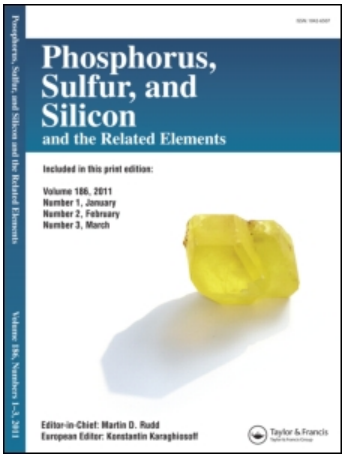

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Novel Free Radical Reactions in Organosulfur Chemistry

Emmanuil I. Troyansky[a]
[a] N. D. Zelinsky Institute of Organic Chemistry the Russian Academy of Sciences, Moscow, Russia

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Novel Free Radical Reactions in Organosulfur Chemistry

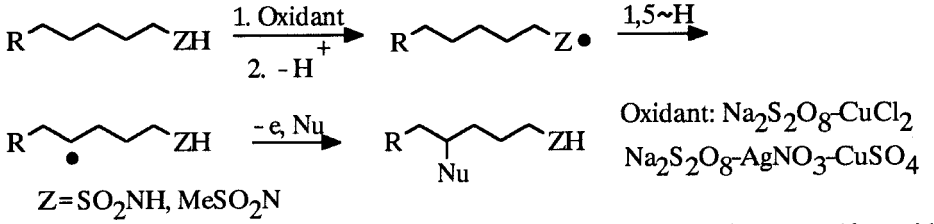
Emmanuil I.Troyansky

N.D.Zelinsky Institute of Organic Chemistry the Russian Academy of Sciences, Leninsky prospect 47, Moscow B-334, Russia

Our studies on homolytic and oxidative transformations of organic compounds of bi- and hexavalent sulfur cover mainly the following trends:

(i) One-step Remote Oxidative Functionalization.

The one-step approach to the regioselective (or regiospecific) synthesis of bifunctional organic compounds of sulfur (VI) has been developed. The method involves the generation of N-centered sulfonylamidyl radicals by single electron oxidation of sulfonamides of various types, regioselective (or regiospecific) rearrangement of these radicals with 1,5 H-migration into C-centered radicals and their oxidation into final reaction products.



Z=SO_2NH, $MeSO_2N$

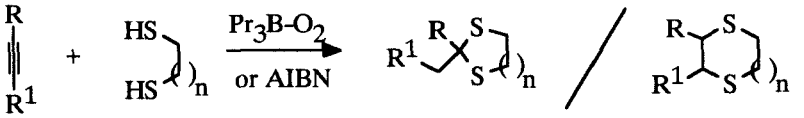
By this way were accomplished regioselective chlorination of alkanesulfonamides into 3-chloroalkanesulfonamides, regiospecific oxidation of alkanesulfonamides into 3-oxoalkanesulfonamides, cyclization of N-mesylalkylamines into pyrrolidines, transformation of acyclic N-mesyl-α-aminoacids into proline derivatives. The approach developed does not operate in the case of dialkylsulfones, the remote oxidation of which proceeds under polar control.

(ii) Homolytic and Oxidative Heterocyclization of Dithioic Acids and Their Derivatives.

It was established that these reactions provide a facile route to the synthesis of 1,2-dithiole-3-thiones and hexathiaadamantanes from dithioic acids as well as to 1,2,4-thiadiazoles from alkanethioamides. Co-oxidation of arenethiohydrazides and alkanethioamides induced by tert-BuOCl leads to formation of comparatively hardly available 2-alkyl-5-aryl-1,3,4-thiadiazoles.

(iii) Free Radical Cycloaddition Including Homolytic Macrocyclization

Intermolecular homolytic cyclization provides an extremely facile approach to the construction of saturated sulfur-containing heterocycles, and the free radical cycloaddition of dithiols to alkynes presents a highly selective and effective route to five-, six- and seven-membered 1,3- and 1,4-dithiacycloalkanes. The mode of the addition to the triple bond as well as the type of heterocycles formed depend strongly on the nature of substituents in alkynes.

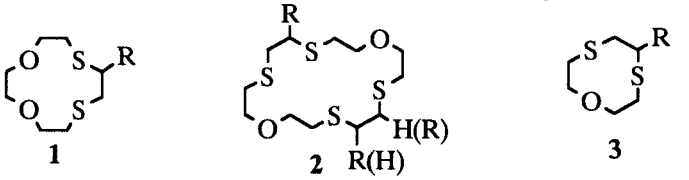


The cycloaddition of dithiols to disubstituted alkynes proceeds with high *cis*-stereoselectivity due to the combination of *trans* - addition to triple bond and subsequent intermolecular *cis* - addition to double bond in the intermediate unsaturated thiol. Conformational analysis of 2-mono- and 2,3-disubstituted 1,4-dithianes is elaborated by NMR spectroscopy and MMX calculations.

Based on the same general idea, we have accomplished, for the first time, an intermolecular homolytic macrocyclization with participation of thiyl radicals, which enabled us to develop the versatile and facile one-step approach to construction of 12-, 14-, 16- and 18-membered thiacrown ethers from alkynes and corresponding dithiols.

Homolytic cycloaddition of 3,6-dioxaoctane-1,8-dithiol with alkynes, induced by tripropylborane in the presence of oxygen, leads to 12-membered thiacrown ethers **1** which are the 1:1 cycloadducts of free radical macrocyclization.

Homolytic cycloaddition of 3-oxa-1,5-pentanedithiol with alkynes proceeds in a completely different manner and leads mainly to the 18-membered thiacrown ethers **2**, which are the 2:2 cycloadducts of free radical macrocyclization, while the corresponding 1:1 cycloadducts, 9-membered thiacrown ethers **3**, are formed only as minor products.



Similarly the corresponding 14- and 16-membered thiacrown ethers are obtained as 2:2 cycloadducts in the homolytic reaction of 1,3-propanedithiol and 1,4-butanedithiol with alkynes. Mechanism of this mode of the design of thiacrown ethers is established.

Thus, free radical cycloaddition - macrocyclization can be considered as a very powerful method of the synthesis of thiacrown ethers with different ring size and number of heteroatoms.

The results obtained demonstrate wide possibilities of free radical reactions in the synthetic and physical organic chemistry of sulfur.