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Tribute

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Professor Oleg Alekseevich Rakitin

A Tribute

This commemorative issue of Arkivoc is dedicated to Professor Oleg A. Rakitin on the occasion of his 65th birthday, to acknowledge his contribution to heterocyclic chemistry

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Oleg Alekseevich Rakitin was born on August 5th, 1952 in Moscow, Russia. In 1974 he graduated from the M. V. Lomonosov Moscow State University with a Diploma in Chemistry. Oleg then began a 40 year research career at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. Starting as a Junior Researcher (1974-1982), Oleg obtained his PhD in 1980 working under the supervision of the late Professor Lenor I. Khmelnitsky. Subsequently, working as a Senior Researcher (1982-1994) Oleg obtained his Doctor of Science (DSc) degree in 1992. From 1994-1995 Oleg was a Principal Researcher and in 1996 he became the Head of the Laboratory of Polysulfur-Nitrogen Heterocycles at the N. D. Zelinsky Institute. In 2009 Oleg attained the title of Professor.

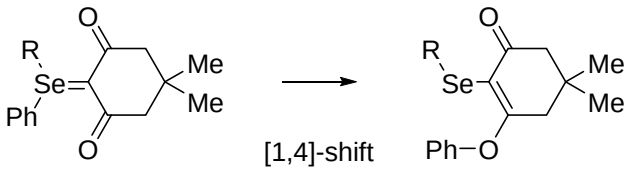
While Oleg's research career was primarily based at the N. D. Zelinsky Institute, he also worked in several foreign laboratories for short periods. In 1990 Oleg worked for 3 months in the laboratory of Professor Mukund Gurjar at the Indian Institute of Chemical Technology, in Hyderabad. Shortly afterwards, in 1992 Oleg began a productive three-way collaboration with Professor Charles W. Rees (Imperial College London) and Professor Tomás Torroba (Universidad de Extremadura, Cáceres and later Universidad de Burgos, Burgos) that led to regular visits to laboratories in both England and Spain. During these visits, Oleg took full advantage of the available research facilities and worked very actively at the bench. Furthermore, he became multilingual learning to speak both English and Spanish fluently. It was in London during these visits that I, as a PhD student in the Rees group, first met Oleg, where I quickly discovered him to be an open and friendly individual with a robust and enthusiastic work ethic.

Oleg's research discoveries have been published in over 150 journal articles, more than 35 scientific reports and his name appears as co-inventor on more than 20 patents. In addition, Oleg has authored over 20 authoritative reviews either as book chapters or journal review articles. To date, 10 students have graduated with PhDs and one with a Diploma in Chemistry from Oleg's research team. Oleg also received several awards for his research activities which include 1st (1984, 1991 & 2008) and 2nd (2000, 2012 & 2014) Prizes for the best scientific work in the N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences. He also received multiple fellowships for the support of his research activities including The Royal Society Kapitza Fellowship (1992), The Royal Society of Chemistry Journals Grant for International Authors (1997, 2000 & 2004), and the Royal Society Joint Projects award (1993, 1999 & 2002). Furthermore, he was awarded the status of Fellow of the Royal Society of Chemistry in 1999. Oleg is also a member of a number of editorial boards including, *Butlerov Communications*, *Universal Journal of Chemistry* and *Cogent Chemistry*. In 1999 Oleg became a Member of Scientific Council of the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences.

Research Interests

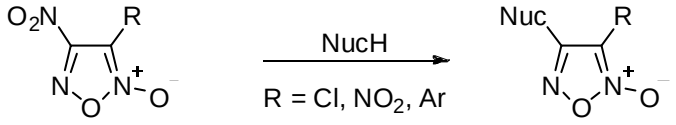
Oleg's scientific interests include acyclic and cyclic heteroatom chemistry with a particular emphasis on the synthesis and chemistry of N,O-, N,S- and polysulfur-heterocycles. While the primary goal of Oleg's chemistry has been to discover new synthetic methods, he also worked closely with collaborators to exploit potential applications in both the biological[1,2] and materials sciences.[3,4]

Oleg's very first publication (1975) was the study of a tentative 1,4-sigmatropic rearrangement of selenonium ylides (Scheme 1)[5] and it is presumably from here that his interest in heteroatom chemistry was born.



Scheme 1. A reaction from Oleg's very first journal publication from 1975.[5]

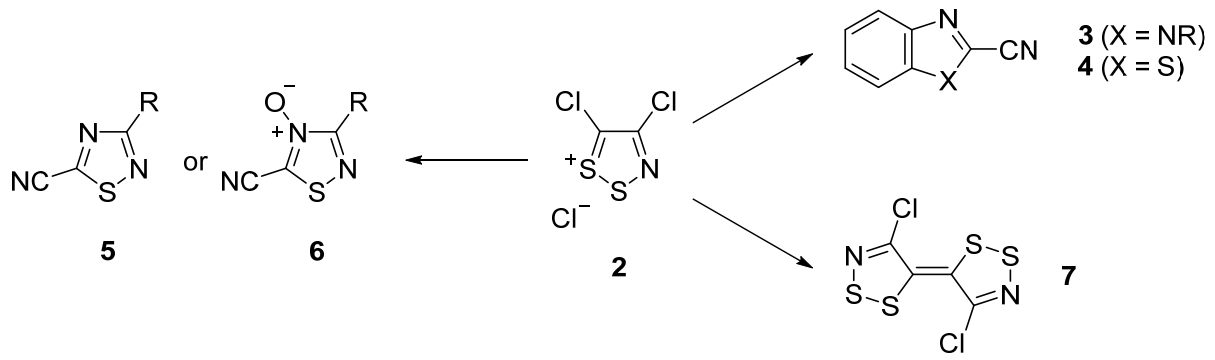
Despite this early baptism in selenium chemistry Oleg spent the next phase of his research career focusing on the synthesis and chemistry of 1,2,5-oxadiazoles (aka furazans)[6] and their N-oxides **1** (aka furoxans), that were typically prepared *via* oxidation of glyoximes,[7,8] or from nitrile oxides.[9,10] A highlight was the chemo- and regioselective nucleophilic displacement of the 4-nitro group from the furoxan **1** (Scheme 2).[8,11,12] Oleg did not hesitate to use less common strategies, such as the use of phosphoranimines[13] and sulfilimines[14] to introduce amino groups that could later be converted to nitroso,[15] nitro[15] and azo[6,16] functionalities.



1

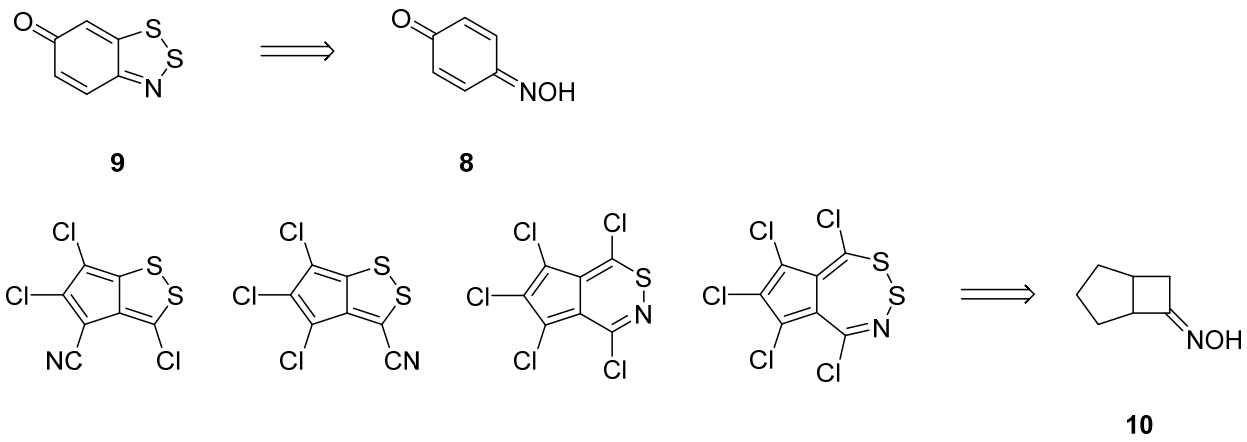
Scheme 2. Nucleophilic substitution behavior of 4-nitro-1,2,5-oxadiazole 2-oxides **1**.

From 1992 Oleg expanded his heterocyclic chemistry "footprint" to cover S- and N,S-heterocycles. Common themes between his early work and this later phase involved the use of oximes as starting materials and not surprisingly, the formation of heterocyclic N-oxides. This transition from O- to S-heterocyclic chemistry was facilitated by a productive collaboration with Prof. Charles W. Rees and Prof. Tomás Torroba. The period led to exciting discoveries of new heterocycles and ring transformations. The work focused on three strategies: i) an investigation of 4,5-dichloro-1,2,3-dithiazolium chloride **2** (Appel salt);[17-19] ii) a study of the chemistry of cyclic oximes on treatment with sulfur chlorides,[20,21] and iii) a study of the highly reactive DABCO/S_2Cl_2 sulfurization protocol. Appel salt **2** highlights include high yielding routes to benzimidazoles **3**,[17] benzothiazoles **4**,[18] 1,2,4-thiadiazoles **5** and **6**,[19] and 5,5'-bi(1,2,3-dithiazolylidene) **7**[22] (Scheme 3). Of particular note is that Oleg expanded his chemistry of Appel salt **2** to include the structurally related 4-alkyl/aryl-5-chloro-1,2,3-dithiazolium chlorides[22,23] and the 3,4,5-tri-chloro-1,2-dithiolium chloride (aka Boberg's salt).[24]



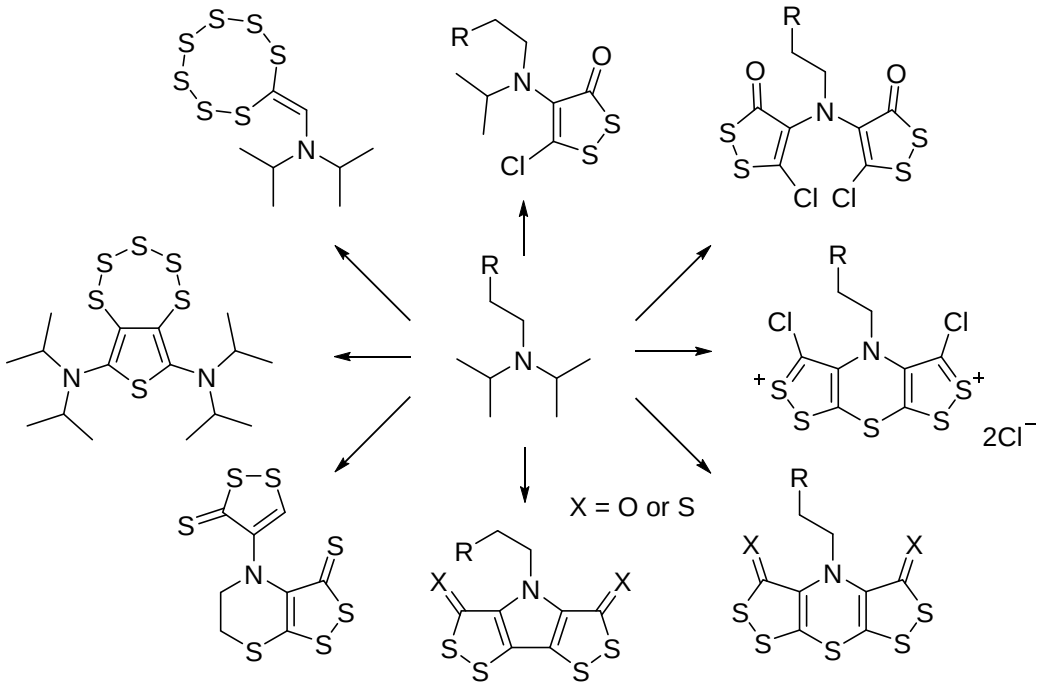
Scheme 3. Selected transformations of Appel salt **2**.[17-19]

During this period Oleg unraveled the complex behavior of cyclic oximes on treatment with sulfur chlorides.[20,21] While the 1,4-benzoquinone monooximes **8** gave the anticipated 6*H*-benzo[*d*][1,2,3]dithiazol-6-ones **9**[21] the reactions of bicyclo[3.2.0]heptan-6-one oximes **10**[20] were more complex and afforded an exciting array of fused 1,2-dithiole**s,** 1,2-thiazines and 1,2,3-dithiazepins (Scheme 4).



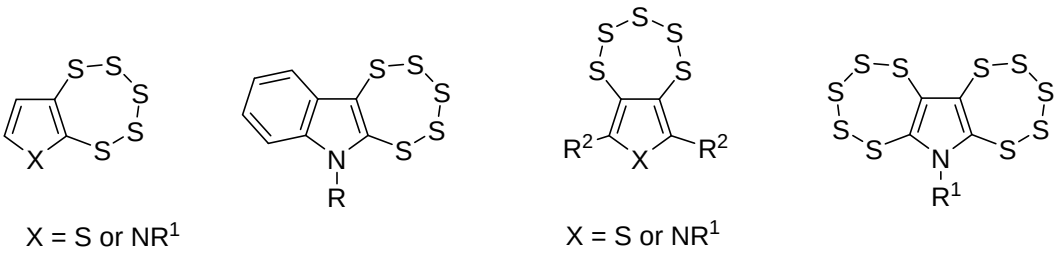
Scheme 4. Selected transformations of cyclic oximes **8** and **10** on treatment with S_2Cl_2.

During sulfurization studies of 1,4-benzoquinones monooximes **8**, Oleg and coworkers serendipitously discovered the mindboggling synthesis of an array of complex sulfur rich heterocycles. Treatment of comparatively simple starting materials such as trialkylamines[25-27] or dialkylsulfides[28] with the powerful DABCO/S_2Cl_2 protocol gave fused 1,2-ditholes, 1,4-thiazines and polysufur systems such as 1,2,3,4,5-pentathiepin and heptathiocanes (Scheme 5).



Scheme 5. Selected reaction products derived from the treatment of *N,N*-diisopropylethylamines with DABCO and S_2Cl_2.

Oleg's fascination with the 1,2,3,4,5-pentathiepin system led to the development of new fused analogues. By using the DABCO/S_2Cl_2 sufurization protocol Oleg was able to carry out one pot transformations of aromatic heterocycles (*e.g.*, pyrroles and indoles) and also fully saturated heterocycles (*e.g.*, pyrrolidines and tetrahydrothiophenes) into pentathiepins often in useful yields (Scheme 6).[3,29,30]



Scheme 6. Selected fused 1,2,3,4,5-pentathiepin structures from Oleg's chemistry.

More recently, Oleg has investigated the formal exchange of chalcogens in fused 1,2,5-heterodiazoles, exemplified by the conversion of fused 1,2,5-oxadiazoles and 1,2,5-seleno-diazoles into 1,2,5-thiadiazoles,[31,32] and the interconversion of 1,2,5-thiadiazoles and 1,2,5-seleno-diazoles.[4,32,33] In collaboration with colleagues Oleg has demonstrated these heterocycles to be useful as electron deficient precursors for the preparation of persistent radical anions.[4]

While most of Oleg's time is actively spent on his chemistry, writing and refereeing scientific papers, he does find time for additional interests which include listening to music (light and rock), watching sport

(football, basketball, snooker), mushroom hunting and spending leisure time in his dacha with his wife Tatiana of over 30 years, his two sons, Alexey and Dmitry, and his granddaughter Alexandra.

On behalf of the heterocyclic community, I thank Oleg for his exciting contributions and, looking forward, wish him continued success in both his chemistry and social activities.

Panayiotis A. Koutentis
University of Cyprus

Selected Publications

1. Konstantinova, L. S.; Bol'shakov, O. I.; Obruchnikova, N. V.; Laborie, H.; Tonga, A.; Sopéna, V.; Lanneluc, I.; Picot, L.; Sablé, S.; Thiéry, V.; Rakitin, O. A. *Bioorg. Med. Chem. Lett*. **2009**, *19*, 136. http://dx.doi.org/10.1016/j.bmcl.2008.11.010
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