachelors and masters in chemistry. At present, the fields of scientific research conducted at the department include activation of the carbon-hydrogen bond in cage substrates, chemistry of sterically hindered alkenes, directed synthesis of viral inhibitors with cage structure [766], benzo-fused heterocycles obtainable by cascade transformations of o-quinone methides (doctoral dissertation of V.A. Osyanina, 2014) [767], stereoselective formation of C-C bonds under catalysis by transition metal complexes with chiral ligands, chemistry of fused pyrimidinone, quinoline, and bithiophene derivatives, and development of technologies for the synthesis of biologically active substances.

# 13. ORGANIC CHEMISTRY IN TVER OBLAST

The chemical education in Tver oblast originates from the P.P. Maksimovich's Women's Teachers' School (1870), though rich Tver entrepreneurs, not having much knowledge of chemical science, built factories for the processing of natural raw materials even at the beginning of the XVIIIth century. Thus, the first large entrepreneurs who manufactured rosin and turpentine were A. Savelov and the Tomilin brothers; they organized a chemical plant in 1720. In the decree

of Peter I (July 10, 1719) it was said that "these persons are allowed to build factories in the Moscow district, ... in Tver, and in the Medyn district, where they should cook and make turpentine and rosin." "There is a turpentine plan in Tver on the bank of the Volga River, where spruce turpentine and rosin are made

ORGANIC CHEMISTRY. HISTORY AND MUTUAL RELATIONS



from sulfur; that factory belongs to P.P. Maksimovich (1817-1892). A. Savelov, and the Tomilins mer-

chant people," the clerk Ivan Kirilov wrote in 1727. The quality of the products was high. Assay master Ivan Schlatter said in 1724 "Turpentine is very good, ... colophony of the most volatile." In 1752, a decree was issued banning the importation from abroad of turpentine and rosin, as these products were produced in sufficient quantities in Tver [768].

In 1890, industrial development of "Galitsky moss" peat began at the Redkino station. Here, the first coke plant was opened. In 1892, entrepreneur A. Nepokoichitskii founded Vyshnevolotsk plant of enzymatic preparations (production of rice starch).

However, despite numerous chemical enterprises, chemical education in Tver began only with the opening in 1870 of P.P. Maksimovich's school for rural teachers (since 1882, the Zemstvo school).

In 1917, the first state high school in Tver, the Tver Teacher's Institute, was founded on the basis of Maksimovich's school by the order of the Minister of Public Education of the Provisional Government with the active assistance of the outstanding natural scientist, chemist, mineralogist, bioecologist, and thinker V.I. Vernadskii. The institute included three faculties, one of which was natural and geographical faculty where chemistry was studied. In the beginning of the 1918/1919 academic year, the Teacher's Institute was transformed into a pedagogical institute. There were 16 professors, including S.G. Krapivin (1922-1927, see also Section 4) who was the first head of the department of chemistry [769].

Sergei Gavrilovich Krapivin (1868-1927) graduated from the natural department of the Faculty of Physics and Mathematics of the Odessa University. He trained in the laboratories of Nernst and Ostwald in Germany (1890). He lectured on organic chemistry and wrote the book "Practical Works on Organic





Maksimovich's Teachers' School in Tver.

Chemistry" (1910). From 1901 to 1924, he headed the department at the Moscow Higher Women's Courses. In 1915 he published the book "Data on the Kinetics of Chemical Reactions" (1915). In the autumn of 1920 S.G. Krapivin consented to take part in the work of the Tver Pedagogical Institute where he taught courses in organic and physical chemistry and every two years a course in chemistry. In the first year he came to Tver for a week every month, and from 1925, for four days every two weeks. He supervised the whole work of the department and was chairman of the methodological commission on chemistry [770].

Professors D.K. Aleksandrov (1928–1930), V.I. Pelevin (1931–1932), and P.I. Kondratskii (1933– 1934) and assistant professors P.I. Lerkh, S.V. Dmitrienko, B.N. Dement'ev, and P.G. Ugryumov worked at the Department of Chemistry until 1934. In the postwar period, assistant professors P.S. Malinovskii (head of the department until 1954), I.I. D'yakonov (head of the department in 1954–1958), and O.S. Popov (1955– 1958) worked there. In 1958, the Department of Chemistry was abolished and restored again only in 1964. On July 29, 1971, the Pedagogical Institute was transformed into the Tver State University, and the Department of Chemistry was divided into two, departments of organic chemistry and department of physical chemistry.

At different times, the Department of Organic Chemistry was headed by candidate of engineering A.A. Aver'yanov (1971–1972), Doctor of Physical and Mathematical Sciences, Professor Yu.G. Papulov (1972–1973), Doctor of Biological Sciences, Professor A.V. Sergeev (1973), Doctor of Chemical Sciences, Professor A.S. Chegolya (1974–1982), and Doctor of Chemical Sciences, Professor I.P. Gorelov (1982–1985). It was with the arrival of Professor **Aleksandr** 

Sergeevich Chegolya (1935–2010), who headed the All-Union Scientific Research Institute of Synthetic Fibers, that studies on the synthesis of surfactants were started at the department. From 1985 to the present time the Department of Organic Chemistry is headed by Doctor of Chemical Sciences, Professor



Lyudmila Ivanovna Voronchikhina. The research lines of the department were preserved but supplemented by applied aspects of surfactant chemistry

and studies on the relations between the surfactant properties and their structure. The applied aspects of surfactant chemistry included the development of metallized materials (mainly thin fibers with a diameter of  $7-10 \mu m$  coated with copper and nickel with a thickness of up to 1 µm) used as radio-absorbing and



radio-reflective masking means in air defense systems. The other applied aspects of surfactant chemistry are the development of effective hydrophobizers, corrosion inhibitors, bactericides, work to preserve the environmental situation and purity of the Upper Volga basin and Lake Seliger (Ostashkov tannery), etc. The results of these studies were covered by 15 inventor's certificates, and 10 candidate dissertations were defended on this basis.

# 14. DEPARTMENT OF ORGANIC CHEMISTRY OF THE DOSTOEVSKY OMSK STATE UNIVERSITY

The Dostoevsky Omsk State University is young; it is only 42 years old. This is a little even for a person and is a child's age for a university. The Omsk State University was founded along with a number of other classical universities that were opened in the 1970s in the USSR. The university network expanded in two ways, via creation of new universities (Omsk, Barnaul, Chelvabinsk, etc.) and reorganization of the existing ones (as a rule, pedagogical) into universities, provided that they were strengthened by scientific and pedagogical personnel and their material and technical base was expanded (Kemerovo, Tyumen. etc.) [771]. The chemical faculty appeared as a separate structural unit in the Omsk State University in 1978; it consisted of three departments: inorganic chemistry, organic chemistry, and petroleum chemistry. The Department of Organic Chemistry was founded in 1975; its staff was represented by former employees of the Irkutsk Institute of Organic Chemistry, namely Doctor of Chemical Sciences, Professor A.S. Atavin (the first head of the department), associate professors, candidates of chemical sciences V.M. Nikitin and E.F. Zorina, and senior lecturer B.F. Kukharev.

Aleksandr Spiridonovich Atavin [772, 773] was born on December 28, 1905. In 1930 he enrolled in the Faculty of Chemistry of the Far Eastern State University, in 1933 transferred to the Faculty of Chemistry of the Samara Pedagogical Institute, and after graduation therefrom worked as a school teacher. Since 1937 he was assistant professor of the Novosibirsk Medical Institute. In 1946 he defended his candidate's dissertation "Study in the field of chlorination of vinyl ethers and their derivatives," and in 1966, doctoral dissertation. Since 1947 he headed the Department of Chemistry of the Novosibirsk Institute of Geodesy, Aerial Photography, and Cartography. From 1960 to 1971 he worked as deputy director of the Favorskii Irkutsk Institute of Chemistry of the Siberian Branch of the Russian Academy of Sciences, where he also headed the laboratory of organic synthesis and was one of the closest associates of the first director and organizer of the Irkutsk Institute of Organic Chemistry, corresponding member of the Academy of Sciences of the USSR M.F. Shostakovskii. B.A. Trofimov (later Academician of the Russian Academy of Sciences, Director of the institute in 1994-2015, Doctor of Chemical Sciences, Professor) and famous scientists E.P. Vyalykh, M.L. Al'pert, A.N. Mirskov, and A.I. Mikhalev worked in A.S. Atavin's laboratory. In 1967 he was elected professor of the Faculty of Chemistry of the Irkutsk University, and from 1975 to 1981 he headed the Department of Organic Chemistry of the Omsk State University.

The research work carried out by A.S. Atavin was aimed at solving glycol vinylation problems, elucidating structure-reactivity relations for chemical compounds, developing methods for the preparation of vinyl ethers containing polyfunctional groups and heteroatoms, and synthesizing biologically active substances and flotation agents [774–776].

In 1981, **R.S. Sagitullin** from the Moscow State University was invited to head the Department of Organic Chemistry in the Omsk State University. R.S. Sagitullin made a lot to raise scientific research to the modern level. Thus, the department was additionally equipped with laboratory furniture, and performing of elemental analysis was organized. Library collections were replenished with foreign journals, which were transferred from libraries of other universities and research institutes. Using his connections in the capital, he achieved the allocation of two NMR spectrometers (Tesla 60 and Tesla 80) to a small



Head of the Department of Organic Chemistry of the Omsk State University, Doctor of Chemical Sciences, Professor A.S. Atavin (third from the left) and staff of the Faculty of Chemistry.

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017

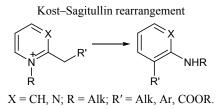
department of a provincial university. R.S. Sagitullin developed and read the main course of organic chemistry and special courses "Chemistry of heterocyclic compounds," "Methods of organic synthesis," and "Demonstration experiments in organic chemistry" and organized a laboratory practicum.



**Reva Safarovich Sagitullin** [707, 708] was born on March 9, 1931 in the village of Elenskoe of the Tyumen oblast. In 1954 he graduated from the Faculty of Chemistry of the Moscow State University. He worked at the chemical enterprise P.O. Box no. 10 in Kirovo-Chepetsk, Kirov oblast, later he taught at the Moscow Polygraphic Institute. In 1958–1981

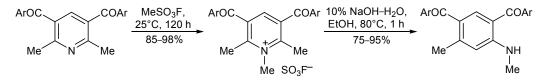
he worked at the Moscow State University at the Department of Organic Chemistry in the laboratory of nitrogenous bases headed by Professor A.N. Kost (see Section 4.1). In 1979 he defended his doctoral dissertation "Reactions of 2-aminoindole and new rearrangements of nitrogenous heteroaromatic compounds," devoted to the discovered family of new rearrangements of six-membered nitrogen heterocycles leading to another heterocycle or carbocycle. The discovered transformations have entered the scientific and reference literature under the name *Kost–Sagitullin rearrangement*.

Gradually, the staff of the department was completely changed. It was based on young teachers, candidates of chemical sciences E.G. Atavin and G.P. Shkil' (Sagitullina), as well as graduates of the

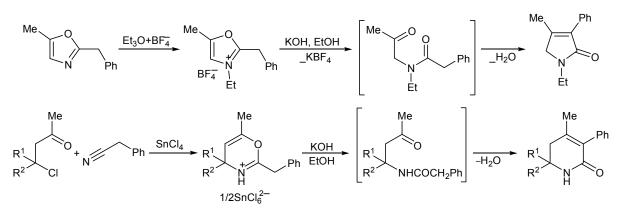


Omsk State University, who had finished at the time post-graduate courses in Moscow (A.S. Fisyuk, Lomonosov Moscow Institute of Fine Chemical Technology, supervisor Professor B.V. Unkovskii; V.M. Zhelyaev, Lenin Moscow State Pedagogical University, supervisor professor E.E. Nifant'ev) and Leningrad (V.V. Dubitskii (Zhdanov Leningrad State University, supervisor Professor L.L. Rodina). The department actively carried out research work aimed at elucidating the synthetic potential of the Kost–Sagitullin rearrangement [777].

Since 1989, a postgraduate course in the specialty "Organic Chemistry" has been opened at the department. The first post-graduate student, who defended in 1993 her candidate's dissertation under the guidance of R.S. Sagitullin and A.S. Fisyuk, was M.A. Vorontsova (currently an associate professor). In these years, the Hantzsch rearrangement of nitropyridines [778] was studied, the possibility of pyrrole synthesis via rearrangement of 3-aminopyridine derivatives was shown [779], a new approach to the synthesis of macrocyclic systems was developed [780], and rearrangement of oxygen-containing heterocycles (1,3-oxazinium [781] and oxazolium salts [782]), formally analogous to the Kost–Sagitullin rearrangement, was studied.



 $Ar = Ph, C_6H_4Me-4, C_6H_4OMe-3, C_6H_4OMe-4, C_6H_4Cl-4, C_6H_4Br-4, 1-naphthyl, 2-naphthyl, 2-naphthyl, C_6H_4Me-4, C_6H_$ 



Intramolecular cyclization of *N*-(3-oxoalkyl)amides and thioamides [783–788] formed during the rearrangement of 1,3-oxazines, as well as of those synthesized independently [789], was also studied. In this way methods for the synthesis of various hydrogenated pyridine derivatives [790–795], including 4,6,6-trimethyl-3,4-epoxypiperidin-2-one [796] (an alkaloid isolated for the first time in 2016 from *Nigella glandulifera* [797]) have been developed. Some reactions of 1,3-isothiocyanatocarbonyl compounds and their derivatives were studied [798–802].

In 1998, the department was visited by one of the most authoritative specialists in the field of chemistry of heterocyclic compounds, the world-famous organic chemist Henk C. Van der Plas.

In 1999, the first graduate of the Faculty of Chemistry of the Omsk State University, Aleksandr Semenovich Fisyuk defended his doctoral dissertation at the Moscow State University (scientific adviser Professor D.G. Bundel'). After defending the dissertation, A.S. Fisyuk founded an organic synthesis laboratory at the Omsk State Chemical University, which worked in cooperation with Bayer AG. For a number of years, the laboratory carried out studies of the cyclization of N-(3-oxoalkenyl)amides to 3-functionally substituted pyridine-2(1H)-ones [803-805], cascade cyclizations of urea and thiourea derivatives to 1,3,4,6,7,11b-hexahydro-2H-pyrimido[6,1-a]isoquinolines and 1,2,3,4,6,7,12,12b-octahydropyrimido-[1',6':1,2]pyrido[3,4-b]indoles, and other domino reactions [806-808]. Studies of the Kost-Sagitullin rearrangement are also in progress [809-811].

Since 2009, Doctor of Chemical Sciences Professor A.S. Fisyuk is head of the Department of Organic Chemistry. During this period, research on luminescent conjugate systems interesting as materials for organic electronics was begun at the department in collaboration with French and Polish scientists [812, 813], new terpyridine derivatives and their luminescent complexes with lanthanides were obtained [814-820], methods of synthesis of 4H-thieno[3,2-c]chromenes and 4,5-dihydrothieno[3,2-c]quinolines [821-823] were developed. The obtained materials were used for the manufacture of efficient light-emitting diodes [824]. The department and the laboratory actively cooperate with Russian scientific centers (Institute of Hydrocarbon Processing Problems of the Siberian Branch of the Russian Academy of Sciences, Omsk; Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences;

Moscow State University; Institute of Theoretical and Experimental Biophysics, Russian Academy of Sciences, Pushchino) and universities of Kokshetau, Astana, and Karaganda (Kazakhstan Republic).

As the Omsk State University, Omsk State Technical University, and Institute of Hydrocarbon Processing Problems formed a scientific and educational center, the department gained access to modern NMR spectrometers and other equipment. A little later, a similar center was organized by the Omsk State University and Novosibirsk Institute of Organic Chemistry. In 2013, Professor A.S. Fisyuk organized a laboratory of new organic materials in the Omsk State Technical University. The staff of the department includes 2 professors, 4 associate professors (candidates of chemical sciences G.P. Sagitullina, M.A. Vorontsova, L.V. Glizdinskaya, and A.K. Kuratova), and 4 employees of the training and research laboratory (researcher, candidate of chemical sciences A.S. Kostyuchenko and junior researchers T.Yu. Zheleznova, A.L. Shatsauskas, and K.S.Varaksin).

The department produces annually 10–12 bachelors and 6–8 masters in chemistry. In 2016, 2 postgraduate students successfully completed their study and defended their candidate's dissertations in organic chemistry.

Priority directions of scientific research at the department are molecular design of organic structures and reactions, targeted search, synthesis and testing of practically important organic compounds, design and synthesis of organic semiconductors and luminophores, intramolecular cyclization of bifunctional compounds, and synthesis and rearrangements of electron-deficient nitrogen heterocycles.

# 15. ORGANIC CHEMISTRY IN THE UNIVERSITIES OF STAVROPOL

The history of the Department of Chemistry of the North Caucasus Federal University originates from the Department of Chemistry, formed in 1930 at the chemical and biological section of the newly opened Stavropol Agropedagogical Institute (in 1932 it was renamed the North Caucasian Pedagogical Institute). The head of the department was **N.N. Rozhdestvenskii**. In the 1960s, the Department of Chemistry (by that time already in the Stavropol State Pedagogical Institute) was headed by candidate of chemical sciences, assistant professor **P.M. Kuznetsov**. Later, in the 1970–1980s the department was headed by asso-



First graduates of the Stavropol Agropedagogical Institute.

ciate professors L.T. Azhipa, G.V. Sakovich, and S.B. Davidyants.

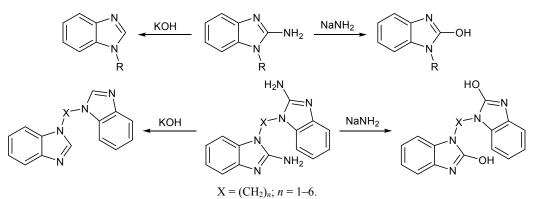
In the mid-1980s, associate professor **A.A. Mikha**lev began to work at the department. Later he headed the department of chemistry until it was divided in 1996 into two departments: organic and physical chemistry and inorganic and analytical chemistry. Until 1994, organic chemistry as an independent trend did not exist in the Stavropol region. Individual works



Main building of the Stavropol Pedagogical Institute (1970s).

were carried out within the framework of dissertational research under the guidance of professors from other regions. M.M. Medvedeva worked in the Stavropol State Pedagogical Institute (which was later included in the North Caucasus Federal University), and in the 1970s she studied at the post-graduate courses of the Rostov State University under the guidance of Prof. A.F. Pozharskii. In 1981 M.M. Medvedeva defended her candidate's dissertation in organic chemistry, which became the first dissertation in this specialty, performed in Stavropol. The dissertation was devoted to amination and hydroxylation of benzimidazole derivatives [825–827].

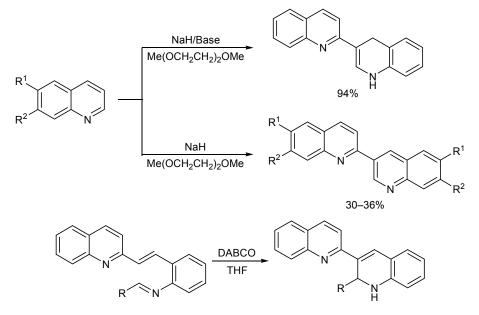
At the same time, a large number of graduates of the post-graduate school at the Rostov State University came to various universities of Stavropol: B.K. Martsokha (Stavropol State Polytechnic Institute, became a unit of the North Caucasus Federal University), V.I. Sokolov (Nevinnomyssk branch of the Stavropol State Polytechnic Institute, became a unit of the North Caucasus Federal University), I.V. Borovlev (Stavropol Agricultural Institute). However, none of them conducted research in the field of organic chemistry until the mid-1990s.



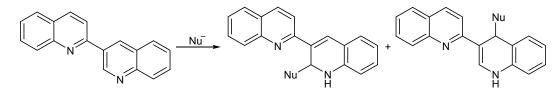
In 1994, A.V. Aksenov and I.V. Aksenova, graduates of the Mendeleev Moscow Institute of Fine Chemical Technology, and A.F. Golota, a graduate of the Crimean State Pedagogical Institute, began to work in the department. By 2001, A.V. Aksenov and A.F. Golota defended their doctoral dissertations and headed the newly formed new chairs: **A.V. Aksenov** headed the Department of Organic and Physical Chemistry, and **A.F. Golota**, the Department of Inorganic and Analytical Chemistry. In 2000, the Department of Biochemistry headed by Professor **S.M. Kunizhev** separated from the Department of Organic and Physical Chemistry.

Since 1994, under the leadership of A.V. Aksenov, research has begun in the field of quinoline chemistry, in particular of the chemistry of 2,3'-biquinolines. These studies were initiated in the early 1990s in the Mendeleev University of Chemical Technology of Russia, where A.V. Aksenov studied in post-graduate school and carried out candidate's dissertation "New areas of application of sodium hydride in organic chemistry" under the guidance of Professor Yu.I. Smushkevich, a representative of the scientific school of Professor N.N. Suvorov. In 1997, A.V. Aksenov invited I.V. Borovlev to the department.

During the development of these studies, a method was proposed for the synthesis of 2,3'-biquinolines and 1,4-dihydro-2,3'-biquinolines by cross-coupling of quinolines under the action of sodium hydride [828, 829]. Extension of the quinoline dimerization methodology to other compounds containing a multiple carbon-nitrogen bond gave rise to development of a method for the synthesis of 1,3,5-triazines by trimerization of nitriles under the action of sodium hydride. Single-electron character of these reactions was shown. Methods have also been developed for the synthesis of 2,3'-biquinolines and their dihydro derivatives by closing one of the quinoline fragments. In the course of this project, the synthetic potential of the Vilsmeier reaction was also investigated. The most interesting result of this part of research was demonstration of the possibility of Baylis-Hillman reaction



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 53 No. 9 2017



with Schiff bases and its application to the synthesis of heterocycles [830].

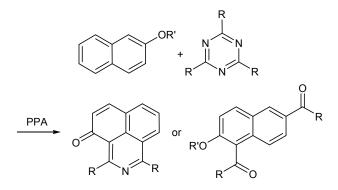
The single-electron reduction of aromatic compounds and properties of the reduction products were studied using 2,3'-biquinoline derivatives as examples. As a result, cation dependence of SET processes [831] was revealed, the reaction of dianions with nucleophilic reagents was discovered, whose mechanism includes previously unknown elementary stage [832], previously unknown hetarylation with N-oxides [833] was accomplished, and the general mechanism of reactions of aromatic dianions with electrophilic and nucleophilic reagents [834] was determined. Nucleophilic and electrophilic substitution in biheterocycles was studied. Factors determining the regioselectivity of nucleophilic substitution in 2,3'-biguinolines and their salts, primarily the role of the metal cation and nucleophile hardness, have been studied [835-838].

The study of nucleophilic substitution in dihydro-2,3'-biquinolines [839, 840] revealed previously unknown hydride-ion replacement with allylic rearrangement. When studying the mechanism of electrophilic substitution in substituted quinolines, it was shown that, depending on the mechanism, the electrophilic substitution involves different quinoline fragments of 2,3'-biquinoline [841, 842]. The results of these studies formed the basis of the first candidate's dissertation (A.V. Aksenov, 2001). A post-graduate course in organic chemistry was organized at the department; N.V. Demidova was the first postgraduate student that defended her candidate's dissertation (1992).

Since 1997, studies in the field of azapyrenes have been started at the department [843–846]. The most significant achievements in this area were methods developed for the synthesis of various polynuclear compounds. In 2004, I.V. Borovlev defended his doctoral dissertation, and in 2007, V.I. Goncharov.

In 2004, the Department of Organic and Physical Chemistry was again reorganized. It was divided into the Department of Organic, Physical, and Pharmaceutical Chemistry (headed by Professor A.V. Aksenov) and the Department of Chemistry of Heterocyclic Compounds (headed by Professor I.V. Borovlev). The latter existed until 2010, when it again merged with the Department of Organic, Physical, and Pharmaceutical Chemistry.

Since 2006, the department has continued work in the field of chemistry of 1,3,5-triazines. A method was proposed for *peri*-fusion of a pyridine ring to phenalenes using 1,3,5-triazines and nitriles in polyphosphoric acid (PPA). To expand the synthetic possibilities of ring opening in 1,3,5-triazines, a new reagent system, 1,3,5-triazine–PPA, was proposed, which can be used alone or in the presence of an additional reagent [847, 848]. The most interesting was change of the regioselectivity in the reaction of 2-naphthyl ethers with triazines in PPA [849].



The result of these works was the doctoral dissertation of I.V. Aksenova (2009). At that time, 13 candidate's and 3 doctoral dissertations (to date 27 and 4, respectively) were defended under the guidance of A.V.Aksenov.

In 2009, the staff of the department organized the first international conference on organic chemistry "New Directions in the Chemistry of Heterocyclic Compounds" in the North Caucasus, which gathered about 300 participants. Subsequently, this conference became traditional: in 2011 it was held in Zheleznovodsk, and in 2013, in Pyatigorsk. In 2016, the conference became a component of the cluster of conferences DOCC-2016 (Dombai) in conjunction with the Moscow State University.

The next direction of research of the department was related to search for new methods of direct electrophilic amination. Two systems of reagents were found for this purpose; in particular, direct electro-



Staff of the Department of Organic Chemistry and Department of Chemistry of Heterocyclic Compounds (2006).



Participants of the International Conference "Modern Trends in Organic Chemistry DOCC-2016." Dombai, 2016.

philic amination of aromatic compounds with the use of sodium azide in PPA was developed. This method was suitable for the amination of azaphenalenes (for example, perimidine [850]), naphthalene, phenols, and phenol ethers, including crown ethers [851, 852].

Another approach to electrophilic amination, developed in A.V. Aksenov's laboratory, involved the use of nitroalkanes in PPA. Benzene and its derivatives containing donor substituents [853], crown ethers [854], etc., enter the reaction. Replacement of nitroethane by nitromethane allowed the development of a method for carboxyamidation of arenes [855], and by 2-nitropropane, for the synthesis of diarylamines [856].

For a number of years, close cooperation has continued between the scientific groups of Professor A.V. Aksenov and M.A. Rubin, an assistant professor of the Faculty of Chemistry of the University of Kansas in the United States. M.A. Rubin graduated from the Faculty of Chemistry of the Moscow State University; in 1994 he completed his candidate's dissertation in the laboratory of organoelement compounds headed by Academician of the Russian Academy of Sciences I.P. Beletskaya, and entered postgraduate courses at the Moscow State University under the guidance of Professor I.G. Bolesov. In 2014 he defended his doctoral dissertation in organic chemistry "Catalytic reactions of cyclopropene addition" at the North Caucasus Federal University. He combines the positions of the leading researcher of the Laboratory of New Synthetic Methods of the Research Institute of Chemistry and Chemical Technology of the North Caucasus Federal University and of assistant professor of organic chemistry at the University of Kansas. This joint work led to another qualitative leap in the work of the department and brought it to the international level. In addition to a fruitful exchange of ideas, data, and materials, the students and staff of the department received the opportunity to undergo an internship in the United States on the basis of the University of Kansas.

This new jump was also reflected in the studies on reactions of nitro compounds in PPA. The idea of "smart" reaction media was formulated. The most striking recent studies are those of transannulation reactions [857, 858].

Thus, in approximately 20 years, the efforts of representatives of the two Moscow schools, Mendeleev Moscow Institute of Fine Chemical Technology and Moscow State University, and the Rostov School in Stavropol made it possible to create a school of organic chemists literally from scratch.

\* \* \*

Concluding this review on the history of organic chemistry in the universities of Russia, let us sum up some results. In all Russian universities, we see very significant changes in the structure of organic chemistry as it develops. There was its differentiation and separation of many independent disciplines therefrom. At the same time, new scientific directions have been formed at the borders of organic chemistry with other sciences, and this trend towards integration with other disciplines is visibly increasing in the modern period. An important role in the development of organic chemistry in Russian universities is played by their mutual connection, as well as by cooperation with the leading foreign scientific centers and institutes of the Academy of Sciences.

Since their foundation, the organic chemistry departments of many universities of Russia are among the leading scientific and educational centers of the country and the world in the field of organic chemistry. Outstanding scientists and educators, who have made a significant contribution to the development of world organic chemistry and created powerful scientific schools, have worked and are working within the walls of Russian universities. In the Soviet and post-Soviet periods, the university departments of organic chemistry were centers of consolidation of the community of organic chemists of the country. Graduates of these departments head collectives in many educational and scientific centers of the country or actively work therein, acting as bearers of university traditions.

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