A CENTURY OF BASE-PROMOTED DECOMPOSITION OF HYDRAZONES: THE EARLY CAREER OF NIKOLAI MATVEEVICH KIZHNER (1867-1935)

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The year 2011 marked the centennial of the first report of the base-promoted decomposition of hydrazones to hydrocarbons (1). The reaction was discovered in 1911 by the 43-year-old inaugural Professor of Organic Chemistry at the Imperial Technological Institute at Tomsk, in Siberia—Nikolai Matveevich Kizhner (Николай Матвеевич Кижнер, 1867-1935) (2, 3). Eighteen months after the appearance of Kizhner's paper, which was in Russian, the reaction was rediscovered by German chemist, Ludwig Wolff (1857-1919), at Jena, and published in German (4). Since 1912, it has borne the name of both chemists, being known in the west as the Wolff-Kishner reaction, and in Russia as the Kizhner-Wolff reaction.

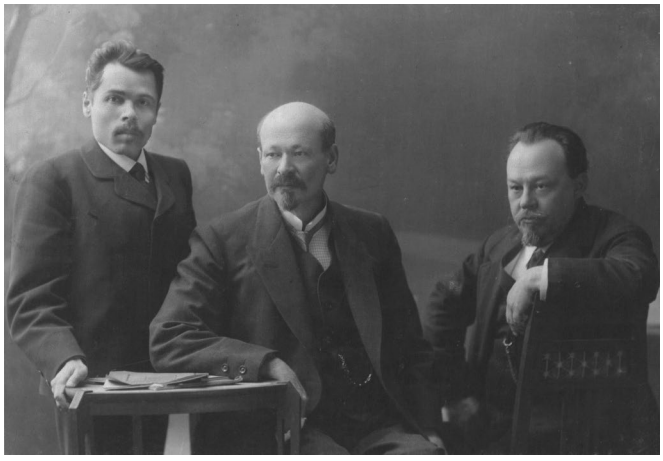


Figure 1. *Members of the Chair of Organic Chemistry at Tomsk Technological Institute ca. 1910: (l-r) Laboratory Assistant (later Professor) Georgii Vasil'evich Khonin (1878-1952), Professor Nikolai Matveevich Kizhner, and an unidentified member. Photograph courtesy of Tomsk Technological Institute.*

Kizhner (Figure 1) is an interesting study as both an individual and as a chemist. Over the course of his career, he faced incredible obstacles—physical, political, and professional—all of which he overcame. It is a tribute to his resilience and tenacity that he not only built a career as an organic chemistry professor, but that he succeeded as well as he did. Some idea of the course of his career can be gauged from the fact that, while other major figures in organic chemistry were frequently memorialized by plaques placed prominently their universities within a short time of their deaths, it was not until over a quarter century after his death, and over half a century after he had left Tomsk, that Kizhner was so memorialized at the Technological Institute.

There are no reliable facts available about Kizhner's early life; it has been speculated that his father held the social rank of a court counselor (i.e. not of the nobility, but of a middle social class), or that he came from a family of army medical assistants. Still, his family did have sufficient status to allow him to enter the First

Moscow Gymnasium, from which he graduated in 1886. He then entered Moscow University (now Lomonosov Moscow State University) as a student in the Natural Sciences Division of the Physics-Mathematics Faculty. This faculty by then included chemistry, which had initially been part of the Medical Faculty of the university (5). By his third year, Kizhner had fixed on organic chemistry as his course of study.

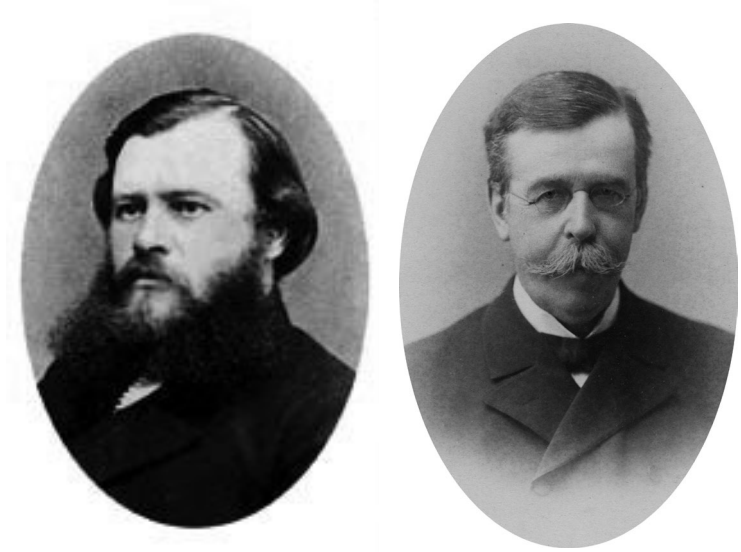


Figure 2. *Kizhner's mentors: Vladimir Vasil'evich Markovnikov (left) and Vladimir Fyodorovich Luginin (Louguinine) (right). Photographs courtesy of the Museum of the Chemistry School of Kazan University (Markovnikov) and Moscow State University Archives (Luginin, provided by Dr. E. A. Zaitseva (Baum)).*

At Moscow, Kizhner came in contact with of two excellent chemistry instructors, who undoubtedly had a strong influence on his eventual choice of a career: organic chemist, Vladimir Vasil'evich Markovnikov (Владимир Васильевич Марковников, 1838-1904), who taught the lectures in organic chemistry, and physical chemist, Vladimir Fyodorovich Luginin (Владимир Фёдоровч Лугинин, 1834-1911), who supervised the laboratory instruction in chemistry (6). Kizhner's attitude towards Markovnikov, especially, appears to have been what today would be called hero-worship: "'I remember how impatiently I waited for Markovnikov's first lecture,' said Nikolai Matveevich. 'His name, in our eyes, was surrounded by a halo of chemical prestige'" (7). It is worthwhile noting that Markovnikov, one of Butlerov's students at Kazan, was one of the few Russian organic chemists to build a lasting international reputation during his own lifetime.

Kizhner rapidly developed as an organic chemist, and his first research publication was published the same year he graduated with the *Diplom*—1890. By that time, Markovnikov's primary focus had shifted to identifying the hydrocarbons of the Caucasus oil, and he was involved in the effort to establish the identity of the hydrocarbon, "hexahydrobenzene," that had been obtained by the reduction of benzene by means of Berthelot's method using hydrogen iodide in a sealed tube at high temperature (8). This hydrocarbon and its constitution were also the subject of intensive research in Western Europe (9, 10).

Kizhner began investigating this problem while still an undergraduate, and he soon supplemented it with two other projects (Figure 3). This ability to focus simultaneously on more than one problem at a time was one of the hallmarks of his entire career. Thus, while studying hexahydrobenzene, he was also investigating the reactions of hydrogen halides with allyl ethyl ether, reactions that resulted in the cleavage of the ether into the two halides and water (11), and the reaction of epichlorohydrin with sodium metal (12) to give 1,3-diallyloxy-3-propanol. He published these two papers and two on hexahydrobenzene (13) in the first years of his association with Markovnikov.

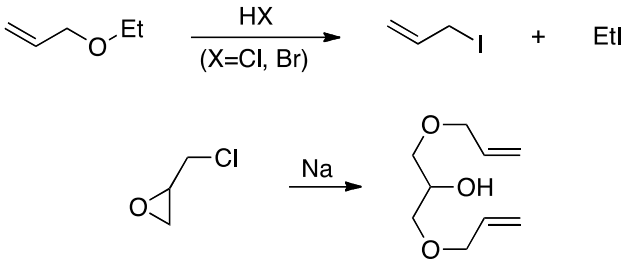


Figure 3. *Kizhner's early research problems.*

Following his graduation with the *Diplom*, Kizhner remained in Markovnikov's laboratory to carry out the research for the degree of *Magistr Khimii* (M. Chem.). He had been identified by both Markovnikov and Luginin as a student with the potential to enter the professoriate, and at their suggestion, he was funded during this time by means of a supernumerary, "outside statute" position—a position funded internally, rather than by the state—as a laboratory assistant in chemistry at Moscow University.

In 1895, he submitted his M. Chem. dissertation (14) to St. Petersburg University. He passed the requisite examinations, and since he now held the M. Chem. degree, he was qualified to hold a junior appointment at a Russian university. He was appointed Docent at Moscow in 1895. During his M. Chem. studies, Kizhner had taught in the laboratories at Moscow, and in his final year (1894) he had been appointed as an instructor at the Alexander Military School; he held this appointment jointly with his position at Moscow until his departure for Tomsk, in 1901.

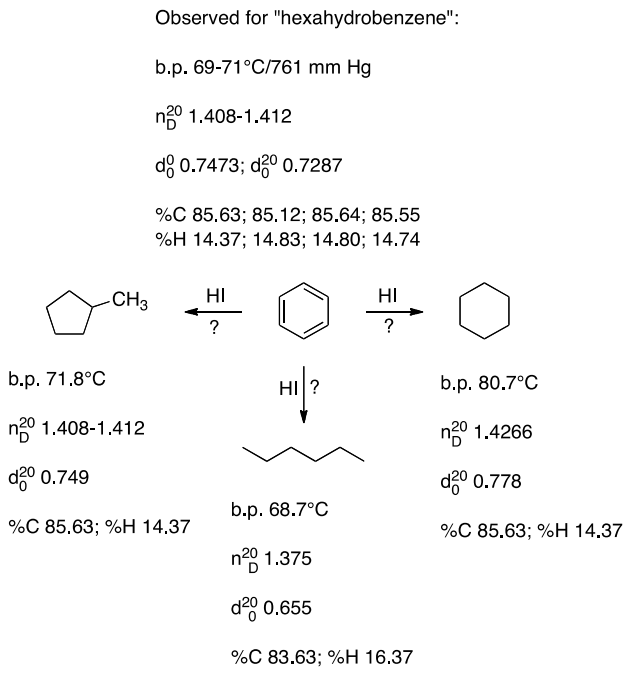


Figure 4. *The candidates for the hydrocarbon produced by reduction of benzene under Berthelot's conditions.*

Kizhner submitted his dissertation to Moscow University for the degree of *Doktor Khimii* (Dr. Chem.) in 1900 (15). During the independent research on which his Dr. Chem. dissertation would be based, Kizhner continued to work on the hexahydrobenzene problem (Figure 4). The fact that the boiling point of hexahydrobenzene (69-71°C/761 mm Hg) was closer to that of hexane, and not cyclohexane, while its combustion analysis gave values equal to those from cyclohexane, and not hexane, had been problematic for chemists of the period looking to establish the six-membered ring in benzene.

It was Kizhner who first realized what had happened—that there had been a rearrangement during the reduction—and showed that methylcyclopentane (Figure 4) had the required physical and chemical properties (16). The publication of Kizhner's paper was quickly followed by papers by Zelinskii (17) and Markovnikov (18), confirming Kizhner's conclusions. Zelinskii's paper was revealing in another way: it showed he had begun working on Markovnikov's problem without informing him of this fact, a breach of professional etiquette, and Markovnikov made clear his claim to the problem in his "Bemerkung" paper (18b).

The Russian poet, Andrei Belyi (Андрей Белый, nom-de-plume of Boris Nikolaevich Bugaev, Борис Николаевич Бугаев, 1880-1934), who had a dim view of science and its practitioners, painted a vivid caricature of Kizhner as Markovnikov's apprentice in Moscow (19):

> 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. You would come across him, awkward, never too far away from 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.
>
> —Who is that?
>
> —Kizhner.
>
> ... *[of the many people in the lab]* ... one whistles, another mumbles something to himself, Kizhner is mute. He displays emotion only when you push his elbow in the hallway. In response, you'll get boxed in the ears with the towel usually draped over his shoulders…It would be strange to find that Kizhner has a house or, God forbid, a wife. His home is the organic laboratory.

This description notwithstanding, not only did Kizhner have a wife (Sofia Petrovna), but a son (Boris Nikolaevich, born in 1894).

In the same work, Belyi suggests that in the eyes of the other students, Kizhner, who worked in the laboratory from dawn until dusk, could be represented by the following rather grotesque description (19):

> ... The crazed look of the small, lidless eyes, like the heads of two rubbed corks, the little red nose, the glasses, the little red beard, and a round bald spot: all parts of his head....

Again, one must recognize in this description the hyperbole used by one with little respect for scientists—in Belyi's eyes a man so dedicated to science could not help but arouse pity and a wry smile.

Graduating with the Dr. Chem. qualified Kizhner to hold a Chair in chemistry as an Ordinary (Full) Professor at a Russian university. The Imperial Tomsk Technological Institute, which had been established by a 1896

decree of Tsar Nicholas II, was officially opened in 1900 under the leadership of Efim Luk'yanovich Zubashev (Ефим Лукьянович Зубашев, 1860-1928), Professor at Khar'kov University, and a sugar chemist and technologist of national standing (Figure 5). Tomsk was somewhat unusual for the time, since its enrollment was open—not subject to the political and religious limitations of most other universities in the empire—and thus was permitted to enroll graduates of technical schools. Its exemption from the enrollment quotas attracted a large number of Jewish students. Zubashev quickly sought candidates to fill the faculty positions there; his efforts to build the chemistry faculty were facilitated by the active assistance of Mendeleev, who helped to attract strong candidates for the positions.

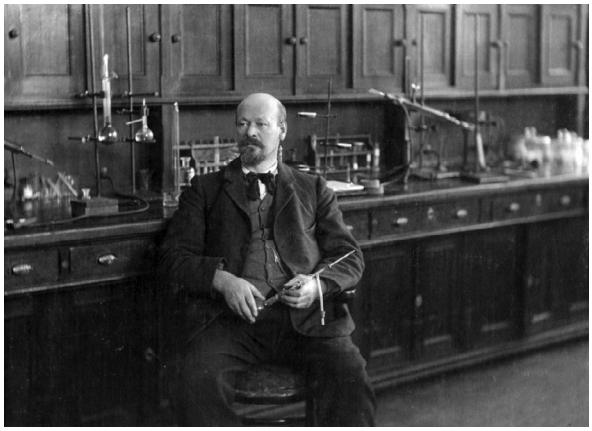
Figure 5. *The first Director of the Tomsk Technological Institute, Efim Luk'yanovich Zubashev ca. 1901 (photograph courtesy of Tomsk Polytechnic University)*

Tomsk is one of the oldest cities in Siberia, having been founded by the decree of Tsar Boris Godunov in 1604. Two centuries later, Tomsk became the seat of the Tomsk Guberniya, and began a rapid expansion that was accelerated by the discovery of gold in 1830. Because the route chosen for the Trans-Siberian Railway passed through Nizhni Novgorod, the growth of Tomsk was surpassed by that city in the mid-nineteenth century. Nevertheless, at the end of the nineteenth century, Tomsk resurrected itself as a major educational center with the founding of the Siberian Imperial University in Tomsk (now Tomsk State University) in 1888, and the Imperial Tomsk Technological Institute of Tsar Nicholas II (now Tomsk Polytechnic University) in 1900.

In July, 1901, Kizhner began the most eventful decade of his life, when he joined the faculty at Tomsk Technological Institute (Figure 6). He began teaching, and immediately set about equipping his laboratory (Figure 7), which soon became one of the best in Russia, and building the collection of the chemistry journals into a major resource. During each of his trips to Western Europe, he sought out apparatus and chemical journals to bring back to Tomsk. In addition to the equipment he imported from Germany, Kizhner also made equipment for his laboratory—he possessed not inconsiderable skill as a glassblower and instrument maker.

Figure 6. *The Chemistry building at Tomsk Technological Institute, ca. 1903. Photograph courtesy of Tomsk Polytechnic University.*

Kizhner's early research work at Tomsk was devoted to a continuation of the chemistry of bromoamines that he had begun during his doctoral research. This was followed some four years later by a major focus on the chemistry of small-ring compounds, especially amines obtained by the Hofmann rearrangement of the corresponding carboxamides (20). He also began studies of Lewis acid-catalyzed reactions of small-ring acid chlorides with benzene under Friedel-Crafts conditions (21). The chemistry of organic nitrogen compounds was to remain a major focus of his research until his death in 1935.



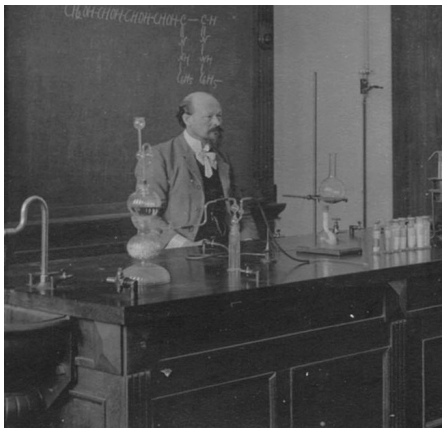


Figure 7. *Kizhner in his Tomsk laboratory (above) and lecturing (on osazones) in the auditorium (below). Photographs courtesy of Tomsk Polytechnic University.*

Just two years after beginning his tenure at Tomsk, Kizhner was diagnosed with the dangerous and painful "gangrene of the limbs." This disease became so threatening to his life that, in 1904, he traveled to Moscow, where his right leg was amputated above the ankle. On his return to Tomsk, he was still able to attend lectures and lead symposia by using crutches. But he ceased research because he could not endure the long hours of standing at the laboratory bench and the supervision of the laboratory passed to another professor. Although the surgery resulted in a brief respite from the pain, within months, gangrenous lesions began to appear on his left leg. Again, the disease ultimately proved to be resistant to treatment, and his left leg was amputated above the ankle in early 1910.

What should have been career-ending surgery at that time, especially for a synthetic organic chemist, had exactly the opposite effect. Although his teaching career in the auditorium was now in tatters (he could only enter the auditorium on crutches), his research program underwent a remarkable transformation. After his first amputation, Kizhner had effectively stopped doing experimental work. Now he returned to the research laboratory—this time confined to a wheelchair—and began working with a vengeance, as if to make up for lost time. In the words of the pioneering organophosphorus chemist, Aleksandr Yerminingel'dovich Arbuzov (Александр Ерминингельдович Арбузов, 1877-1868), "One must wonder at his powerful spirit and willpower: an invalid in every sense of the word, he continued his experimental work, publishing one paper after another" (22). It undoubtedly also helped that his apartment—like many Russian universities at this time, the Chair carried with it the fringe benefit of an apartment—was close to his laboratory.

In 1911—the year *after* he had become wheelchair-bound—he published the first report of the base-promoted decomposition of hydrazones to give hydrocarbons, and he followed this a year later with the first report of the synthesis of cyclopropanes now known as the Kizhner cyclopropane synthesis; he continued to pursue this research for decades (23). What is even more remarkable is the fact that most of Kizhner's research publications, including those where the work was carried out after his amputations, carry the name of only one author: Kizhner did the work himself, and allowed his students to publish under their own names. In the case of the reaction that is the topic of this paper, after the initial publication with Belov, which described the preparation of cyclohexanone hydrazone hydrate, Kizhner extended the work alone (although paper 1a does carry a section titled, "In collaboration with A. Proskuryakov").

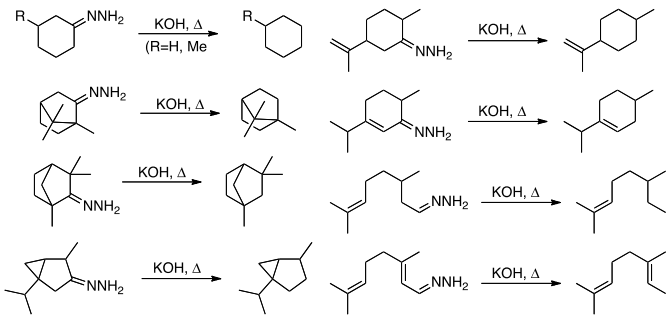


Figure 8. *Kizhner's first demonstrations of the base-catalyzed decomposition of hydrazones to give hydrocarbons (the Wolff-Kishner reduction).*

Kizhner's study of the base-catalyzed decomposition of hydrazones was carried out initially (1a) using a

variety of saturated ketone hydrazones, including those of some highly hindered ketones, such as camphor and fenchone (Figure 8). In the second publication (1b), Kizhner extended the reaction to a study of aldehyde hydrazones and hydrazones of unsaturated ketones (Figure 8). It is typical of the era that the most common substrates for investigation were terpene-based. In every case but one, the major product of the reaction, isolated by distillation and steam distillation, was the corresponding hydrocarbon. The reactions with the dihydrocarvones also showed that unsaturation—whether in conjugation with the carbonyl group or not—did not alter the course of the reaction. The decomposition of cyclohexanone hydrazone, however, was unusual, in that it also provided cyclohexanol in an amount approximately equal to the amount of cyclohexane produced.

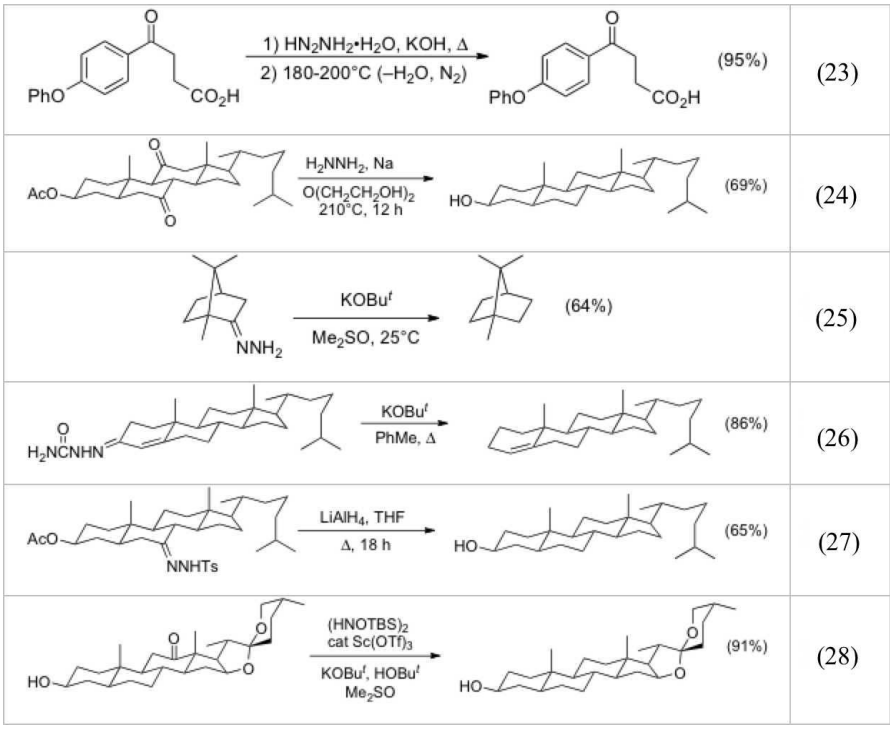


Figure 9. *Variants of the Wolff-Kishner reduction developed since the original discovery in 1911.*

Some idea of the importance of this reduction can be gathered from its longevity as a method for reducing aldehydes and ketones, and from the observation that nine decades after its discovery, the reaction was still inspiring research into developing variants that would circumvent or overcome deficiencies in the original method (Figure 9). In the nine decades since the discovery of the reaction by Kizhner, no less than six major variants have appeared (23-28), from the Huang-Minlon modification, developed in 1946 (23), to the variant reported by Myers in 2004 (28).

The year after he had described the deoxygenation of ketones by means of the base-promoted decomposition of their hydrazones, Kizhner described the base-promoted decomposition of pyrazolines in the presence of platinized clay (29). In this case, the product was not an unsaturated hydrocarbon, but an isomeric cyclopropane instead (Figure 10). As shown in Figure 10, the pyrazolines were generally formed by the reaction of hydrazine with an α,β-unsaturated ketone, but in one case, the pyrazoline was formed from the ketazine by the method developed by Curtius and Zinkeisen (30).

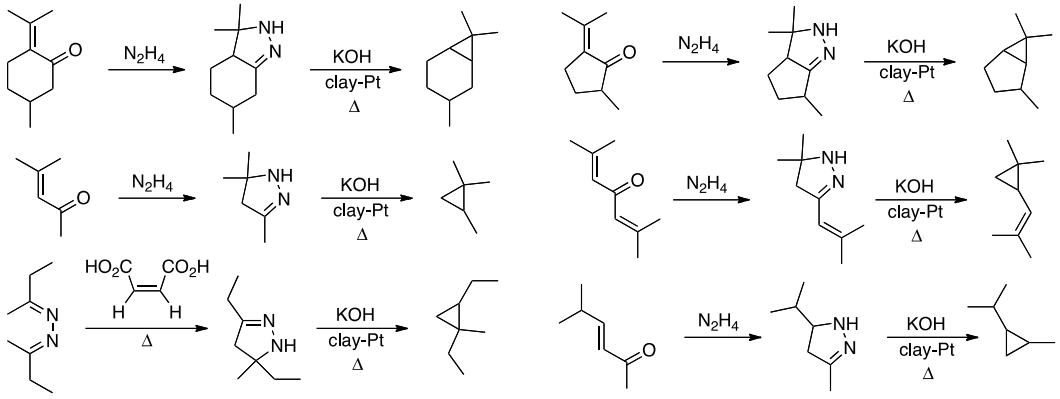


Figure 10. *The first cyclopropanes prepared by pyrolysis of pyrazolines with base and platinized clay.*

It was not only his scientific accomplishments that made his Tomsk years eventful for Kizhner. The beginning of the twentieth century saw the political crises that had been building during the reign of Nicholas II begin to grow out of control, culminating in the first of the Russian revolutions: the Revolution of 1905, which led to a curtailing of the absolute powers of the Tsar. The beginnings of this political unrest were quite evident in Moscow at the end of the nineteenth century. Kizhner may have hoped that by working in far-off, conservative Tomsk, he would be shielded from this unrest and its effects on his research program, and that the Siberian city would become a peaceful haven to pursue his science. Unfortunately for him, it was not to be, as political unrest broke out in Tomsk.

Like all the faculty members at the Institute at the time, Kizhner eventually had to declare for one side or the other. He chose to side with the striking students, and strongly supported the students' demands for the independence of the educational system from what had become oppressive rule by bureaucrats. For this, he was reported (anonymously) to be involved in organizing student and faculty strikes, and in addressing revolutionary groups (31). He was also accused by his enemies of abetting the student strikes by cancelling his lectures. While Kizhner did not punish the students for striking, there is actually little objective evidence to brand him as an agitator, and his writings and speeches were much more concerned with the science he was teaching than the politics of the students (3d).

Regardless, the success of the revolution should have protected Kizhner from serious repercussions of his supposedly revolutionary activities, but the testimony of his personal enemy, Leonid Ivanovich Lavrent'ev (Леонид Иванович Лаврентьев, d. 1914), a curator (trustee) of the Tomsk educational district (this was a powerful position, whose occupant reported directly to the Minister), and the anonymous accusations against him carried substantial weight with the local government, and he was branded a "dangerous free-thinker" (3e). In 1906 he, Zubashev, and other "disloyal" staff members were exiled from Tomsk on 48 hours' notice by the Interim Governor-General of Western Siberia (31). They were saved from a worse fate by sheer luck: the day before his arrest, Zubashev had been summoned to a council on the reform of higher education in Moscow by the Minister of Public Enlightenment, Count Tolstoy. Kizhner and the other exiled professors followed immediately thereafter, and also participated in the council. Even so, Kizhner spent a year and a half in exile, in St. Petersburg, while Zubashev, who had some connections in higher government circles, remained in Moscow, where he petitioned the Ministry of Education for their reinstatement.

In response to a private letter from the influential minister, Count Sergei Yul'evich Witte (Сергей Юльевич Витте, 1849-1915) to the new Governor-General, Baron Nol'ken, and thanks to the influence of Pyotr Arkad'evich Stolypin (Пётр Аркадьевич Столыпин, 1862-1911), Zubashev and Kizhner were ordered reinstated in the middle of 1907. But, resentment among their colleagues at Tomsk remained. Within a year, Zubashev had been forced to resign. In 1912—the year he was awarded the Greater Butlerov Prize—Kizhner, also, was forced to resign.

It is symptomatic of the times that anonymous denunciations and petty dislikes should overshadow world-class accomplishments, but this is what happened to Kizhner. The overt reasons for his resignation were his health, but his colleagues at Tomsk knew that the real reason was, in fact, that Kizhner had been "advised" that there were local elements in the area, such as the violent gangs known as the "Black Hundreds" (32) who disapproved of his "disloyal" activity; his resignation was simply the result of extortion by threats against his life and his family (31). Another factor that made Kizhner's departure from Tomsk inevitable was the loss of his apartment, which was close to the laboratory. This apartment was one of the perquisites of the *kafedra*, or chair, and on resigning from his position, Kizhner also forfeited the apartment. For a man confined to a wheelchair, this added hardship eventually became too much to take.

Leaving Tomsk was extremely hard for Kizhner: he was being forced to leave the laboratory he had built from nothing, to leave behind students with whom he had established a close bond, and to abandon research problems that were not yet completed. Although he spent a further two years at Tomsk teaching, his departure was inevitable, and in 1914 he returned to Moscow, where he spent the rest of his career and life.

Kizhner's career in Moscow lacked much of the vibrant creativity that he had shown in Tomsk, although this may be traced, in part, to the dramatic shift from pure to applied research under the Soviet regime. Immediately on his return to Moscow, Kizhner obtained an appointment at the short-lived Shanyavskii People's University, with financial support from "Society to promote the success of the experimental sciences and their practical applications," funded by the philanthopist Khristofor Semënovich Ledentsov (Христофор Семёнович Леденцов,

1842-1907) (33). After the Revolution, he assumed a leadership position at the Aniline Trust Institute ("Anil-trest"), where he became a very conscientious leader of the Russian synthetic dye industry. His research during this period consisted largely of work to improve the synthesis of dyes, but he did continue, somewhat sporadically, with work on the two reactions he had discovered in Tomsk. In 1934, he was elected an Honorary Member of the Academy of Sciences of the U.S.S.R.

References and Notes

1. (a) N. M. Kizhner, "Kataliticheskoe razlozhenie alkilidengidrazinov, kak metod polucheniya uglevodorodov [Catalytic reduction of alkylidene hydrazines as a method for producing hydrocarbons]," *Zh. Russ. Fiz.-Khim. O-va.*, **1911**, *43*, 582-595. (b) N. Kizhner, "O kataliticheskom razlozhenii alkilidengidrazinov: St. 2-ya [On the catalytic decomposition of alkylidenehydrazines: Second part]," *Zh. Russ. Fiz.-Khim. O-va.*, **1911**, *43*, 951-962.
2. Russian uses the Cyrillic alphabet, and so names must be transliterated to the Roman alphabet. The exact transliteration used depends on the language into which the transliteration occurs, and even this is not a constant within the same language. In keeping with our previous practice (D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer-Verlag, Heidelberg, 2012) throughout this paper, the BGN/PCGN romanization system for Russian is used as the most intuitive for English speakers. In citations of articles in western journals, names are given as transliterated by the journals. The English transliteration most frequently encountered is "Kishner," which was first used by *Chemical Abstracts* in Kizhner's early papers. It was subsequently replaced in English by the more intuitive, "Kizhner," but since the predominant use of *CA* has been to refer to Kizhner's original papers, the early transliteration became widespread. German does not have a consonant or combination of consonants corresponding to the Russian, ж, but this is now addressed by using the Czech letter, "ž"; the modern German transliteration of Kizhner's name is "Kižner." The German transliteration used by Kizhner himself was "Kijner." Clearly, this spelling does not transliterate the correct pronunciation of Kizhner's name by a German reader, but it does so (or to a closer approximation than in German) in French. This suggests that Kizhner may have used a French transliteration for his name for his three publications in the German journals (although, interestingly, in his sole publication in French, he uses the form, "Kishner").
3. There are relatively few biographies of Kizhner available, and almost all are in Russian. Most are focused on his scientific accomplishments, and contain relatively little personal information: (a) S. S. Nametkin, *N. M. Kizhner. Issledovaniya v Oblasti Organicheskoi Khimii [N. M. Kizhner. Investigations in the Field of Organic Chemistry]*. Akad. Nauk SSSR, Moscow, 1937. (b) S. Shch. Rodionov, in V. M. Rodionova, Sr. Ed., *Voprosy Anilinokrasochnoi Khimii, Trudy VIII Sovyeshchaniya khimii i tekhnike 8-11 Dekabrya, 1947 g. [Issues in Aniline Dye Chemistry. Proceedings of the VIII Council on aniline chemistry and techniques, December, 1947*; henceforth *Voprosy Anilinokrasochnoi Khimii]*, 5-17. (c) T. V. Boratova, E. A. Zaitseva, "Nikolai Matveevich Kizhner," *Khimiya*, **1996**, *39*, 2. For biographical sketches containing more personal details, see: (d) V. D. Yushkovskii, "IV. Iz istorii Tomskogo Politekhnicheskogo Universiteta. Protivostoyanie Tomsk v sud'be professora Kizhnera [IV. From the history of Tomsk Polytechnic University. Confrontation in the fate of Professor Kizhner at Tomsk]," *Izv. Tomskogo Pol-ka. Univ-ta.*, **2002**, *305*, 208-221. (e) O. Magidson, in *Voprosy Anilinokrasochnoi Khimii*, 18-20. (f) V. A. Ismailskii, in *Voprosy Anilinokrasochnoi Khimii*, 21-24. For biographical materials in English, see: (g) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer, Heidelberg, 2012, 105-106. (h) D. E. Lewis, "Disabilities, despots, and deoxygenation—from exile to Academy Member. Nikolai Matveevich Kizhner (1867-1935)," *Angew. Chem. Int. Ed.*, **2013**, *52*, 11704-11712.
4. L. Wolff, "Methode zum Ersatz des Sauerstoffatoms der Ketone und Aldehyde durch Wasserstoff," *Justus Liebigs Ann. Chem.*, **1912**, *394*, 86-108.
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