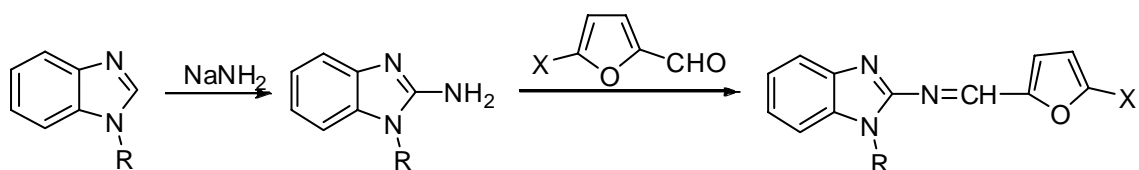


Professor Alexander F. Pozharskii

A Tribute



Alexander F. Pozharskii was born in Rostov-on-Don on December 8, 1938. He performed his first research work (under the supervision of Professor A.M.Simonov) as a student at Rostov State University. The research dealt with benzimidazole chemistry and included the preparation of a series of 1-R-benzimidazoles, their sodamide amination and subsequent synthesis of 2-furfurylideneaminobenzimidazoles which were then tested for antibacterial activity (Scheme 1).



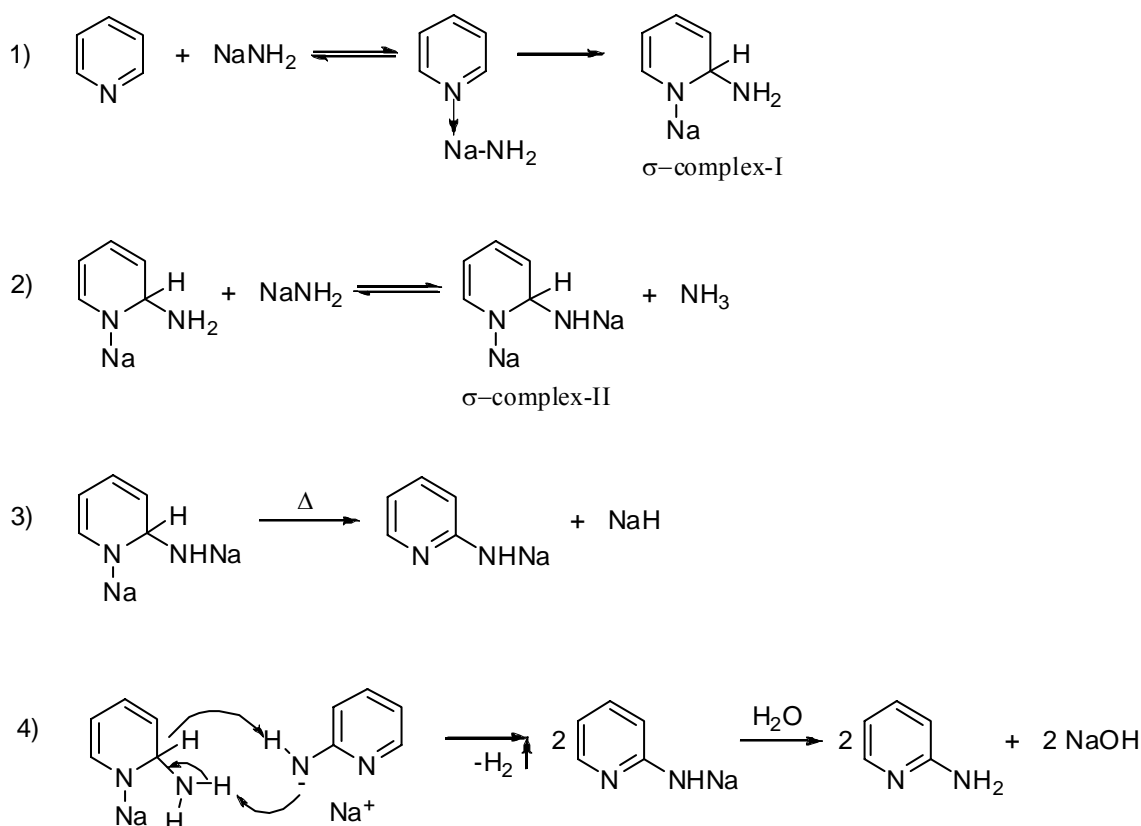
R=Pr, *i*-Pr, Bu, *tert*-Bu, C₆H₁₁, Ph etc.
X= Cl, Br, I, NO₂

Scheme 1

After graduating in 1961 he was recommended by the Faculty Scientific Council to continue research as a postgraduate student. In 1963 Alexander was awarded his Ph.D. degree and in 1964 took a position as assistant professor. In 1968-1969 he was a postdoctoral fellow in Professor A.R. Katritzky's laboratory in the University of East Anglia where he studied the application of physical methods in organic chemistry. In 1972 he was awarded a Doctor of Science degree and in 1975 he was appointed full professor at Rostov University. From 1981 and until the present Prof. Pozharskii has served as head of the department of organic chemistry at Rostov University (Southern Federal University from 2006). He was a visiting professor at the Slovak Technical University, Antwerpen, Salford, Vilnius, Wroclaw, and Szczecin universities, the Institute of Organic Synthesis of the Latvian Academy of Sciences and the Institute of Organic Chemistry of the Ukrainian Academy of Sciences. Prof. A. F. Pozharskii's research interests include heterocyclic and naphthalene chemistry, strong organic bases ("proton sponges") and theoretical organic chemistry. His research interests also include the field of surfactants and biologically active heterocyclic compounds.

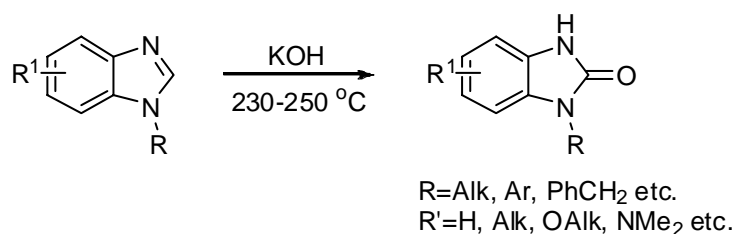
The systematic scientific carrier of Alexander began from the investigation into the classical (heterogeneous) version of the Chichibabin reaction which does not require the use of an external oxidant. For the first time amination of perimidines, benzoquinolines, numerous benzimidazole derivatives and several other condensed azines and azoles was achieved and various aspects of the kinetics of the reaction, including the relative activity of nitrogen heterocycles towards sodium amide were studied successfully. The suggested mechanism for the heterogeneous

Chichibabin reaction that explained its autocatalytic character included the formation of anionic and dianionic σ -complexes (Scheme 2).



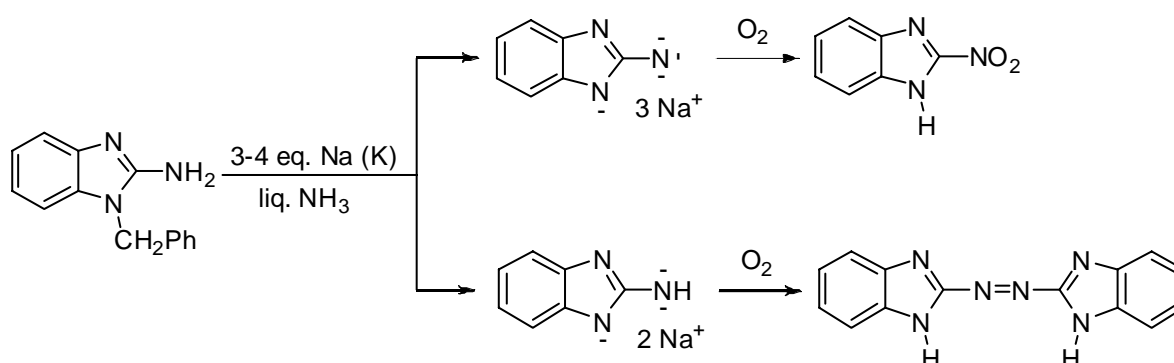
Scheme 2

An oxygen analogue of the Chichibabin reaction developed by Prof. Pozharskii involved direct hydroxylation of 1-substituted derivatives of perimidine, benzimidazole, naphtho[1,2-d]- and naphtho[2,3-d]imidazoles with powdered potassium or sodium hydroxide (Scheme 3). This method is recognized as the best approach to 1-R- imidazolones and perimidones.

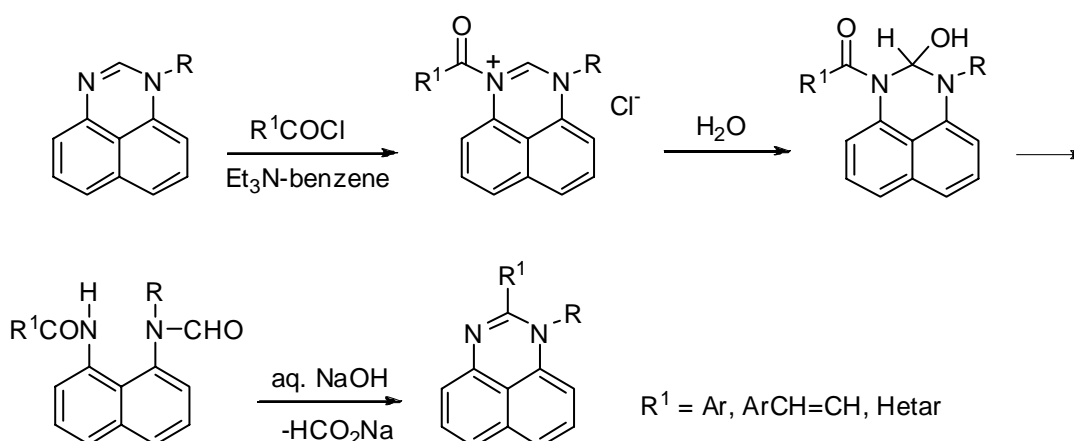


Scheme 3

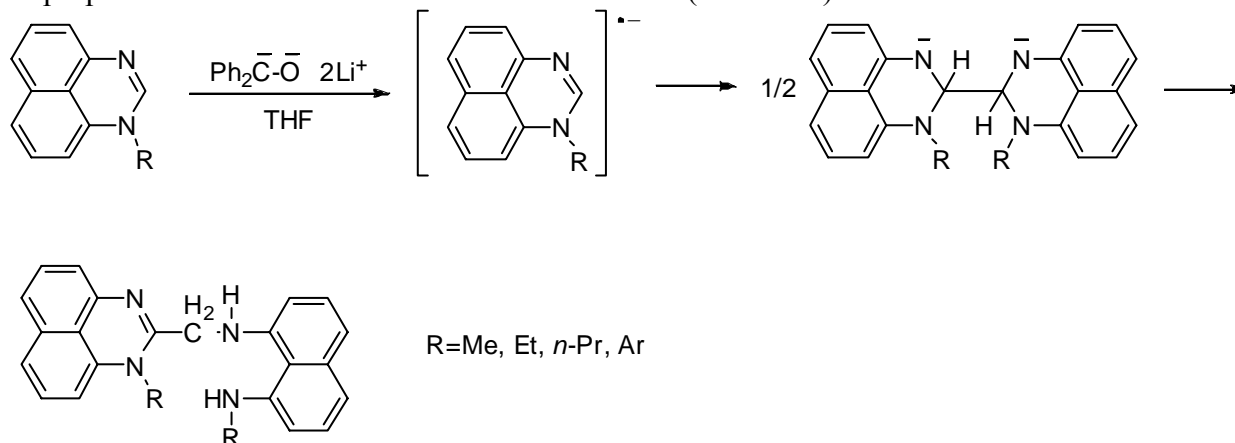
In an attempt to prepare the unsubstituted 2-aminobenzimidazole by debenylation of 1-benzylbenzimidazole with sodium or potassium in liquid ammonia Prof. Pozharskii unexpectedly observed the formation of 2-nitro- (a close analogue of the natural antibiotic azomicine) and 2,2'-azobenzimidazoles in quantitative yield (Scheme 4). This transformation represents an example of an extremely easy oxidation of an aromatic amino group to a nitro group. The reaction was later extended to other 1-R-2-amino-benzimidazoles and 2-aminonaphthoimidazoles.

**Scheme 4**

By studying the π -amphoteric heterocyclic system of perimidines Prof. Pozharskii demonstrated that these compounds are not only prone to the amination and hydroxylation reactions occurring at position 2, but also readily react with many electrophiles that substitute hydrogen atoms of the naphthalene moiety. Thus, unlike most of the azaheterocyclic perimidines, they enter into Friedel-Crafts reactions and are susceptible to a mild nitration when treated with NaNO₂-AcOH. Starting from perimidine derivatives, the synthesis of many previously unknown heterocyclic systems, for instance 1,3-diazapyrenes, was achieved. A useful reaction discovered by Prof. Pozharskii in the perimidine series concerns the recyclization *in situ* of 1-R-3-aryloperimidinium salts (Scheme 5).

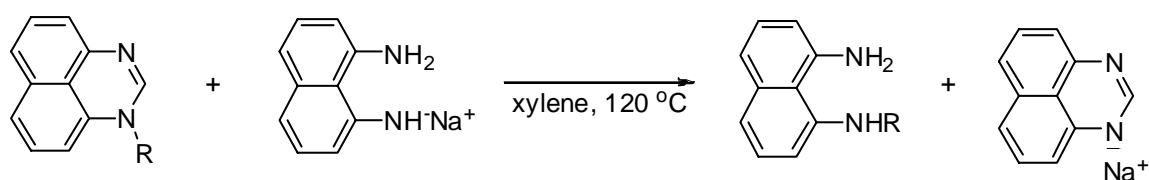
**Scheme 5**

Another new reaction occurring by treatment of 1-R-perimidines with dilithium benzophenone involves 2,2'-dimerization with subsequent oxidative-reductive disproportionation of the dianion dimer intermediate (Scheme 6).

**Scheme 6**

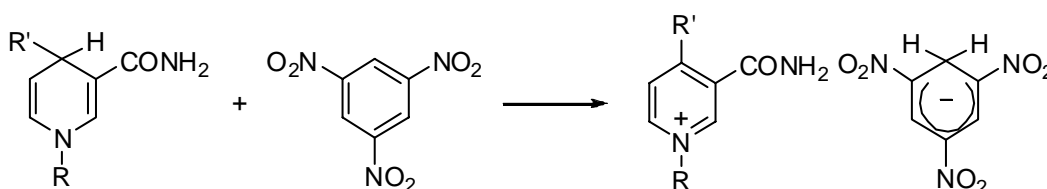
Using 1-R-perimidines as the starting material Prof. Pozharskii prepared various N-substituted 1,8-diaminonaphthalenes. It was shown that the anion of 1,8-diaminonaphthalene is

able to substitute a μ -CH fragment of 1-R-perimidines to give less accessible mono-N-substituted 1,8-diaminonaphthalenes (Scheme 7).



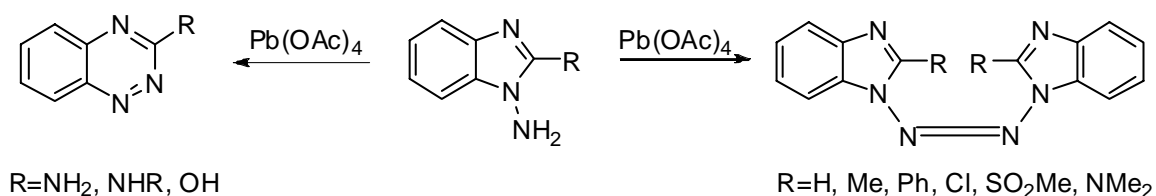
Scheme 7

Hydride transfer from 1,3-dimethyl-2,3-dihydroperimidines to 1,3,5-trinitrobenzene has been shown to result in the formation of 1,3-dialkylperimidinium salts. The reaction has been extended to the synthesis of dihydroderivatives of other heterocycles, e.g. 1,4-dihydropyridines and coenzyme NAD-H (Scheme 8).



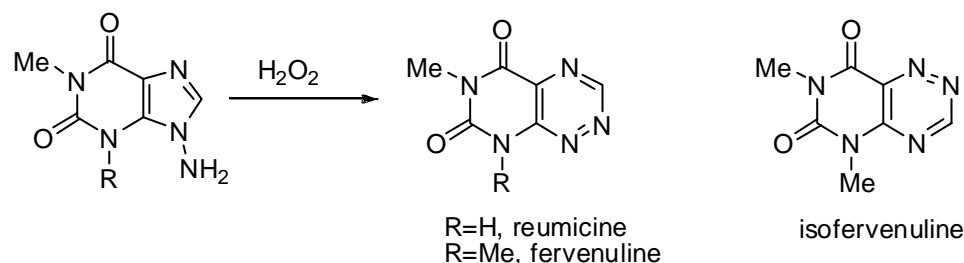
Scheme 8

A significant contribution was made by Prof. Pozharskii to the chemistry of N-aminoazoles. A wide series of N-aminobenzimidazoles, indazoles, purines, perimidines, triazoles were prepared by direct amination of NH-azoles or via cyclization and functionalization reactions. Through an analysis of the molecular structure and key physical chemical parameters of N-aminoazoles he reached the conclusion that the origin of the electronic interaction between the azole ring and the N-amino group was almost purely inductive in character. For N-aminobenzimidazoles, two different types of reactivity were characterized. Whereas 1-aminobenzimidazoles form 1,1'-azobenzimidazoles, their 2-amino derivatives produce 3-amino- and 3-hydroxybenzo-1,2,4-triazines (Scheme 9).



Scheme 9

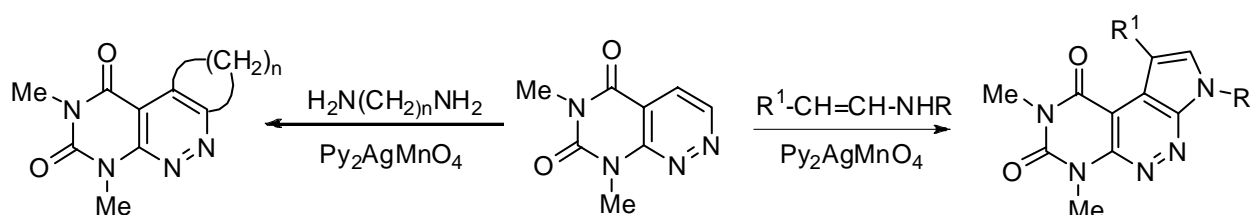
It was found that N-amino-2-azidoimidazoles undergo thermal transformation with a loss of dinitrogen to form 3-amino-1,2,4-triazines. By oxidation of 7- and 9-aminoxanthines natural antibiotics reumicine and fervenuline were obtained as well as preparatively useful isofervenuline (Scheme 10).



Scheme 10

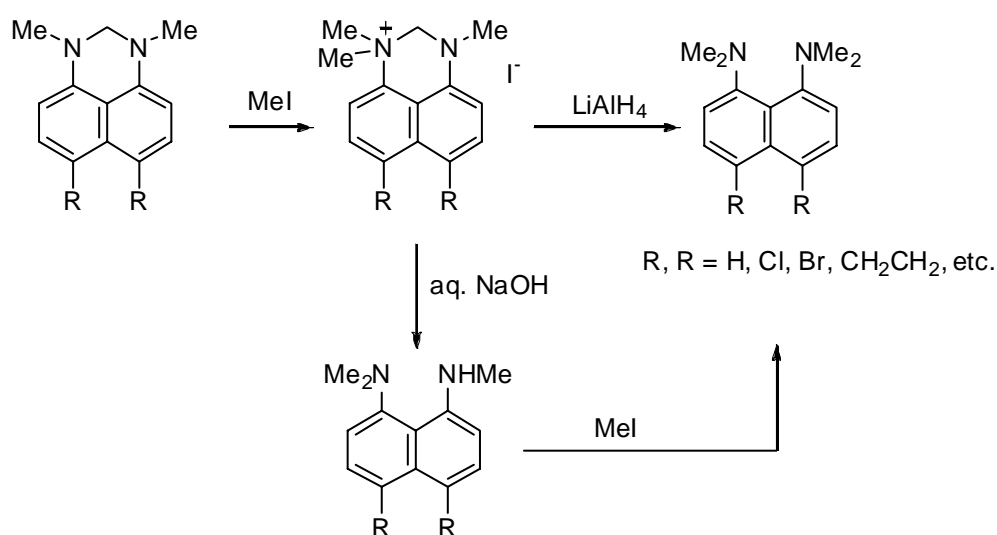
For the first time the N-amino group was employed as a convenient protecting function in the preparation of less accessible derivatives of azoles and xanthines. By treatment of N-alkylaminoazoles with nitrous acid their N-nitrosoderivatives were isolated and described for the first time. It was also shown that these compounds exist as mixtures of *E*- and *Z*-forms.

A significant part of the activity of Prof. Pozharskii and his group was devoted to the study of the chemistry of heterocyclic systems containing condensed uracil and azine rings. In the 1980s it was found that isofervenules readily undergo [4+2]-cycloaddition reactions when treated with alkylvinyl ethers, enamines or even diethyl- or triethylamine producing derivatives of pyrido[2,3-*d*]pyrimidine-2,4-dione. In a series of papers published together with Dr. Anna Gulevskaya, Prof. Pozharskii described oxidative S_N^H amination and alkylation of azinouracils and the first reactions of tandem substitution of two hydrogen atoms in the azine ring leading to annulation of pyrrole, imidazole, imidazoline and other heterocyclic rings (Scheme 11).



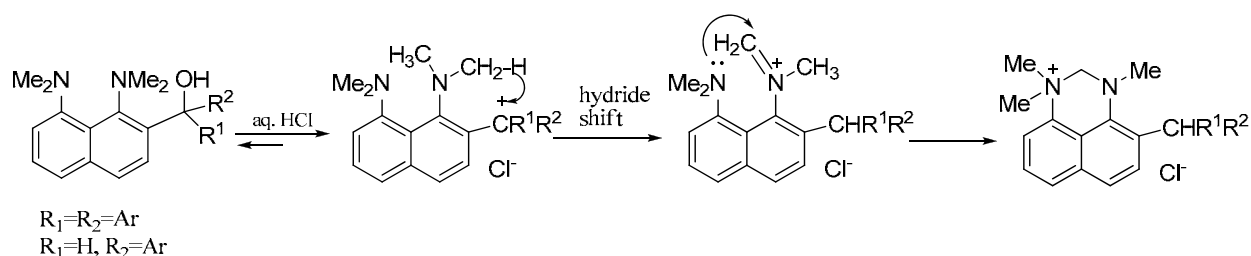
Scheme 11

During the past decade, the scientific interests of Prof. Pozharskii have been primarily concerned with the investigation into naphthalene proton sponges. Novel approaches have been developed for the preparation of these compounds. In one of them 2,3-dihydroperimidinium salts were employed as starting materials (Scheme 12). In another approach, octafluoronaphthalene was subjected to the action of lithium dialkylamides to obtain earlier unknown hexa- and heptakis(dialkylamino)naphthalenes. Proton sponges of this new type, e.g. acenaphthene- and acenaphthylene sponges were prepared and rearrangements of some of these were accompanied by drastic basicity changes.

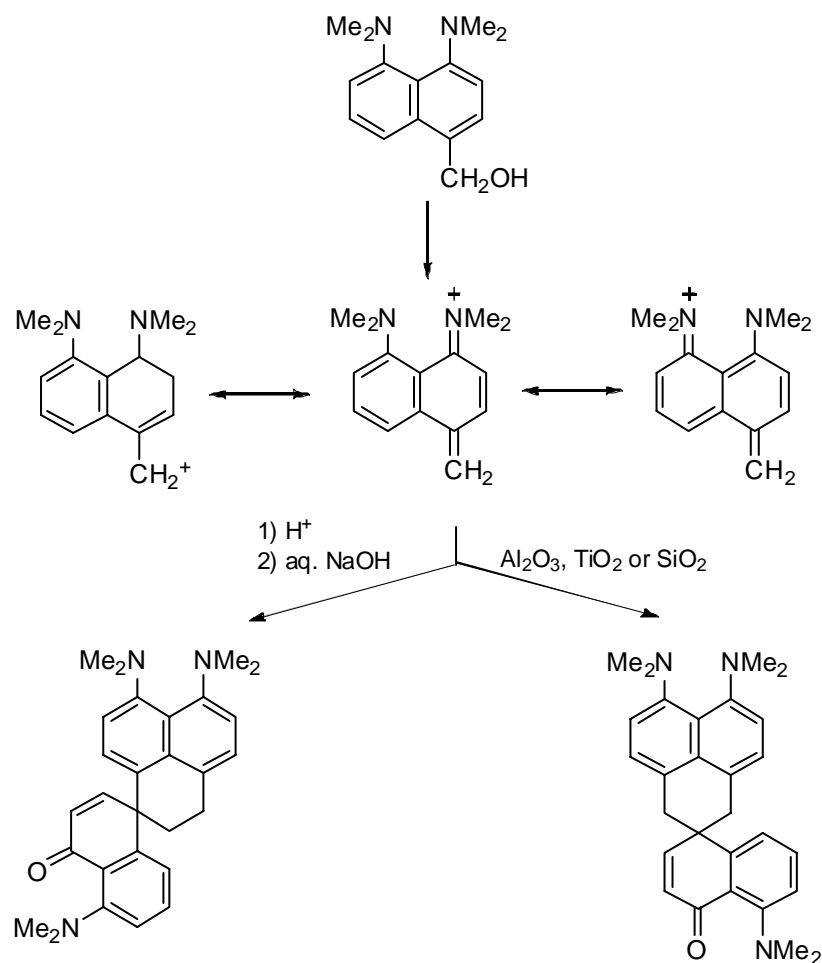


Scheme 12

The Pozharskii group has pioneered studies of proton sponge reactivity. Contrary to expectations, it was demonstrated that proton sponges possess surprisingly high C-nucleophilicity. Many reactions of these compounds are not typical for naphthalenes and arenes as illustrated by the spectacular behaviour of proton sponge-based naphthylmethyl carbocations (see for example Scheme 13, 14).

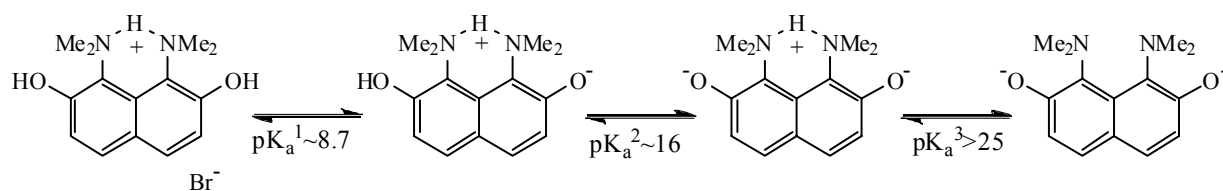


Scheme 13



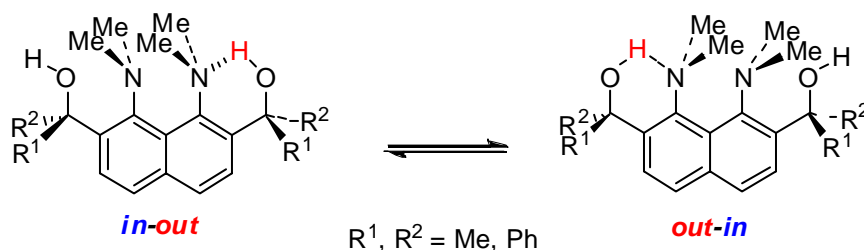
Scheme 14

A preparative method developed by Prof. Pozharskii and his co-workers for selective *ortho*-dihalogenation of proton sponges opened a way to the synthesis of their 2-substituted and 2,7-disubstituted derivatives. The investigation of the properties of these compounds elucidated the nature of the so-called “buttressing effect”. It was demonstrated that there is no dependence between the bulkiness of the *ortho*-substituents and the pK_a of the compounds. At the same time, the proton sponge basicity was shown to increase with the enhancement of the electron donor ability of *ortho*-substituents. Based on this observation it was found that the dinaphtholate of 2,7-dihydroxy-1,8-bis(dimethylamino)naphthalene possesses a basicity comparable with that of amide- and hydride ions ($pK_a > 27$) (Scheme 15). At present this species seems to be the strongest arylamine nitrogen base.



Scheme 15

A number of the so-called double proton sponges as well as enantiomerically pure chiral proton sponges were also prepared. Basicity, molecular structure and spectral characteristics of a large number of proton sponges were studied. A convenient NMR-based procedure for quantitative evaluation of asymmetry of the intramolecular hydrogen bond in proton sponge cations was advanced. A phenomenon of in/out-isomerism of the NMe₂ groups was discovered and first representatives of proton sponges existing in non-conventional in/out-form were obtained and studied. For tertiary 2,7-dialcohols, the superimposed equilibrating in/out-out/in nitrogen invertomers were observed in solution (Scheme 16).



Scheme 16

Prof. Pozharskii paid special attention to theoretical organic chemistry. A chapter in his monograph “Theoretical Principles of Heterocyclic Chemistry” is devoted to the detailed analysis of the concept of π -excessive and π -deficient heteroaromatic compounds that was introduced by A. Albert. New definitions of “ π -amphoteric heterocycles”, total and local π -excess (π -deficiency), π -balance helped to create a clearer classification of heterocyclic systems. In 1985, Prof. Pozharskii suggested the use of a structural index of heteroaromaticity, $\Delta\bar{N}$, that evaluates the degree of alternation in bond orders of all ring bonds. A number of papers published by Prof. Pozharskii are concerned with the problem of tautomerism of heterocyclic compounds. He studied a prototropy of 2-aminoderivatives of perimidine, imidazole and condensed imidazole systems.

Professor Pozharskii has published 7 books, almost 400 scientific papers, 35 reviews and chapters in collective monographs. He is a member of Editorial Boards of three scientific journals. He was a plenary or invited lecturer at a number of conferences on heterocyclic and organic chemistry (Bratislava, 1982, Antwerpen, 2004, Moscow, 2005, Novosibirsk, 1979, 1986, 2007, Ekaterinburg, 1985). He supervised more than 30 PhD students and was elected as Soros professor.

On the occasion of his 70th birthday, I wish Alexander many fruitful years ahead.

Vladimir Minkin

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