

IN MEMORIAM



**LEONID BORISOVICH
VOLODARSKII**
(18.07.1931-25.03.2010)

With the passing of Professor Leonid Borisovich Volodarskii, the world community of chemists has suffered a heavy blow and has lost a talented organic chemist, an outstanding specialist in the chemistry of nitrogen heterocyclic compounds and stable nitroxyl radicals, purposeful and efficient person, erudite in many fields, with talent for organization.

Professor Volodarskii was born on July 18, 1931 in Moscow. He entered the D. I. Mendeleev Moscow Institute of Chemical Technology in 1949 and, in 1952, transferred to the Lensovet Leningrad Technological Institute, from which he graduated with honors in 1954. In 1959, at the invitation of Prof. N. N. Vorozhtsov, Jr., he began graduate studies at the Novosibirsk Institute of Organic Chemistry. After successful completion of his studies, Prof. Volodarskii was appointed a junior research worker at this institute. In 1963, he defended his Candidate's dissertation *Transformations of N-(1-oxyimino-1,2,3,4-tetrahydronaphthyl-2)hydroxylamine*, which he completed under the direction of Prof. V. A. Koptug, and, in 1972, he completed his doctoral dissertation *Investigation of the Chemistry of α -Hydroxylaminooximes*.

Already at the beginning of his scientific career, Professor Volodarskii laid the foundation of his work in heterocyclic chemistry by developing a synthesis for hydroxylaminooximes and showed that these compounds hold considerable promise as precursors for a broad range of heterocyclic compounds. The future of this field was so promising that a Nitrogen Compounds Group was soon founded at the Novosibirsk Institute of Organic Chemistry headed by Prof. Volodarskii. In 1980, this group was expanded into a Laboratory, which

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then gained truly worldwide renown, primarily, in recognition of work on α -hydroxylaminooximes and their derivatives, which serve in the synthesis of stable heterocyclic nitroxyl radicals derived from 3-imidazoline.

Subsequently, these species were termed Volodarskii radicals in both the Russian and world literature. In addition, the use of monooximes of α -diketones was found promising for the synthesis of various heterocyclic compounds. Original methods were developed under the leadership of Prof. Volodarskii for the synthesis of N-oxide derivatives of imidazoles pyrazine, and pyrimidine.

Professor Volodarskii combined his research with teaching and was a professor at the Department of Organic Chemistry of Novosibirsk State University. He was a brilliant lecturer with a unique style. His fanatical devotion to organic chemistry was the reason that none of his students remained unmoved. Prof. Volodarskii knew how to ignite a love for chemistry in the hearts of his students and this brought many talented young people to the Nitrogen Compounds Laboratory. He was able to form a group of like-minded chemists as devoted to organic chemistry as he himself. Many of these students went on to obtain Candidate's and Doctoral degrees, to become professors, and head laboratories. His students continue to develop the major themes in Prof. Volodarskii's research. More than ten Candidate's degrees and four chemical sciences Doctoral degrees were awarded under his direction. Prof. Volodarskii was the author of more than 300 research articles published in the leading Russian and international journals, 70 Russian Inventor's Certificates, and six foreign patents. He was an organizer and participant in many international and Russian scientific conferences.

A very important characteristic of Prof. Volodarskii was his great appreciation of everything new like promising of developments in his own scientific field and, especially, in combined areas of scientific knowledge where the results of his research were used. As a consequence, Prof. Volodarskii was able to locate investigators and interest them in using compounds synthesized in the Nitrogen Compounds Laboratory for the efficient solving of their scientific problems.

We cannot fail to recall that Professor Volodarskii was always interested in biologically active compounds and used all means for the large-scale testing of the activity of the compounds synthesized in his laboratory. When these tests proved positive the synthesis of a whole series of analogs was carried out in order to search for the optimal and most promising structures. But the major object for study by Prof. Volodarskii was undoubtedly stable nitroxyl radicals known as Volodarskii radicals. An enormous number of spin labels and probes was synthesized for molecular biology, biochemistry, and biophysics. Here and in all other cases, combined studies were carried out for a set of structures, which might be useful for solving problems in ESR spectroscopy.

As a consequence of such close and active cooperation, completely new possibilities arose for using nitroxyl radicals in biophysics, for example, a pH-sensitive spin probe, spin labels for biological substrates, whose action is based on the thiol-disulfide replacement. We should note that the use of pH-sensitive probes opened new horizons as in the spin probe method in general. This field is being actively developed by students of Prof. Volodarskii and their biophysics colleagues in Russia and other countries.

The contribution of Professor Volodarskii and his laboratory has undoubtedly been very important in the chemistry of coordination compounds with nitroxyl radicals as paramagnetic ligands. All this work started with the use of nitroxyl radicals capable of forming chelate complexes with metal ions in the development of a new analytical method for the quantitative determination of ions of various metals using ESR spectroscopy. A whole series of analytical procedures was developed.

Since the complexes with paramagnetic metals themselves at that time held considerable theoretical interest as multispin systems consisting of several different paramagnetic sites an enormous number of complexes with different metals were synthesized and characterized using Volodarskii radicals. For some of these complexes he discovered low-temperature phase transition to a magnetic state when spin ordering occurred in the crystal structure such that the entire crystalline phase became a magnetic material while remaining a dielectric. A new field involving the synthesis and study of molecular magnets has been created and is presently developing from these pioneering studies.

Professor Volodarskii sought the practical application of his discoveries for solving industrial problems, for example, furthering petroleum output, for which tracers were developed. These compounds are nitroxyl radical precursors that are stable under conditions of a petroleum-bearing stratum and capable of undergoing oxidation directly in the tube of a portable ESR spectrometer right beside an oil rig.

All this does not exhaust the range of Professor Volodarskii's scientific interests characterizing him as a Scientist with very broad viewpoints and possessing truly encyclopedic knowledge. His contributions were recognized when he was awarded the Russian Federation State Prize in 1994 along with his students and colleagues. In 2002, he was awarded the prestigious Voevodskii Prize for his research on nitroxyl radicals.

Professor Volodarskii was a very committed individual with a burning interest in everything new in science and the development of Russian science. His straightforward nature, unusual temperament, and charisma of a real scientist, teacher, and leader attracted many talented scientists, which led to a huge scientific heritage left by him. Professor Volodarskii's bright memory will live in the hearts of his students, colleagues, and all those who knew him, encouraging them to love life, to approach Science with excitement, and retain interest in everything new throughout life. He was a man devoted to science and generous in sharing his knowledge.

Professor Volodarskii was seriously ill during the past few years. His resilient nature, willingness to hide his own problems in essentially dictated his way of life. Up until his last days, he retained his lucidity and regretted leaving some of his ideas unrealized. The life of Prof. Volodarskii left a great mark. His works remain as do his grateful students.

Professor Volodarskii was buried in the United States at the Arlington Cemetery in Atlanta, Georgia. His is a bright memory.

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