A. YE. ARBUZOV: FATHER OF ORGANOPHOSPHORUS CHEMISTRY IN RUSSIA

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The year 2016 marked the 110th anniversary of the first publications by Kazan chemist, Aleksandr Yerminingel'dovich Arbuzov (1) (Арбузов, Александр Ерминингельдович, 1877-1968, Figure 1), describing the reaction that now bears his name (2). Arbuzov became a major pioneer of organophosphorus chemistry—he was nominated for the Nobel Prize in Chemistry four times (3)—and his long career at Kazan established it as a world center for research in that field (4).

***Figure 1**. Aleksandr Yerminingel'dovich Arbuzov (1877-1968, left) and Aleksandr Mikhailovich Zaitsev (1841-1910, right).*

The city of Kazan is 600 miles east of Moscow, on the Volga River. Today, it is the capital city of the Tatarstan Republic of the Russian Federation and the eighth-largest city in Russia, but in 1804 it was effectively the easternmost European outpost of the Russian empire. In fact, to many Russians resident in the western capitals of Moscow and St. Petersburg, Kazan was not a European city but an Asiatic one, and this made recruiting faculty members rather more difficult than the same task in the contemporary new universities at Dorpat (now Tartu, in Estonia) and Khar'kov (now Kharkiv, in Ukraine), which were much closer to western Russia and therefore viewed automatically as European. This difficulty in recruiting faculty members was a major reason why it took an unusually long time—a decade—for Kazan to become a full, independent university, rather than subordinate to the local Gymnasium.

Despite this less-than-auspicious beginning, by the turn of the twentieth century, Kazan had risen to become one of the pre-eminent universities in Russia (5). In fact, at the turn of that century, almost half the Professors of Chemistry in the Russian empire had a connection with the Kazan School of Chemistry, either by receiving part or all of their education there, or by studying under one of the graduates of the Kazan school.

Arbuzov's Early Life and Education

Arbuzov was born to a member of the lesser nobility in the village of Arbuzov-Baran, in Kazan Province; his father's estate was next to that of the great Russian organic chemist, Aleksandr Mikhailovich Butlerov

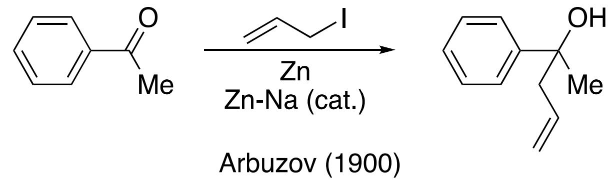
(Бутлеров, Александр Михайлович, 1828-1886). He began his schooling in the one-room schoolhouse in the village; shortly after Butlerov died, he was enrolled in the classical Gymnasium in Kazan. He graduated in 1896 and immediately entered the Physics-Mathematics faculty of Kazan University. Here he met Aleksandr Mikhailovich Zaitsev (Зайцев, Алкксандр Михайлович, 1841-1910, Figure 1) (6).

As a student, he taught himself to blow glass, and over time, he became a true virtuoso glassblower—one of the few chemists who did not need a professional glassblower in his laboratory. His skills as a glassblower were particularly invaluable in Novo-Aleksandriya, for the Institute did not have a glassblower (Figure 2). In 1912, he published a self-study guide to learning glassblowing (7a). Two decades later, while fractional distillation was still the only recourse for separating mixtures of liquids, Arbuzov published at least one paper on particularly effective fractionating columns/reflux condensers for distilling turpentine (7b).

Figure 2. *Two views of Arbuzov at the glassblowing table.*

Arbuzov earned his diplom in 1900. One month later, he passed the examinations for the degree of kandidat in the natural sciences, and he prepared to undertake his research for the degree of Magistr Khimii (M. Chem.).

Zaitsev had continued the work of his own mentor, Butlerov, in developing methods for the synthesis of tertiary alcohols based on organozinc nucleophiles (Scheme 1); his students Yegor Yegorovich Vagner (Вагнер, Егор Егоревич, Georg Wagner, 1849-1903, Figure 3) and Sergei Nikolaevich Reformatskii (Реформатский, Сергей Николаевич, 1860-1934, Figure 3) further extended Zaitsev's work to the synthesis of secondary alcohols (8) and β-hydroxyesters (9).



Scheme 1. *The final synthesis at Kazan of a homooallylic alcohol by the Zaitsev method.*

Figure 3. *Yegor Yegorovich Vagner (Georg Wagner, 1849-1903, left) and Sergei Nikolaevich Reformatskii (1860-1934, right).*

During the year that Arbuzov graduated, Victor Grignard (1871-1935, Figure 4) published his method for the synthesis of alcohols (10). This completely revolutionized alcohol synthesis, because it did not require the strong experimental skills that the Zaitsev synthesis required. With the lone exception of the Reformatskii reaction (9), the use of organozinc nucleophiles fell into an eight-decade decline. The synthesis of secondary alcohols by means of organozinc nucleophiles was eventually resurrected by the work of Ryoji Noyori (1938-, Figure 4) in the asymmetric synthesis of secondary alcohols with organozinc nucleophiles (11).

Figure 4. *Victor Grignard (1871-1935, left) and Ryoji Noyori (1938-, right).*

The Grignard method required much less experimental skill than the organozinc approach, and so alkylmagnesium halides, which are inherently more reactive nucleophiles than the corresponding zinc species, quickly displaced alkylzinc halides or dialkylzinc reagents as the preferred nucleophiles for this purpose. Arbuzov thus has the distinction of being the last Zaitsev student to carry out an alcohol synthesis (2-phenylpent-4-en-2-ol) using allylzinc iodide (12). However, the timing of Grignard's discovery placed the young Arbuzov in a difficult position, since the proposed research problem for his M. Chem. degree was now rendered obsolete. In fact, in the same paper (12), Arbuzov described carrying out the same synthesis with magnesium by adding a mixture of allyl iodide and acetophenone dropwise to magnesium turnings in ether. This general reaction had been reported in 1899 (13) by Grignard's mentor, Philippe Antoine Barbier (1848-1922), but organomagnesium reactions did not achieve popularity until after Grignard's papers had appeared.

Arbuzov's Early Independent Career

Immediately following his graduation as kandidat, it had been Zaitsev's intent to retain Arbuzov at Kazan to train for the professoriate, and Zaitsev had submitted the paperwork for him to do so, to St. Petersburg for action. At the same time, Arbuzov had moved to the Petrovskii (now Timiryazev) Agricultural Academy, where he enrolled in the third course. Then, before his stipend as *Aspirant* could be approved, the Professor of Inorganic chemistry at Kazan, Flavian Mikhailovich Flavitskii (Флавитский, Флавиан Михайлович, 1848-1917, Figure 5), urged kandidat Arbuzov to follow Zaitsev's student, Wagner, to the Novo-Aleksandriya Institute of Agriculture and Forestry (Figure 6) as Assistant in the Department of Organic Chemistry and Chemical Analysis. On his arrival there, Arbuzov sought out Wagner, and passed on greetings from their mutual mentor, Zaitsev.

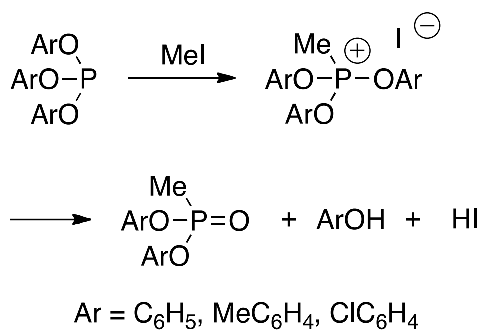
Figure 5. *Flavian Mikhailovich Flavitskii (1848-1917, left) and Karl Arnold August Michaelis (1847-1916, right).*

Figure 6. *The Novo-Aleksandriya Institute of Agriculture and Forestry, in the Pulavski Palace.*

Today, Novo-Aleksandriya is the Polish city of Puławy. In 1842, after the November uprising of 1830-1831 had been quashed, it was renamed Novo-Aleksandriya. Poland had long been a thorn in the side of the Russian government, and after this uprising, a deliberate move was made to Russify Poland and to suppress Polish culture; the renaming of Puławy was one part of this effort. Following World War 1, after the defeat of a numerically much larger Soviet army and the restoration of Polish sovereignty, it reverted to Puławy.

At Novo-Aleksandriya, Arbuzov's duties were to manage the department and the practical classes of students in a large and complex laboratory—he was the only assistant for a laboratory with 80 student places. In the Fall, students studied quantitative analysis, and in the Spring they studied the analysis of soils and fertilizers. In addition, his duties included assisting in lectures on organic chemistry. And still, he found time for research. The head of the department, F. F. Selivanov, proposed that he carry out the synthesis of *tert*-butylacetic acid, but this project proved to be much more difficult than Selivanov had envisaged. Arbuzov's progress on the project was agonizingly slow, especially for such a meticulous experimenter. Selivanov had an excellent and expansive mind, but Arbuzov reported that his experimental technique was so sub-standard, that he was a poor leader in the laboratory (4c). Certainly, he had little grasp of the practical difficulties that young Arbuzov would encounter. Although Selivanov wanted to publish their meager results, Arbuzov withheld his permission, so the work remained unpublished.

With the failure of this initial project, Arbuzov radically changed the focus of his research, and began to study phosphorous acid and its derivatives, largely as a result of studying Mendeleev's *Osnovy Khimii* during his preparation for the M. Chem. degree. This was a much more daring move than it might seem, since it meant that he would be pursuing research for the M. Chem. without a formal research supervisor and in a totally new field. Nonetheless, he obtained enough results (2a) to prepare and submit his M. Chem. dissertation (14) to Kazan University in 1905. In this dissertation, Arbuzov discussed the structure of phosphorous acid and its derivatives, and he investigated the nature of the hydrogen that is not replaced by metals. His first independent research results were presented in 1903, at the meeting of the Society of Naturalists at the University of Warsaw (15), and concerned the use of copper(I) salts to distinguish tricoordinate phosphite esters, $P(OR)_3$, from tetracoordinate "phosphite" esters, $RP(=O)(OR)_2$, (which he later showed were actually dialkyl alkylphosphonates).

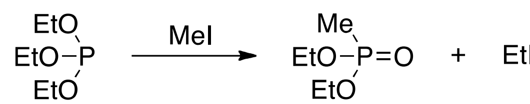


***Scheme 2**. The Michaelis rearrangement of triaryl phosphites to diaryl alkylphosphonates.*

Arbuzov's dissertation research extended earlier work by August Michaelis (1847-1916, Figure 5) at Rostock. In 1876, as part of a lengthy article (16), Michaelis had proposed that the structure of phosphorous acid was $HPO(OH)_2$, and in a later paper (17), he studied the reactions of phosphorous acid esters, and noted that diethyl ethylphosphonate, prepared by reaction of diethyl phosphite and sodium metal, followed by alkylation with ethyl iodide, was in fact, identical to the triethyl phosphite reported by Zimmermann (18).

A year later, Michaelis and his student, Kaehne published the paper describing the reaction of triaryl phosphites with methyl iodide. They reported that the initial reaction gave a methyl(triaryloxy)phosphonium iodide that decomposed on boiling in water or dilute base to give the diaryl methylphosphonate. If the same salt were simply heated above 200°C, the diaryl methylphosphonate, the phenol, and hydrogen iodide (19) were obtained (Scheme 2). Interestingly, Michaelis did not follow up on this particular discovery—this was his only report of the reaction—but shifted his research more toward the chemistry of nitrogen heterocycles, especially the pyrazolones and their phosphonyl derivatives.

Arbuzov's discoveries nicely complemented those of Michaelis. During the course of his M. Chem. research, he had discovered the reaction that now carries his name (Scheme 3) (2), and had obtained strong evidence that the structure of phosphorous acid was, in fact, not $P(OH)_3$, but $HPO(OH)_2$, as had been proposed earlier by Michaelis. His studies were also much more wide-ranging. The Arbuzov rearrangement had the advantage that it required only one formal step (unlike the Michaelis reaction, which required a base hydrolysis to complete the rearrangement), and that it did not require such extreme conditions (his reactions were typically carried out between 100 and 130°C). At the same time, Arbuzov discovered the catalyzed version of the reaction.



***Scheme 3**. The Arbuzov rearrangement of trialkyl phosphites to dialkyl esters of alkylphosphonic acids.*

As a result of the successful defense of his M. Chem. dissertation at Kazan, Arbuzov was appointed to the Chair of Organic Chemistry at Novo-Aleksandriya in 1906, and in 1907, he was awarded a *komandirovka* (rather like a modern sabbatical), which he spent in western Europe, working with Emil Fischer in Berlin, and Baeyer in Munich. Many years later, Arbuzov recalled how Fisher asked him, referring to Arbuzov's discovery of the catalytic effect of copper(I) salts on the conversion of phenylhydrazones to indoles (20), "Have you patented your discovery?" When he received a negative answer, Fischer was terribly surprised at his selflessness and, perhaps, at the naiveté of his Russian colleague (4e). Arbuzov returned to Novo-Aleksandriya in 1910—the year that his mentor, Zaitsev, died.

Arbuzov's Return to Kazan

Two candidates were initially considered to replace Zaitsev at Kazan: Vladimir Vasil'evich Chelintsev (Челинцев, Владимир Васильевич, 1877-1933), a student of Zelinskii, and Aleksandr Nikolaevich Reformatskii (Реформатский, Александр Николаевич, 1864-1937, Figure 7), a student of both Zaitsev and Markovnikov. Reformatskii, in particular, had strong ties to Kazan through his mentor, Zaitsev. Nevertheless, both declined to compete for the position, and chose to remain at Moscow.

Figure 7. Aleksandr Nikolaevich Reformatskii (1864-1937)

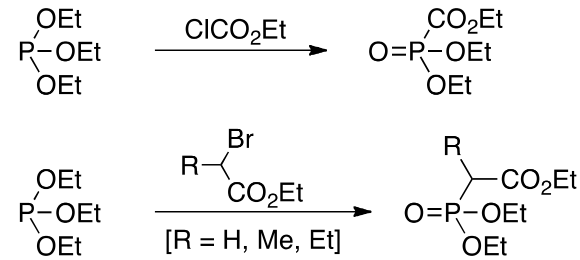
Once again, Flavitskii stepped forward, this time to champion Arbuzov as a candidate for the vacant chair. He actively promoted his nominee by describing Arbuzov's work and potential in glowing terms in his written assessment (21):

> In all these studies, A. Ye. Arbuzov has proved to be a careful and skilled experimenter. All his works are distinguished by the ingenious formulation of the questions and the comprehensiveness of his investigations of them. Questions about isomerizations or rearrangements involving catalysts are currently very common in chemistry, and the results of A. Ye. Arbuzov in this area witness to his general initiative and are what we are entitled to expect from the head of a scientific school. This is exactly what the traditions of the Chair of Organic Chemistry at our University, established by Butlerov, Markovnikov and, most recently, Zaitsev, demand.

Arbuzov became Extraordinary Professor of Chemistry at Kazan in September 1911, with the condition that he write and defend a dissertation for the degree of Doktor Khimii (Dr. Chem.) within three years. In February 1915, his Dr. Chem. dissertation (22), containing full descriptions of the reaction he had developed, was presented to the University Council by Flavitskii and approved.

Arbuzov's career at Kazan was long and distinguished, culminating in his election to the USSR Academy of Sciences and the establishment of the Institute of Organic and Physical Chemistry that bears his name; he was the first Director of the Institute. During his entire career, he continued his work with organophosphorus compounds, and with his rearrangement. In the ensuing five decades, he published 73 papers in Russian and four in German in the area of organophosphorus chemistry (23).

In 1914, with his student, A. A. Dunin, he reported the reactions of triethyl phosphite with ethyl α-bromocarboxylates and with ethyl chloroformate (24) (Scheme 4). The resultant phosphonocarboxylate esters and similar phosphonic acid derivatives have become stock reagents for the synthesis of *E*-α,β-unsaturated esters by the Horner-Wadsworth-Emmons reaction (25).



Scheme 4. The Arbuzov rearrangement of trialkyl phosphites to dialkyl esters of alkylphosphinic acids and the alkylation of dialkyl phosphites with α-haloesters.

Around the same time, with his student A. A. Ivanov, he reported further investigations of the isomerization of trialkyl phosphite esters to the isomeric dialkyl alkylphosphonates by the alkyl halide (26).

There is a hiatus of eight years in Arbuzov's publication record, between 1915 and 1923, a period that encompassed both World War I and the Russian Revolution. Although there were no refereed publications by Arbuzov during this time, an abstract (27) of a talk given by him to the Third Mendeleev Congress of Pure and Applied Chemistry, held at the National Chemical Technological Institute in Kazan, detailing the activities of the Laboratory of Organic Chemistry at Kazan for the period 1915-1921, was published in 1923.

A Russian-German commercial agreement of 1904 prohibited Russia from refining coal tar, meaning that Germany held a monopoly on the raw materials for many important medications in Russia. Early on, the pioneering pyridine chemist, Aleksei Yevgen'evich Chichibabin (Чичибабин, Алексей Евгеньевич, 1871-1945), saw the danger for Russia posed by shortages of essential medicines. He was one of the organizers of the Moscow Committee for the Development of the Chemical Pharmaceutical Industry and became its first head.

In 1915, Arbuzov had just been promoted to Ordinary Professor, the same year that Chichibabin launched a public appeal to enlist the help of chemists for the production of medicines (28). Arbuzov answered the call, and he began consulting with the Krestovnikov Brothers chemical plant in Kazan (Figure 8). This plant, which was noted for its production of soap and high-quality glycerine (suitable for conversion to nitroglycerine and dynamite), had been founded in 1855 with the aid of the Professor of Chemical Technology at Kazan, Modest Yakovlevich Kittary (Киттары, Модест Яковлевич, 1825-1880). The plant was nationalized by the Soviet government in 1919.

***Figure 8**. Arbuzov (front row, third from left) with the workers and specialists of the Krestovnikov Brothers plant.*

It was Arbuzov's task to direct the production of phenol, salicylic acid and aspirin from benzene, itself obtained from local crude oil. The aspirin produced there was an essential medicine, and in quality it proved to be the equal of the important Bayer product that it was intended to replace. As an aside, a sample of Arbuzov's phenol is kept at the Butlerov Museum of the Kazan School of chemistry, and above a pool of dark liquid, it consists of the only pure white, crystalline sample of this compound that this author has ever seen.

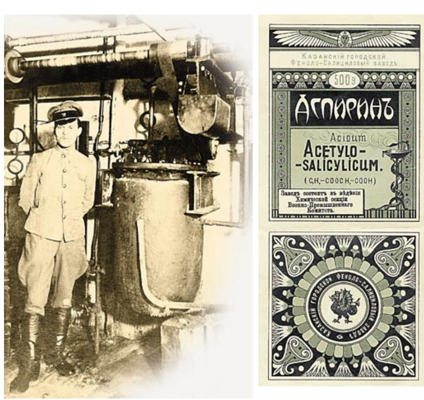
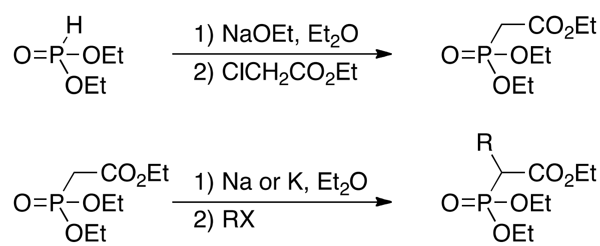


***Figure 9**. An aspirin kettle at the Krestovnikov Brothers plant (left) and the aspirin box designed by Arbuzov (right).*

Before the Russian Revolution, rosin and turpentine, obtained from the gum resin produced by Scots pine (*Pinus sylvestris*), were imported—despite the abundance of this species in Russia. This was due, in large part, to the belief that the severity of the Russian climate would render the process unprofitable. In 1924, the Supreme Council of the National Economy sought to test this. Under the leadership of Arbuzov and his son, Boris Aleksandrovich Arbuzov (Арбузов, Борис Александрович, 1903-1991, Figure 10), an acre of the Raifa forest near Kazan was set up for experiments to investigate this in the Volga region, and to develop the most rational methods of producing gum-resin. After numerous experiments, Arbuzov showed that it was, in fact, possible to extract gum resin from conifers in forests in the middle of Russia (29). Thanks, in part, to B. A. Arbuzov's continuation of this work, Russia became a large producer of turpentine before World War II (4c).

***Figure 10**. Boris Aleksandrovich Arbuzov (1903-1991)*

In 1929, Arbuzov published two papers reporting the synthesis of ethyl phosphonoacetate by alkylation of the sodium salt of diethyl phosphite with ethyl α-bromoacetate (30). This was an extension of the early independent work of Swedish chemist, Paul Nylen (1892-1976) who had formed α-phosphonocarboxylate esters by the alkylation of the sodium or potassium salt of phosphonoacetate esters with methyl iodide and benzyl chloride (31) (Scheme 5).

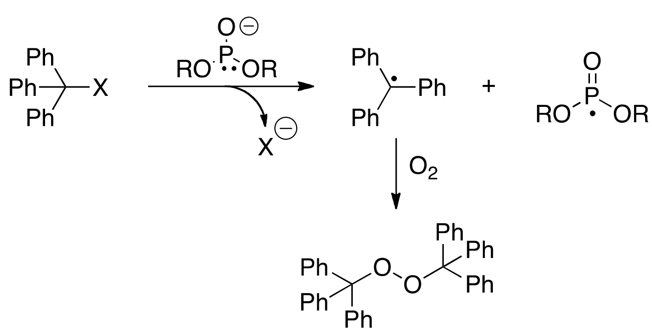


***Scheme 5**. The alkylation of the sodium salt of dialkyl phosphites, and salts of α-phosphonocarboxylate esters.*

The same year, he reported two important observations on the reaction of triphenylmethyl derivatives with trivalent phosphorus compounds. In the first (32), Arbuzov and his son reported studies aimed at elucidating the structure of "Boyd's acid chloride," a compound reported by Boyd and Chignell to have predominantly (78%) the trivalent phosphorus structure, $Ph_3CO–PCl_2$ (33) rather than the phosphonyl dichloride, $Ph_3C–P(:O)Cl_2$.

One key observation leading to this deduction was the fact that, on boiling in ethanol, triphenylmethyl ethyl ether was obtained from this acid chloride. The Arbuzovs proposed that the product was, in fact, the phosphonyl dichloride. In 1933, Hatt (34) provided evidence that the Arbuzovs had been correct, and also suggested a mechanism involving the triphenylmethyl cation, that rationalized the formation of the ethyl ether. In 1947, Arbuzov and Nikonorov provided evidence that the phosphonyl structure was, in fact, correct (48).

As part of their analysis, the Arbuzovs suggested that a free radical reaction may be required to rearrange this product. Their study of the reaction between the sodium salt of a dialkylphosphite and a triarylmethyl halide, published the same year (35), revealed that this did, indeed, provided a useful method for the generation of free radicals (Scheme 6). The formation of the triphenylmethyl radical was demonstrated by the isolation of *bis*(triphenylmethy) peroxide from the product mixture.



***Scheme 6**. The generation of triarylmethyl radicals from triarylmethyl halides and sodium dialkylphosphites.*

Arbuzov served as Professor of Chemistry at Kazan University until 1930, the last eight of those years as Dean of the Physico-Mathematical Faculty. In 1930, he became Professor of Chemistry and Director of the Kazan Technical Institute of the USSR Academy of Sciences. Two years later, in 1932, he was elected a Corresponding Member of the USSR Academy of Sciences.

Arbuzov in World War II

In June 1941, when Arbuzov was already 63 years old, Operation Barbarossa began, bringing Russia into the war on the Allied side. The German advance caused major interruptions to the scientific life of the Soviet Union. As the Nazis advanced towards Moscow and Leningrad during July 1941, the decision was taken to evacuate the Academy of Sciences from those two cities to Kazan. A total of eleven Institutes and the Academy laboratories were evacuated from Moscow to Kazan by the middle of July.

From the beginning, Arbuzov was the key individual at Kazan during these evacuations, finding places for the evacuated scientists to live and work. During this time, beds were so scarce in Kazan that the scientists were sleeping in shifts (36), and all were assigned to a term of work in the fields during the summers (37) to help feed the ballooning population. Less than a year after the evacuation, he received the news that he had been elected a Full Academician of the USSR Academy of Sciences.

Arbuzov continued his research during the war, and in 1943 he personally developed and perfected a method of obtaining dipyridyl. He also led a team of scientists who were seconded to carry out secret, war-related research. Not surprisingly, there are no contemporary accounts of this work. Beginning during this period, and continuing for the remainder of his life, Arbuzov devoted considerable effort to recording the history of organic chemistry in Russia, including his 1948 classic book (38).

The Post-war Years

After the war, in 1945, Arbuzov was named the permanent Director of the Kazan Technical Institute of the USSR Academy of Sciences. This may have been a recognition of his performance during the administrative nightmare that was the evacuations from Moscow and Leningrad. His strong administrative skills were evident in this position, and in 1959 he was appointed as Head of the Institute of Organic Chemistry of the USSR Academy of Sciences. In 1965, the two Institutes merged, and the new body was named the A. Ye. Arbuzov Institute of Organic and Physical Chemistry in his honor; it celebrated its 50th anniversary in 2015.

Arbuzov rose to a position of great prominence towards the end of his life. He was five times a Deputy to Convocations 2-6 of the Supreme Soviet—the Soviet Union's highest legislative body—between 1946 and

1966. He was awarded the Stalin Prize, second class, in 1943, and first class in 1947, and he received the Order of Lenin five times. In 1957, he was awarded the Hero of Socialist Labor medal, the highest civilian decoration of the Soviet Union.

Arbuzov the Man

There were three passions in Arbuzov's life: chemistry, music, and painting. He often said: "I cannot imagine a chemist who is not familiar with the heights of poetry, with pictures of masters of painting, and with good literature." The walls of the Dom-muzei (Home-museum) of the Academicians Arbuzov (Figure 11) are adorned with his paintings.

Figure 11. *The Dom-muzei (Home-museum) of the Academicians Arbuzov.*

There is a grand piano in the Dom-muzei, which was played by his wife, Yekaterina Petrovna (Krotova), and his granddaughter, Marina Borisovna (1935-1997). Arbuzov's favorite instrument was the violin, and he had gone to the length of taking lessons from a professional teacher. He organized an amateur string quartet of Kazan scientists in which he played second violin (Figure 12). One of Arbuzov's favorite pieces was one written by the chemist-composer, Aleksandr Porfir'evich Borodin (1833-1887): the nocturne from String Quartet #2. Arbuzov's copy of the music for this piece is still kept at the Dom-Muzei in Kazan. During World War II, he organized concerts in Kazan for the military personnel and scientists assembled there.

Figure 12. *The string quartet of Kazan scientists. (l-r) V. V. Yevlampiev, A. E. Arbuzov, Prof. Burgsdoror and L. N. Parfent'ev. Arbuzov's son, Boris, is in the background.*

Figure 13. *Arbuzov's family: (back) Ekaterina Petrovna; (front, l-r) Boris, Yurii and Irina.*

Arbuzov had three children: Boris, Yurii Aleksandrovich (1907-1971) and Irina Aleksandrovna (1905-1989) (Fig, 13). All three became chemists. Boris followed his father into the Chair of Organic Chemistry, and was himself elected to the USSR Academy of Sciences. Yurii became a Professor at Moscow State University; Irina began her research career with her father, and then moved to Leningrad (St. Petersburg), where she worked in the Institute of Organic Chemistry, and, later, the Institute of Macromolecular Compounds of the USSR Academy of Sciences.

Arbuzov died on January 21, 1968, and was buried in the Arsk Kazan cemetery (Figure 14); his children and granddaughter are buried with him.

Figure 14*. The graves of Arbuzov and his family at the Arsk Kazan cemetery, June 2017.*

Arbuzov's Scientific Legacy

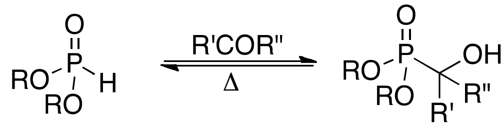
Like some his predecessors at Kazan (Butlerov, Markovnikov and Zaitsev, at least), Arbuzov inspired great loyalty in his students, and he was admired by his colleagues.

Arbuzov's legacy in organophosphorus chemistry was ensured by the continuing work of his students, among whom were his son, Boris Aleksandrovich, Gil'm Khairovich Kamai (Камай, Гильм Хайревич, 1901-1970, Figure 15), and B. A. Arbuzov's student, Arkadii Nikolaevich Pudovik (Пудовик, Аркадий Николаевич, 1916-2006, Figure 15), whose careers were all at Kazan State University, and Vasilii Semyonovich Abramov (Абрамов, Василий Семёнович,1904-1968, Figure 15), whose career was spent at Kazan Chemical-Technological Institute.

Boris Aleksandrovich Arbuzov faithfully continued his father's legacy of organophosphorus chemistry at Kazan, as well as expanding the research into natural products (especially terpenes), petroleum chemistry and polymer chemistry. His important contributions to the development of the turpentine industry in Russia have already been alluded to.

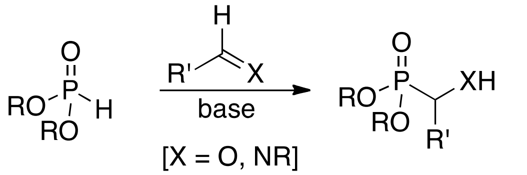
Figure 15*. Top: Gil'm Khairevich Kamai (1901-1970). Bottom (l-r): Arkadii Nikolaevich Pudovik (1916-2006) and Vasilii Semyonovich Abramov (1904-1968).*

In a series that eventually rose to a total of 40 papers between 1950 (39) and 1969 (40), Abramov reported that dialkyl phosphites react with aldehydes and ketones to give α-hydroxyalkylphosphonate esters (Scheme 7).



Scheme 7*. The Abramov reaction.*

Pudovik modified the reaction by incorporating a base, and this allowed the reaction to be used with imines to generate α-aminoalkylphosphonate esters (Scheme 8) (41). The Pudovik reaction has been used to generate chiral α-hydroxyalkyl- and α-aminoalkylphosphonate esters with good enantioselectivity (42).



***Scheme 8**. The Pudovik reaction.*

After early work with his mentor (43) in the area of organophosphorus chemistry, Kamai (who became the youngest Rector in the history of Kazan University) moved his research focus to organoarsenic chemistry (44).

The contributions of Arbuzov and his son in organophosphorus chemistry are celebrated by the award of the International Arbuzovs Prize in the field of organophosphorus chemistry (Figure 16). The award has been presented biennially on the anniversary of A. Ye. Arbuzov's birth since 1997.

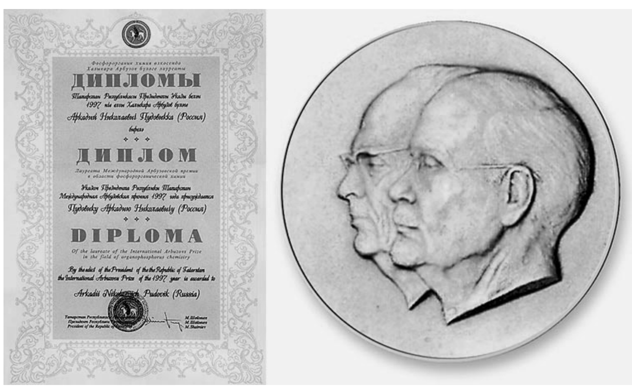
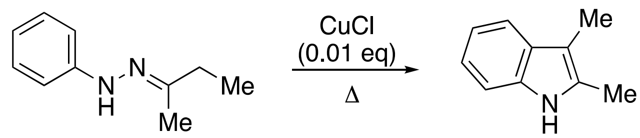
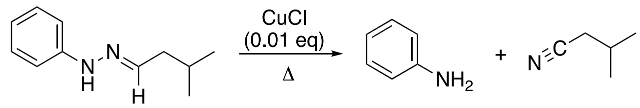


***Figure 16**. The Diploma and Medal for the International Arbuzovs Prize in the field of organophosphorus chemistry.*

Although Arbuzov is best known for his work with organophosphorus compounds, he also made seminal contributions in other areas of organic chemistry. In *A. E. Arbuzov. Izbrannye Trudy*, selected papers from his long career are given as full text (45). Beginning in 1910, he studied the catalytic action of copper(I) salts on phenylhydrazine (46) and phenylhydrazones (20). In the course of this work, he discovered the high catalytic activity of copper(I) halides on the Fischer indole synthesis (alluded to earlier). The importance of the discovery was that only 1-2% of this catalyst was needed, compared to a full molar equivalent of zinc chloride (Scheme 9). On occasion, the catalyzed reaction has been referred to as the Arbuzov-Fischer reaction. Interestingly, Arbuzov also noted that the same reaction conditions with the phenylhydrazones of aldehydes with more than four carbons preferentially gave mixtures of nitriles and aniline (Scheme 10) (47).



***Scheme 9**. The Arbuzov-Fischer reaction*



***Scheme 10**. The conversion of aldehyde phenylhydrazones to nitriles and aniline.*

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References and Notes

1. Russia uses the Cyrillic alphabet, and transliterations are a perennial problem. In this manuscript, the BGN/PCGN romanization system for Russian has been used as the most intuitive for English speakers, in keeping with previous practice by this author: D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*. S. Rasmussen, Ed. *SpringerBriefs in the History of Chemistry*, Springer, Heidelberg, 2012. The Russian letter "E" at the beginning of names is rendered by "Ye."
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