History of Chemistry

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Disability, Despotism, Deoxygenation—From Exile to Academy Member: Nikolai Matveevich Kizhner**

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1905 Revolution · cyclopropane synthesis · history of chemistry · physical disability · Wolff–Kishner reduction

Political activism by chemists is nothing new: Linus Pauling received the Nobel Prize for Peace in 1962 for his nuclear disarmament activities; Stanislao Cannizzarro (1826–1910) fought with Garibaldi in 1848 and with John Alexander Reina Newlands (1837–1898) during the second war for Italian independence. Ignacy Mościcy (1867–1946) was President of Poland from 1926 to 1939, Margaret Thatcher (1925–2013) was Prime Minister of Great Britain from 1979 to 1990, Angela Merkel (born 1954) became Chancellor of Germany in 2005, and Chaim Weiszmann (1874–1952) was the first President of the State of Israel. Frédéric Joliot-Curie was an active member of the French Resistance during World War II.

In most cases, the consequences of activism by chemists have been fairly innocuous: Cannizzarro escaped capture, and spent his time in exile in the Paris laboratory of Eugène Chevreul (1786–1889); he returned from exile and ultimately became Vice President of the Italian Senate. After his service with Garibaldi, Newlands returned to Britain to continue his social reform work. Linus Pauling's passport was revoked, but that decision was reversed when he won his second Nobel Prize. Joliot-Curie became High Commissioner for Atomic Energy after the war. François-Vincent Raspail (1794–1878) was imprisoned and also exiled for his activities, but was twice elected a Deputy of France on his return from exile. Joseph Priestley, on the other hand, had to flee to America to avoid persecution. The "father of modern chemistry," Antoine Laurent Lavoisier (1743–1794), was even less fortunate: despite being renowned for his scientific work, he was a member of the detested *Ferme Générale* (the tax collectors of France), and was guillotined during the French Revolution. Kizhner's forcible exile from Tomsk is reminiscent of Wislicenus' exile from Germany, and Priestley's exile from England, but the fundamental change in the national politics had a much more drastic effect on Kizhner's career—he was never able to make up for the lost time.

Chemists with disabilities have also made important contributions to science. For example, the Swedish chemist Anders Gustaf Ekeberg (1767–1816), the discoverer of tantalum, was deaf, as was Australian chemist, Sir John Cornforth (born 1917), who shared the Nobel Prize in Chemistry in 1975. Dorothy Crowfoot Hodgkin (1910–1994), the recipient of the Nobel Prize for Chemistry in 1964, suffered from rheumatoid arthritis that eventually confined her to a wheelchair. Alfred Nobel (1833–1896) himself was an epileptic who suffered from crippling migraines and depression; and Wallace Hume Carothers (1896–1937), the inventor of nylon, suffered from mental depression so severe that it eventually led him to commit suicide. Henry Gilman (1893–1986), regarded by many as the father of organometallic chemistry, and the author of over 1000 papers, had vision problems beginning in his early adulthood, and was totally was blind by 1947, yet he published over half his papers after the total loss of his sight.

The name of Nikolai Matveevich Kizhner (transliterated variously as Kijner, Kižner, Kishner, or Kizhner; 1867–1935, Figure 1)[1] is permanently linked to the reaction he discovered just over a century ago: the Wolff–Kishner reduction.[2] Since its discovery by Kizhner in 1911,[3] and a second

Figure 1. Nikolai Matveevich Kizhner (1867–1935) as a young man. Photograph courtesy of Tomsk Polytechnic University.

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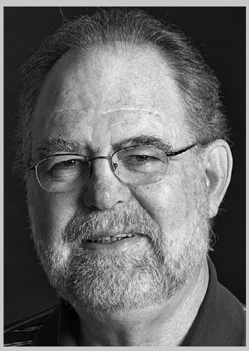
independent discovery eighteen months later[4] by Ludwig Wolff (1857–1919) at Jena, this reaction has become a mainstay of organic synthesis. In the ensuing century, the reaction has been modified in a number of ways, including the variant[5] reported by Huang Ming-Long (1898–1979, Figure 2), and the reduction of tosylhydrazones by sodium cyanoborohydride[6] (Scheme 1).

Figure 2. Huang Ming-Long (1898–1979). Photograph courtesy of the National Science Library, Chinese Academy of Science.

Details of Kizhner's early life are sketchy. According to Yushkovskii,[1d] some accounts state that he was born into a family of military medical assistants, while others assert that his father was a court counsellor. What is known is that Kizhner graduated from the first Moscow Gymnasium, and that he entered Moscow University as a student in the Natural Science Division of the Faculty of Physics and Mathematics in 1886. Although he had chosen a career in science, it was not until his third year at the university that Kizhner came to the decision that his interests included organic chemistry.

This decision was likely influenced by two professors at Moscow, Vladimir Vasil'evich Markovnikov (1838–1904, Figure 3), Butlerov's brilliant student who taught the lectures in organic chemistry, and Vladimir Fyodorovich Luginin (1834–1911, Figure 3), a physical chemist and thermodynamicist who supervised the laboratory instruction in chemistry, and worked in Markovnikov's laboratory. Between them, these two professors supervised the first independent work of the young chemist. Kizhner himself later spoke of the awe that



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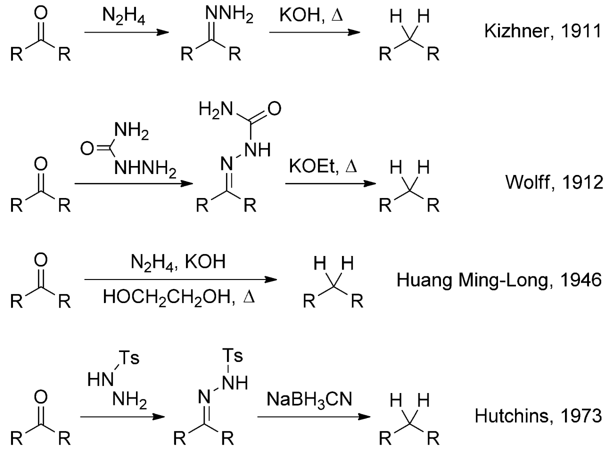


Scheme 1. The Wolff–Kishner reduction over six decades of development.

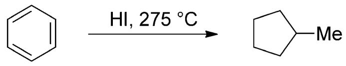
Figure 3. Vladimir Vasil'evich Markovnikov (1838–1904, left), and Vladimir Fyodorovich Luginin (1834–1911, right). Photographs courtesy of the Museum of the Kazan School of Chemistry (Markovnikov) and Moscow State University.

Markovnikov elicited from the students at Moscow: "*'I remember how impatiently I waited for Markovnikov's first lecture,' said Nikolai Matveevich. 'In our eyes, his name was surrounded by a halo of chemical prestige.'*"[7]

In his third year at the university, Kizhner became Luginin's assistant, and a year later (1890) he began to work directly under Markovnikov. Under Markovnikov's guidance, he published his first papers in the *Journal of the Russian Physical-Chemical Society*. These papers concerned two of Markovnikov's areas of research: the reactions of hydrogen halides with alkenes, and the structures of the hydrocarbons of the Caucasus oil. Kizhner's first papers described results from three widely disparate projects: a) the reactions of excess hydrogen chloride and hydrogen bromide with ethyl allyl ether, which resulted in cleavage of the ether to the two halides and water;[8] b) the action of sodium on epichlorohydrin, which had been proposed to form dioxepane,[9] but which Kizhner showed to give allyl alcohol and glycerol 1,3-diallyl ether;[10] and c) the hydrogenation of benzene.[11]

Kizhner graduated from Moscow in 1890, and received a supernumerary appointment to the staff as a laboratory assistant in organic chemistry that lasted until 1898. In this capacity, he taught qualitative and quantitative analysis. When he graduated with the M. Chem. degree four years later, he was elected privatdozent, and permitted to deliver lectures to students. From 1894 to 1901, Kizhner also taught chemistry and electrical engineering at the Alexander Military School.

By 1894, Kizhner was working independently in Markovnikov's laboratory, and he published his first papers, in which he suggested an explanation for why the physical properties of the "hexahydrobenzene" obtained by reducing benzene using Berthelot's method[12] (Scheme 2) did not match those of

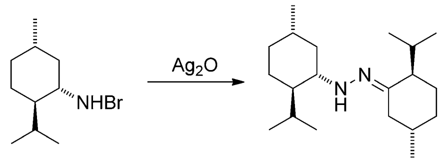


Scheme 2. The reduction of benzene with hydrogen iodide by Berthelot's method does not give cyclohexane.

cyclohexane produced by other routes.[13] The boiling point of the "hexahydrobenzene" (69–71 °C at 761 mm Hg) was much closer to that of *n*-hexane (68.7 °C) than that of synthetic cyclohexane (80.7 °C), which caused considerable consternation among those who championed the cyclic structure for benzene.[14] It was Kizhner who first realized that the boiling points of both *n*-hexane and methylcyclopentane (71.8 °C) were actually within experimental error of the boiling point of the "hexahydrobenzene," and that this might resolve the problem. He suggested, based on the comparison of their boiling points and other physical and chemical properties, that "hexahydrobenzene" was, in fact, methylcyclopentane.[15] This hypothesis was later confirmed by Markovnikov[16] and Zelinskii.[17] (Zelinskii had been appointed to the faculty of Moscow University following Markovnikov's ouster in 1893, and was working on this project—*Markovnikov's* project—without informing him of the fact. If nothing else, this was certainly a breach of professional etiquette.)

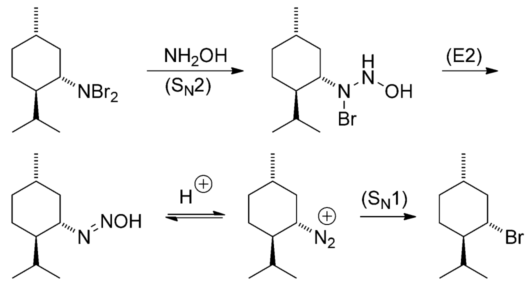
During his work with the saturated hydrocarbons, Kizhner studied the reaction between alkanes and potassium permanganate. It was well known that this reagent would react with alkenes[18] to give glycols, and that it did not react with alkanes. What Kizhner found, however, was unexpected: he found that it was not possible to remove all the alkene from a mixture of saturated and unsaturated hydrocarbons without causing substantial oxidation of the alkane, also.[19] He also observed that the alkane was oxidized to a greater extent if it possessed methine groups, rather than being composed solely of methyl and methylene groups, which is consistent with the modern view that the oxidation of alkanes generally involves free radicals.

In 1895, Kizhner submitted his dissertation for the degree of *Magistr Khimii* (M. Chem.) to St. Petersburg University.[20] The dissertation, entitled "Amines and hydrazines of the polymethylene series, methods of their formation and transformation," reported the preparation of both cycloalkyl and open-chain amines and hydrazines. Much of this work involved the preparation and reactions of *N*-bromoamines and *N*,*N*-dibromoamines, and the link to his later work with hydrazine derivatives of organic compounds is obvious. In this dissertation and the subsequent paper[21] Kizhner reported a study of the reactions of *N*,*N*-dibromoamines (especially menthylamines) with silver oxide to give hydrazones, from which the corresponding hydrazines could be liberated by acid hydrolysis (Scheme 3).



Scheme 3. Kizhner's general synthesis of hydrazines involves the coupling of *N*-bromoamines with silver oxide to generate hydrazones.

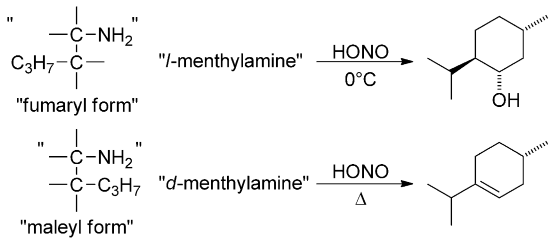
At the same time, Kizhner also studied the reactions of dibromoamines with hydroxylamine hydrochloride. This reaction provided the alkyl bromide and nitrogen, and, as Kizhner himself proposed, almost certainly proceeds through the diazonium ion, which gives a carbocation that is then trapped by the bromide anion. The isolation of a small amount of menthene (by elimination from the cation) from the reaction supports this view. A possible reaction pathway is provided in Scheme 4.



Scheme 4. A possible reaction pathway for Kizhner's synthesis of alkyl halides from dibromoamines and hydroxylamine hydrochloride.

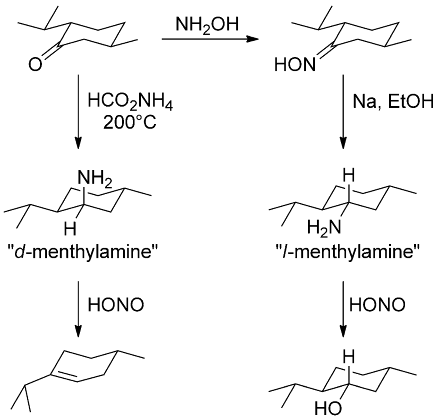
In addition, he reported (Scheme 5) that "*d*-menthylamine" reacted with nitrous acid at room temperature to give the hydrocarbon, menthene, but that "*l*-menthylamine" required heating, and gave *l*-menthol as the major product.[22] These results are, of course, totally incompatible with the two menthylamines referred to, being enantiomers.

The most rational explanation of Kizhner's result leads to the inference that the two menthylamines are, in fact,



Scheme 5. Kizhner's reported divergent outcomes from the treatment of *d*- and *l*-menthylamine with nitrous acid.

diastereoisomers rather than enantiomers. They were both obtained from the same enantiomer of menthone by methods described by Wallach,[23] which means that both share the same absolute configuration at C2 and C5 of the menthane ring system. The "*d*-menthylamine" was obtained from menthone by reduction of the ketone with ammonium formate at 200°C, while the "*l*-menthylamine" was obtained from the same ketone by reduction of its oxime with sodium



Scheme 6. A modern interpretation of the synthesis and observed reactions of *d*- and *l*-menthylamine with nitrous acid.

in ethanol (Scheme 6). In a striking foreshadowing of what is the most likely modern explanation of his observations, Kizhner himself provides a stereochemical diagram with the two forms, labeled "fumaryl form" for the *l*-menthylamine, and "maleyl form" for the *d*-menthylamine (Scheme 5).[21b]

Thus, it is not unreasonable to suggest that, while the "*l*-menthylamine" was, in fact, what is known today as menthylamine, with all three substituents equatorial on the cyclohexane ring, the "*d*-menthylamine" may, in fact, have been the axial amine epimer. Both amines should give the alkanediazonium ions, but the equatorial diazonium ion, cannot undergo rapid *anti* elimination, and so slowly dissociates to the menthyl cation, which then undergoes rapid attack by water to give *l*-menthol. The axial epimer of the alkyldiazonium ion, on the other hand, can rapidly give menthene by *anti* elimination (Scheme 6).

On graduating with the degree of M. Chem., Kizhner was elected privatdozent at Moscow University. For his original work in this dissertation, he was awarded the Minor Butlerov Prize. Five years later, in April 1900, Kizhner presented his dissertation for the *Doktor Khimii* (Dr. Chem.) degree at Moscow University.[24] The dissertation, which comprised two topics, "On the action of silver oxide and hydroxylamine on bromoamines. On the structure of hexahydrobenzene," was successfully defended. Among other things, it contained the general method for the preparation of substituted hydrazines reported the previous year.[22] On graduating with the Dr. Chem. degree, Kizhner was qualified to assume a professorship in a university in the Russian empire.

In 1896, the Imperial Tomsk Technological Institute (Figure 4), named for Tsar Nicholas II, was founded in the

Figure 4. The chemistry building of Tomsk Technological Institute around 1903. Photograph courtesy of Tomsk Polytechnic University.

largest city of Siberia by imperial decree, and became the first technical institute east of the Urals. The city of Tomsk was founded in 1604 by decree of Tsar Boris Godunov (1551–1605), on the Tom River, 3600 km east of Moscow, in Siberia. Its growth was accelerated by the discovery of gold, but the building of the Trans-Siberian Railway through what was to become Novosibirsk meant that this latter city eventually overtook Tomsk in importance. Tomsk returned to prominence at the end of the 19th century as the educational center of Siberia, with the founding of the Imperial Siberian University in Tomsk (1878), and then the Technological Institute. Politically, like much of Siberia, Tomsk was very conservative, and the townenthusiastically espoused the tsarist cause during the Revolutions of 1905 and 1917. Following the Bolshevik Revolution, Tomsk became a major center for the White Russian movement.

In 1899, the carbohydrate chemist Efim Luk′yanovich Zubashev (1860–1928, Figure 6)[25] was appointed the first Rector of the Technological Institute. Zubashev had been Professor at the Khark′ov Technological Institute and worked as a chemist at the Khark′ov sugar refinery. He immediately set about assembling a staff, and, thanks to the assistance and encouragement of Mendeleev (himself a native of Siberia, from the Tobolsk region), he was able to convince a number

Figure 5. Efim Luk′yanovich Zubashev (1860–1928). Photograph courtesy of Tomsk Polytechnic University.

of eminent scientists to join the faculty. The inauguration of the Institute (Figure 5) took place on December 18 (December 6, Julian calendar), 1900. Seven months later, Zubashev was able to persuade the new Dr. Chem, Kizhner, to join the Institute as the inaugural Professor of Organic Chemistry.

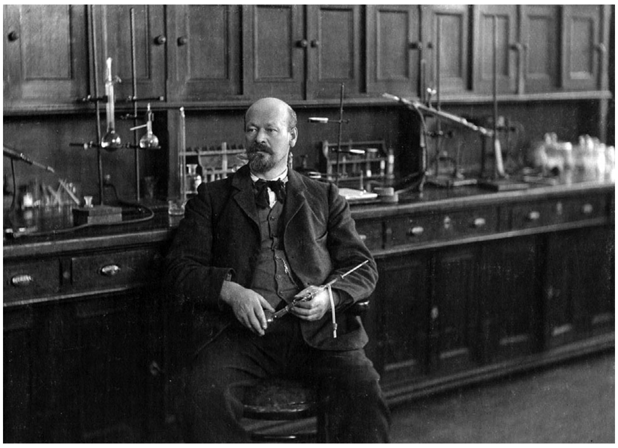


Figure 6. Kizhner in his laboratory at Tomsk Technological Institute. Photograph courtesy of Tomsk Polytechnic University.

Kizhner joined the Institute in July 1901, and embarked on the most eventful decade of his life. He immediately set about equipping the laboratory. Amongst other things, he filled his laboratory with equipment from Germany, and he assembled a chemistry library of journals and books from the leading academic centers of Europe. All this made his laboratory (Figure 6) one of the best in Russia, and certainly the equal of any in the European Russian universities. At the same time, he built such a strong rapport with his students that the metallurgist, Vladimir Andreevich Vanyukov (1880–1957) noted:[26]

"*'My spiritual father was Professor Kizhner,' recalled Vanyukov, the first graduate in chemical separations of that period. 'He clearly related to the students, but was strict in the laboratory. He guided my first work on refining copper and recommended it for publication.'*"

However, even before the first paper had appeared from his new institution, Kizhner had been diagnosed with "gangrene of the limbs," which appears to correspond to the modern, "gangrene of the extremities." This particular malady is common in advanced diabetes, and this raises the question of whether Kizhner was diabetic. The answer is not known, but it is interesting to note that hydrazine sulfate can induce both hyperglycemia and hypoglycemia depending on the glycogen load of the individual.[27] The effects of the chronic exposure to low levels of hydrazines and hydrazones may well include the genesis of diabetes-like medical complications. Kizhner himself refused to admit the possibility of any link between his health problems and his work because he didn't want his reputation as a careful chemist damaged. According to Yushkovskii, Andrei Belyi, a poet with a very low opinion of science and scientists, gave a caricature of Kizhner at Moscow[28] that hints that as a young man he may not have been as careful as he would have one believe:

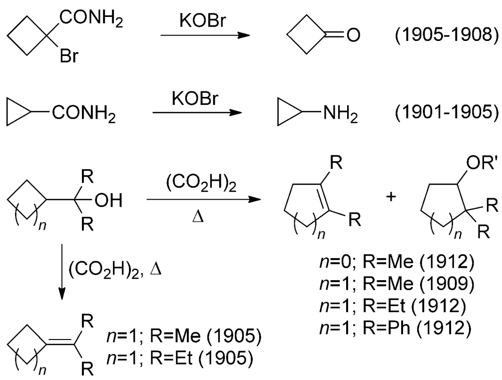
"*The memoirs of Andrei Belyi, one of the brightest representatives of the 'Silver Age', describe the figure of a young Kizhner as fairly lively and, at the same time, slightly grotesque. 'For two years I encountered a bald, red, strangely pink bespectacled man, dressed in devil knows what: something red-soiled and burnt through with holes. He was found foolishly with bromine, in the basement, in the hallway; you push him here, you stumble across him there, he is not a person, but a dumb animal.'*"

Whatever the cause of the disease, Kizhner's 1903 leave of absence to obtain treatment was to no avail, and 1904, his right leg was amputated below the knee. As soon as he was able, Kizhner returned to Tomsk, but the disease continued its progression, and painful gangrenous lesions soon appeared on his left leg. In 1905, he visited a specialist in Berlin, who prescribed a course of treatment. Postcards he sent back to his wife, Sofia Petrovna, and his son, Boris Nikolaevich, were very upbeat, and for a while he did, in fact, show considerable improvement. Unfortunately, however, the disease resumed its inexorable path, and, in 1910, after several futile trips abroad to seek treatment, he lost his left leg to amputation below the knee.

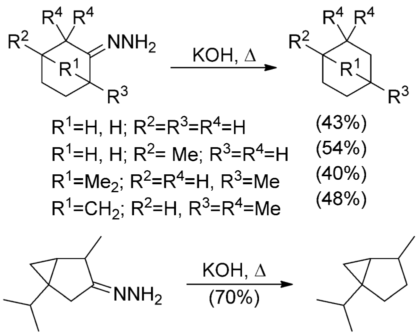
Kizhner was determined that the loss of his leg would have a minimum impact on his professional life. After the loss of his right leg, he continued to give lectures and lead colloquia, but he was now unable to stand for prolonged periods, and so temporarily ceased laboratory work. The loss of his second leg should have had a much greater impact on Kizhner's career, but its effects were not what one would expect, given his reaction to the first amputation. His ability to deliver lectures was seriously compromised, since he was now confined to a wheelchair, and only occasionally entered the auditorium, using crutches and prostheses to do so. But, he resumed his scientific research with a passion. In the words of A. E. Arbuzov, "*His powerful spirit and will are something to marvel at: an invalid in the full sense of the word, he continued to conduct experiments, publishing works one right after another.*"[29]

Kizhner's first papers from Tomsk involved the conversion of α-haloacids to the next-lower carboxylic acid by means of the action of bromine and base on their amides.[30] The remainder of the Tomsk period of his work can be divided into two major areas: 1) the chemistry of small-ring compounds, especially cyclopropane- and cyclobutanecarboxylic acid derivatives (Scheme 7) and 2) the chemistry of hydrazines and azines (Scheme 8). His studies of small-ring compounds resulted in a series of papers[31] detailing rearrangements of small-ring compounds under the influence of a variety of electrophiles and reaction conditions. In these publications, he initially assigned the structures of the products incorrectly, later correcting them to the ring-expanded structures.

What few people realize is the truly remarkable fact that that the discovery of the two reactions that carry his name—the catalytic decomposition of hydrazones by strong base, known as the Wolff–Kishner reduction,[2] and the decomposition of pyrazolines to give cyclopropanes, known as the



Scheme 7. Reactions of small-ring compounds reported by Kizhner while professor at Tomsk.

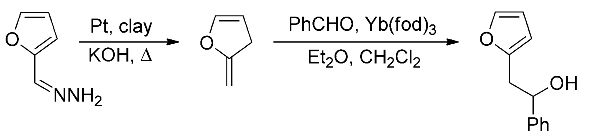


Scheme 8. The first base-promoted decompositions of hydrazones to hydrocarbons reported by Kizhner in 1911.

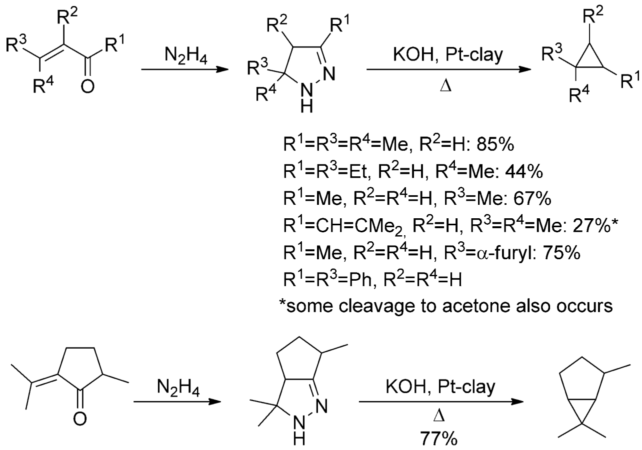
Kishner cyclopropane synthesis[32]—were actually made after Kizhner had become confined to a wheelchair. Kizhner lost his second leg in 1910, and every single paper concerning these two reactions appeared after this date.[33] His disability may have impacted his teaching duties, but Kizhner did not allow it to interfere with his scientific research, and he continued to publish regularly—and quickly—throughout his time at Tomsk.

The Wolff–Kishner reduction occasionally gives unexpected products. In 1931, Kizhner reported an unusual decomposition of furfural hydrazone that gave, under appropriate conditions, an isomer of 2-methylfuran that reacted with benzoquinone to give a product with a 2:1 stoichiometry.[34] This unstable isomer has since been used as a highly reactive ene in the ytterbium-catalyzed Alder ene reaction (Scheme 9).[35]

Kizhner's work with hydrazones also led to the discovery of the formation of pyrazolines from α,β-unsaturated aldehydes and ketones, and their pyrolysis to give cyclopropanes. This reaction is now known as the Kishner cyclopropane synthesis[32] (Scheme 10). For his work with hydrazine derivatives of organic compounds, Kizhner was awarded the prestigious Major Butlerov Prize in 1912. The Kishner cyclopropane synthesis has been the subject of several mechanistic studies,[36] and yet the mechanism is still not completely elucidated. Stereochemical and crossover experiments have largely eliminated the simplest mechanism, the elimination of nitrogen to give a simple diradical. Improvements in the synthesis have largely focused on methods for the generation of the pyrazoline.[37]

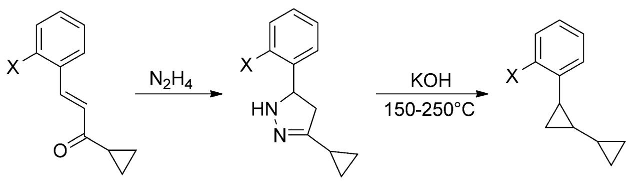


Scheme 9. The unusual product of the decomposition of furfural hydrazone is a highly active ene in the Alder ene reaction.



Scheme 10. The Kizhner cyclopropane synthesis.

The Kishner cyclopropane synthesis remains an important reaction, as attested by its recent use in the synthesis of biologically active cyclopropane derivatives. For example, it is a key reaction in the preparation of intermediates for the synthesis of fungicidal cyclopropylcyclopropane derivatives[38] (Scheme 11).



Scheme 11. Biologically active cyclopropylcyclopropanes prepared by the Kizhner cyclopropane synthesis.

Kizhner had hoped that his move to Tomsk would provide him with a quiet haven where he could pursue chemical research and teaching. This hope was shattered four years later, when the Revolution of 1905[39] erupted. Even in far-off Tomsk, the fires of revolt blazed, and Kizhner found himself in the thick of things. Kizhner's personal politics were decidedly progressive at a time when that was not necessarily wise, especially in ultraconservative Siberia. Sympathetic to the views of the reformers, he helped organize strikes by students and professors, and regularly addressed revolutionary gatherings. His activities during the 1905 Revolution branded him as an agitator, and this was not a good thing in a city that had ardently sided with the tsarist forces.

This reputation as a "free thinker" was quickly used against him. In February 1906, Kizhner and Kubashev were summarily dismissed from their positions by the Governor-General of Western Siberia, and ordered to leave Tomsk and the steppes region (Siberia). Kizhner was given just 48 h to leave the city of Tomsk. This was a reaction to his support of the "disloyal" students, which had been reported anonymously to the school district trustee, writer and lawyer Leonid Ivanovich Lavrent′ev (deceased 1914), by a "reliable source." It is likely that this "reliable source" was a disaffected colleague: At least one of his colleagues felt that a disabled person had no business occupying a professorship.[40] "'*Professor Kizhner does not hold any position in the institute and has no permanent employment,' one of his colleagues angrily said in a report*."

Although this should have been the end of Kizhner's professional career, he was fortunate in that Kubashev had powerful friends at court. Consequently, both were eventually reinstated to their positions as a result of the persistent requests from the Ministry of Education—albeit after over a year of exile. Kizhner returned to his research, but Kubashev was not so lucky: Within a year he had resigned his position at the university over a financial scandal that he neither knew of nor was involved in. Despite having been a strong a supporter of the democratic reforms that led to the Bolshevik Revolution, he was arrested in 1922, and expelled from Russia; he spent the remainder of his life in Czechoslovakia.

It was after Kizhner's return to Tomsk that he completed the research that led to his enduring fame. In 1911, he published a series of three papers. The first of these described the reaction of cyclohexanone with hydrazine hydrate.[41] The next two papers in the series[33] described the decomposition of the hydrazone, which Kizhner called an alkylidenehydrazine, with base. Later that same year, he reported the first paper on the Kishner cyclopropane synthesis.[31] However, his growing national and international stature as a synthetic organic chemist did not erase the memories of his efforts on behalf of the Revolution from the minds of his enemies, nor the hostility of at least some of his colleagues to the difficulties with which he contended due to his disability.

In 1911, Lavrent′ev renewed his attacks on the progressive faculty members of the Technological Institute, this time abetted by the Minister, Lev Aristidovich Kasso (1865–1914), who would decimate Moscow University by dismissing a large fraction of its faculty and students. Kizhner was asked to leave the institute in 1911, and in May 1912, he resigned his position. Ostensibly, the reasons for his departure were to seek improvements in his health, but it appears fairly clear that the administration of the institute was actively trying to force him out (there were surreptitious hints that the safety of the entire Kizhner family could not be guaranteed against the actions of violent ultraconservatives). He taught on a one-term contract for another year at Tomsk, then, in 1914—the same year he won his second Butlerov Prize (this time the major prize)—he finally left the institute that he had done so much to build.

Kizhner moved back to Moscow, where he had spent happier days as a student, and he joined the faculty of the Shanyavskii People's University. This interesting institution had been formed in 1911 by students who had been expelled from Moscow University for antitsarist activities by Education Minister Kasso, and by professors who resigned en masse in sympathy with three colleagues who had also been expelled.[42] These expulsions accounted for most of the students, and over a hundred of the professors, among whom were many of the best instructors at Moscow University. Because it was not an official university, Shanyavskii People's University could not confer degrees, but its academic rigor was fully equal to that of the official Moscow University. In 1918, it was taken over by the state, and in 1920 it ceased operations as a separate institution.

Kizhner remained at Shanyavskii until the Russian Revolution in 1917, and gradually his health improved. From 1917 to 1918, he served in the chemical testing laboratory of the emerging Commissariat Department, and in 1919 he became the Director of the Aniline Trust Institute—essentially responsible for the development of the Soviet dye industry. This largely thankless position required a huge investment of effort by Kizhner, and he did the job well. The most widely disseminated portrait of Kizhner (Figure 7) dates to this period.

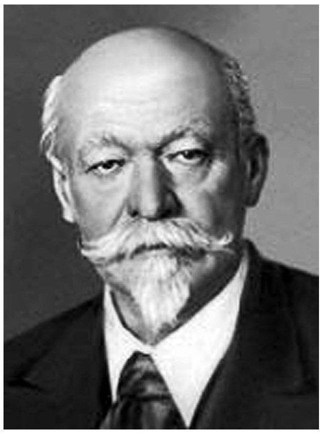
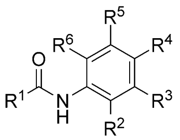


Figure 7. Nikolai Matveevich Kizhner in his later years in Moscow.

Leaving Tomsk was difficult for Kizhner for a variety of reasons: he was leaving work unfinished, and the laboratory that he had built, and where he had made his seminal discoveries; he was leaving his students, with whom he had formed a strong bond; he was being pushed out by political enemies who used his health as a very transparent pretext; and he continued to be subjected to the same petty despotism that had led to his first ouster. The effect of this forced departure on Kizhner may have been exactly what his enemies wanted—never again did his creativity reach the heights it had attained while he was in Tomsk, although this may also have been due largely to the paradigm shift towards applied chemistry under the Soviets.

Kizhner's focus during the last two decades of his career shifted from basic chemistry to technology, and his output of original research fell. He continued his studies on hydrazines, however, and in 1925[43] he confirmed the observation by Benary[44] that 2,6-dimethyl-γ-pyrone reacts with phenylhydrazine to give a product devoid of oxygen. Kizhner's dye work generally appeared in specialty industrial publications rather than in the more mainstream chemical journals. For example, work with aniline dyes is exemplified by two publications on crystal violet derivatives in *Anilinokrasochnaya Promyshlennost* ([*Aniline-dye Industry*]), an industry periodical devoted to aniline dyes.[45] Examples of derivatives of Fast Violet B prepared by Kizhner are shown in Figure 8.



R^1=Ph, R^2=Me, R^3=R^6=H, R^4=NH_2, R^5=OMe
R^1=2-furyl, R^2=Me, R^3=R^6=H, R^4=NH_2, R^5=OMe
R^1=Ph, R^2=R^5=H, R^3=Me, R^4=NH_2, R^6=OMe
R^1=Ph, R^2=R^5=H, R^3=Me, R^4=NH_2, R^6=OEt
R^1=Ph, R^2=R^5=H, R^3=Cl, R^4=NH_2, R^6=OMe
R^1=Ph, R^2=R^5=H, R^3=R^6=Cl, R^4=NH_2

Figure 8. Variants of Fast Violet B prepared by Kizhner.

In 1929, Kizhner was elected a Corresponding Member of the Academy of Science of the USSR, and in 1934, he became an honorary Full Member. In addition to the two Butlerov Prizes for his work, Kizhner was also awarded the Order of St. Stanislaus, 3rd Class and 2nd Class, as well as a medal "In memory of the Reign of Alexander III" for his services to chemistry during the reign of Nicholas II. A scientist to the end, Kizhner died in his laboratory, working at the bench, a week before his 68th birthday, and was buried in Moscow.

We cannot know how being confined to a wheelchair affected Kizhner's productivity. Certainly, while he was confined to the wheelchair, his output was prolific. However, one can only speculate about how productive he might have been with the full use of both legs (or did his disability simply give him an enormous incentive to produce and succeed?). It is also worthwhile examining Kizhner's life in the light of those of other disabled and politically active chemists. He was a member of a very small fraternity: a disabled chemist who was also a political activist. Although he had moved to Tomsk in the hope of avoiding political unrest and its incursions into his scientific life, when the time came, he was willing to stand up for his beliefs. The cost to him was lost time from a career that would soon be changed forever by the October Revolution, with its accompanying dramatic change in the national emphasis to applied, rather than fundamental, science. In Kizhner's case, this meant a change from investigating fundamental questions and discovering new reactions to devising better, more efficient ways to make dyes. In this he also excelled. His career may not have been as productive after his departure from Tomsk, but what he did accomplish in the last two decades of his life certainly made it clear that the official reasons for that departure were undeniably specious.

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