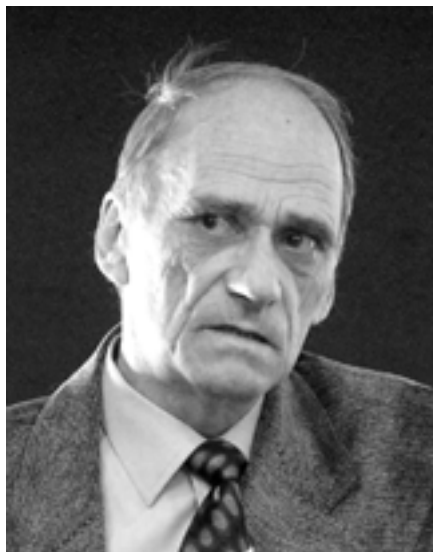


IN MEMORIAM



VADIM ALEKSANDROVICH PESTUNOVICH

(January 6, 1942 - July 4, 2004)

Late in the evening of July 4 the life of Vadim Aleksandrovich Pestunovich – talented scholar, scientific administrator, teacher, and friend – was unexpectedly interrupted.

His love of science, carried on through many years, originated even in his school years. An important role in the establishment of Vadim Aleksandrovich as a scientist was played by his first teacher Academician Grigorii Alekseevich Razuvaev. After finishing with distinction at the chemical faculty of Gorky State University and post graduate study he was invited to work at the Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, where with the active participation of and under the guidance of Doctor of Chemical Sciences J. Stradins the NMR method was first introduced into the daily routine of organic chemists in Latvia.

In the seventies the young specialist became acquainted with future academician M. G. Voronkov, who opened up to him the broad and exciting world of organosilicon chemistry and invited him to join him in investigations in distant Irkutsk. From that time his main interests were concentrated on investigations in the region of NMR spectroscopy and the physical and structural chemistry of heteroorganic compounds. At the Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR (now the A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences), he headed

the Laboratory of Radiospectroscopy (later the Laboratory of Structural Chemistry). The creative duo – M. G. Voronkov and V. A. Pestunovich – formed a team of like-minded persons, making a considerable contribution to the chemistry of the heterocyclic compounds of hypervalent silicon and, particularly, silatranes.

In 1970 V. A. Pestunovich successfully defended a candidate's thesis on "Investigation of the structure of alkoxy and aminoalkoxy derivatives of silicon and certain other elements by PMR," in 1985 he skilfully defended a doctoral thesis on "NMR and the structure of organic compounds of pentacoordinated silicon," and in 1988 he was given the title of professor.

The researches of V. A. Pestunovich devoted to investigation of the structure of heteroorganic compounds by multinuclear and dynamic NMR spectroscopy, including the nuclei of rare isotopes, have made a substantial contribution to the development of the chemistry of familiar and novel types of heteroatomic compounds. They led to discovery of the slow (on the chemical time scale) inversion of the nitrogen atom in derivatives of aziridine and many novel reactions and rearrangements of organosilicon, organogermanium, and organotin molecules. These investigations led to the widespread introduction of ^{29}Si NMR spectroscopy into research and analytical practise worldwide. The greatest recognition was given to the extensive range of his pioneering experimental and theoretical investigations in the field of the organic chemistry of compounds of hypervalent (penta- and hexacoordinated) silicon.

In conjunction with Irkutsk and Moscow colleagues Vadim Aleksandrovich worked on the general principles of the construction and synthesis of various classes of (poly)chelate and zwitterionic compounds of hypervalent silicon formerly considered extremely exotic and difficult to obtain. Here V. A. Pestunovich established the relationships governing the mutual effect of substituents at the trigonal-bipyramidal silicon atom, features of the electronic, orbital, and stereochemical structure, their thermodynamic and stereochemical stability, and the reactivity of their molecules. He was the first to use and develop, as applied to compounds of pentacoordinated silicon and its neighbors in the subgroup, a model of three-center four-electron bonding that explains their structural and chemical uniqueness. The concept of hypervalence proposed by V. A. Pestunovich became central to the chemistry and theory of the structure of compounds containing a highly coordinated silicon, germanium, or tin atom. He was the first to model the optimum paths of intramolecular nucleophilic substitution at a tetracoordinated silicon atom by the Burgi-Dunitz method. He first studied systematically and substantiated theoretically the effect of the medium, the state of aggregation, and the temperature on the structure of silatranes and the (O–Si)-chelate and zwitterionic derivatives of pentacoordinated silicon. In conjunction with American colleagues he studied the effect of the pentacoordinated silicon atom on the stereoelectronic effects in the XSiO_3N coordination unit of silatrane molecules and the proton affinity of the endocyclic heteroatoms in their five-membered rings.

A series of previously unknown reactions and rearrangements of hypervalent molecules were discovered, and the prospect of using their enhanced reactivity in organic and heteroorganic synthesis was discovered. The experimental investigations and concepts of V. A. Pestunovich initiated rapid development of the structural chemistry of highly coordinated silicon compounds and largely determined the present-day level of theoretical concepts and experimental investigations in this field.

The researches of V. A. Pestunovich and his learners on molecular design of the organic derivatives of hypervalent elements of the silicon subgroup with concurrent coordination interaction between several donor or acceptor centers and on determination of the conditions for their stable existence and the stereodynamic features of their behavior, laid the foundation for study of the structure of novel polyheteroatomic analogs of metallatranes and donor-stabilized silenes. In particular, the possible existence of 1,1-bis[N-dimethylaminoacetimidato]silene, which is the first example of a bischelate silaethylene containing a pentacoordinated unsaturated silicon atom with the unusual square-pyramidal structure, was demonstrated.

Pestunovich was coauthor in the scientific discovery of the configurational stability of trivalent nitrogen. The results of his investigations are reflected in more than 370 scientific publications and also in three reviews and four headed chapters in monographs. His learners include 12 candidates and four doctors of chemical sciences.

Pestunovich was member of the Scientific and Specialized Councils of the A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, a member of the Expert Commission of the Russian Fundamental Research Fund and the organizing committees of many national and international conferences. He actively collaborated with the chemical companies and universities of Russia and with a series of foreign laboratories, taught as invited professor in the university of Texas (Austin) and the Israeli Ben Gurion (Negev) and Beer-Sheva universities, and played an active role in many foreign international symposia and conferences in the USA, England, Japan, and other countries. In 2002 he presented a brilliant plenary report at the 35th International Symposium on Organosilicon in Guanajuato (Mexico).

Pestunovich's scientific activity was marked by the prizes of the Mendeleev Chemical Society (1968), the Siberian Branch of the Russian Academy of Sciences (1976, 1986), the Irkutsk City Administration (for many years of creative work and a great contribution to the development of national science and the training of highly qualified scientific staff, 2004), and the medal of Labor Veterans (1988). He received a state grant of the Russian Federation for outstanding scientists (1994-2003). For research in the region of pentacoordinated silicon in 1997 he was awarded the State Prize of the Russian Federation.

Pestunovich was always open to discussion of scientific problems and ready to hear out the opinions of others, to help them with advice or deeds, and ready to collaborate.

Pestunovich was always distinguished by his capacity for work and endless devotion to science. In addition to this he had remarkable humanitarian qualities, including modesty and democracy, intellect, respect for the environment, and adherence to traditions. His distinctive features were honesty, decency, benevolence. He sincerely rejoiced in the successes of his colleagues and was able to see the positive aspects of other people's work that even the authors themselves had not noticed. This in no way prevented him from behaving critically toward any shortcomings in decisions and publications, including his own. The demands that he made on the articles, reviews, and projects issuing from his pen were very high.

Vadim Aleksandrovich Pestunovich departed from life at the peak of his talent and creative abilities. Many of his ideas and plans have remained unrealized.

The happy memories of Vadim Aleksandrovich Pestunovich will always remain with his friends, colleagues, and acquaintances.

M. G. Voronkov and B. A. Trofimov

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In the life of the Riga chemists of the Latvian Institute of Organic Synthesis Vadim played an exceptionally useful but not, perhaps, not outwardly such a striking role. He came to our institute from Gorky at the very time when conditions were being created for the introduction of the modern NMR spectrometric procedures that made it possible to establish the structure and configuration of organic molecules with a much greater degree of reliability than the previously employed spectroscopic methods. He headed the NMR group in the Laboratory of Physical Organic Chemistry and directed its work for seven years.

At the Institute in this time investigations were developing on the chemistry of aziridine, and Vadim was the first to turn his attention to features of the NMR spectra of N-aminoaziridine and related compounds. Simultaneously with the researches conducted at the Institute of Chemical Physics, Academy of Sciences of the USSR (R. G. Kostyanovsky), he established the configurational stability of the trivalent nitrogen atom in nonbridging structures at room temperature. This happened in 1968 and after some tribulations was recorded as scientific discovery No. 110. Its coauthors were S. A. Giller, A. V. Ereemeev, and also some Moscow colleagues. In due course such an assessment raised a real sensation in Riga chemists' circles, but Vadim continued to remain the same quiet, modest, and benevolent colleague who was not that much excited by the various honors.

He educated several capable students, among them Juris Popelis and Ivars Turovskis; it is desirable to mention in particular Eduard Liepinsh, now Academician of the Latvian Academy of Sciences, who subsequently worked with Nobel prize winner Kurt Wuthrich and with him completed about 15 scientific works. This provides evidence for the fact that the NMR method occupied a high position in Vadim's works at both the theoretical and the practical level, although the availability of the equipment in Riga at that time was extremely limited (60 and 90 MHz instruments), but he looked to the future and exhorted his students to do this.

It was very pleasant to be associated with Vadim, and I personally formed the most cordial and closest of relationships with him in spite of the fact that we worked in different fields but in the same laboratory.

I remember the day when he said with the greatest embarrassment that he had just decided to move from Riga to Irkutsk. He supposed that in Siberia broader possibilities would open up for him for scientific work in his favorite field. Our ties did not, however, break up, and Vadim was a special guest at the conferences and anniversaries of the laboratory that he considered his own.

All colleagues who knew and loved Vadim received the tragic news with distress and express their condolences to his relatives and friends. Early, too early we have lost a colleague of outstanding ability, a warmhearted and honest person.

J. Stradins

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THE PRINCIPAL PUBLICATIONS OF V. A. PESTUNOVICH

Discovery

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