

ANNIVERSARIES AND DATES



Sixty Fifth Birthday of ALEKSANDR FEDOROVICH POZHARSKII

On December 8, 2003 the celebrated heterocyclic chemist Prof. Aleksandr Fedorovich Pozharskii, member of the Editorial board of the *Journal of Heterocyclic Compounds*, will be 65 years old. He is an outstanding member of the Rostov school of organic chemists and acquitted himself well in the 1960's. The school was founded by Prof. A. M. Simonov – a native of Moscow who moved to Rostov-on-Don in 1957. In 1958 turned A. F. Pozharskii, a third-year student at the Chemical Faculty of Rostov University, turned to him for a subject for scientific research. Pozharskii's scientific researches during his student years culminated in a paper in the *Journal of General Chemistry* and a major project for entry to post-graduate work in 1961. After only two years Pozharskii presented a candidate's dissertation on "Investigation in the region of N-substituted benzimidazoles." In 1972, already an associate professor at the chemistry department of Rostov State University, he presented a doctoral dissertation on the subject on "Investigation in the region of

N-heteroaromatic amines." In 1975 he was awarded the title of professor. Since 1981 Prof. Pozharskii has headed the Department of organic chemistry at Rostov State University.

An important role in the subsequent scientific and pedagogical activity of Pozharskii was played by his practical training in England in 1968-1969. He worked in the laboratory of Prof. A. R. Katritzky, and their friendship and creative collaboration have continued to this day.

Pozharskii devoted the period between 1958 and 1974 to a fundamental study of the Chichibabin reaction and the N-anions of heteroaromatic amines. The amination and hydroxylation of a series of condensed azines and azoles were realized for the first time, the acid autocatalysis of this reaction, and the dependence of the ease of its occurrence on the basicity, and the "*ortho*-dimethoxy effect" were discovered. By measuring the reaction rate and investigating the side processes it was possible to introduce substantial refinements into the Ziegler mechanism of the Chichibabin reaction. Methods were developed for generation of the N-anions of hetaryl amines, and this made the dialkylamino derivatives of nitrogen heterocycles accessible. The autooxidation of the polyanions of 2-aminoimidazoles, leading to the formation of 2,2'-azo- and 2-nitroimidazoles, was discovered.

Pozharskii's comprehensive investigations into the chemistry and physical chemistry of perimidines have become renowned. It was shown that they exhibit simultaneously the characteristics of π -excessive and π -deficient hetero systems, reacting readily both with nucleophilic and with electrophilic reagents. A series of unusual transformations in this heterocycle were discovered: simple nitration by nitrous acid leading right up to the production of the trinitro derivatives, the recyclization of 1-R-3-arylperimidinium salts, the disproportionation of 1,3-dialkylperimidinium cations in an alkaline medium and of 1-R-perimidines by the action of dilithiobenzophenone, hydride transfer from 1,3-dimethyl-2,3-dihydroperimidines to 1,3,5-trinitrobenzene, etc. A series of new polynuclear heterocyclic systems, including 1,3-diazopyrenes, were synthesized from the obtained perimidine derivatives.

In the 1980's Pozharskii's main scientific interests were focused on N-aminoazoles: Methods were developed for their synthesis; the key physicochemical characteristics and the reactivity of the amino group were investigated. Important results were obtained during study of the oxidation of N-aminoazoles; the natural antibiotics reumycin and fervenulin and also isofervenulin were synthesized; various derivatives of benzo-1,2,4-triazine and uracil were obtained.

A series of extremely interesting discoveries at the theoretical and synthetic level "awaited" Pozharskii during a study of purines, pyrimidines, and condensed systems based on them; they included some important results on oxidative amination, the first tandem nucleophilic substitution of two hydrogen atoms at once in a series of neutral heterocycles, and a new annelation of a pyrrole ring to an azine ring. A fine and elegant reverse diazadiene synthesis made it possible to change from triazinouracils to pyridouracils. Two methods were developed for the synthesis of the natural antitumor antibiotic reumycin and its analogs.

However, Pozharskii considered the most successful direction in the work of his department in the 1990's and at the beginning of the 21st century to be the chemistry of "proton sponges". Numerous methods were developed for their synthesis and included the so-called "double proton sponges". Methods for the selective introduction of all kinds of substituents were developed on the basis of electrophilic substitution reactions and metal-halogen exchange, and the first hexasubstituted "proton sponges" were synthesized.

Initially the aim of the investigation was to study the effect of the molecular structure of these compounds on their basicity. Analysis of the spectral characteristics of a large series of proton sponges and their cations made it possible to work out a method for assessing the degree of asymmetry of the intramolecular hydrogen bond in the latter. Factors affecting their basicity were established, and the first cases of the *in/out* isomerism of dimethylamino groups were identified. Subsequently focus of the investigations was shifted to the chemistry of the proton sponge. In the case of 4,5-bis(dimethylamino)-1-naphthylmethyl carbocation and its analogs a new direction in the chemistry of naphthalene was discovered – the chemistry of resonance-stabilized naphthylmethyl carbocations. Methods were developed for their generation, and the previously unknown

cyclodimerization of these cations, leading in particular to the formation of spiro compounds with a cyclohexadienone fragment, was discovered.

Even from the student's bench Pozharskii was attracted to the theoretical aspects of organic chemistry. His work is characterized by profound comprehension of the nature of events, widespread application of computational and physical methods of investigation, and scrupulous analysis of the results. It is not surprising, therefore, that his contribution to theoretical organic chemistry has been momentous. He developed and quantitatively expanded the concept of the π excess and π deficiency put forward in the middle of the fifties by Albert. The concept of π -amphoteric heterocycles was introduced, and the first system of such a type was discovered in perimidine. A structural index of heteroaromaticity, based on a quantitative assessment of the degree of leveling of the orders of the cyclic bonds in the molecules of heterocycles, was proposed. In the case of certain 2-trifluoromethylperimidine derivatives the first representatives of 1,3-diazoles with greatly hindered annular prototropy were discovered. It was shown that the susceptibility of 2-aminoperimidines to change into the imino form is one of the strongest in the heteroaromatic series and is an order of magnitude stronger than in 2-aminoimidazoles; this fact is explained by the reduced aromaticity of the perimidines.

Professor Pozharskii is the author of 410 publications, including six books, 33 reviews, 36 author's certificates for inventions, and 277 scientific papers in journals. The most important of his books is the monograph entitled "Theoretical Principles of the Chemistry of Heterocycles," and the most prestigious is the "Handbook of Heterocyclic Chemistry" (second edition in coauthorship with Prof. A. R. Katritzky). The appendix of the present article contains references to some of his most significant works.

One doctoral and 23 candidate's dissertations have been completed and defended under Pozharskii's leadership. Aleksandr Pozharskii has been somewhat profligate with regard to students; after graduation they have departed in various directions among the cities and towns, but he has never suffered from a lack of youthful talent.

On the eve of his birthday Aleksandr Fedorovich still has a profusion of new ideas and thoughts. He loves to cite Prof. Katritzky: "Take your own decision!" It remains only to wish him good health; everything else needed for the realization of his plans he has created for himself.

I. V. Borovlev

THE MOST IMPORTANT PUBLICATIONS OF A. F. POZHARSKII

Books, Reviews

1. A. F. Pozharskii and A. M. Simonov, *Chichibabin Amination of Heterocycles* [in Russian], Izd. RGU, Rostov-on-Don (1971), 133 p.
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