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### SOME NEW HOMOLYTIC HETEROCYCLIZATION REACTIONS IN CHEMISTRY OF BIVALENT SULFUR COMPOUNDS

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## SOME NEW HOMOLYTIC HETEROCYCLIZATION REACTIONS IN CHEMISTRY OF BIVALENT SULFUR COMPOUNDS

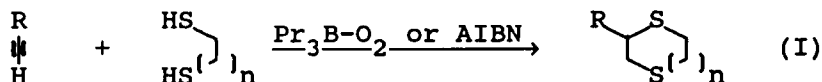
NIKISHIN GENNADY I., TROYANSKY EMMANUIL I., and  
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**Abstract.** The novel approach to one-pot synthesis of various heterocycles based on the heterocyclization reaction of bivalent sulfur compounds (thiols, dithiocarboxylic acids and their derivatives) are reported.

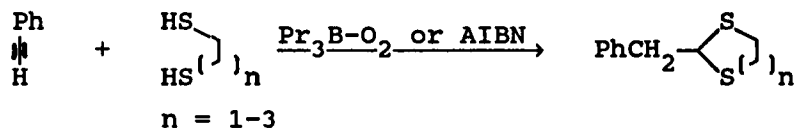
Homolytic and related reactions can serve as an effective tool for the synthesis of heterocyclic compounds from acyclic synthons. This communication is devoted to the new reactions of homolytic heterocyclization of sulfur (II) compounds - thiols and thiocarbonyl compounds such as dithiocarboxylic acids and their derivatives, performed in the last five years in our laboratory.

A new approach to constructing sulfur-containing saturated heterocycles based on the reaction of intermolecular homolytic addition of thiyl radicals to multiple bonds was developed. We established the radical addition of 1,2- or 1,3-dithiols to alkynes to be a general method for the synthesis of five-, six- or seven-membered 1,3- or 1,4-dithiacyclanes. Alkynes with alkyl-type substituents in the reaction with 1,2-ethanedithiol or 1,3-propanedithiol form regiospecifically 1,4-dithianes (I, n=1) or 1,4-dithiepanes (I, n=2), yield 40-70%.



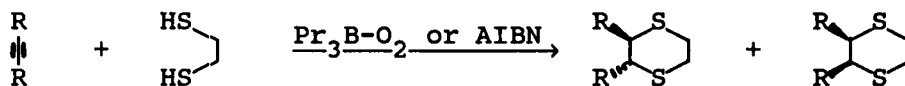
R=Bu, CH<sub>2</sub>OH, CMe<sub>2</sub>OH, CH<sub>2</sub>Cl, etc.; n=1,2.

With phenylacetylene regiospecific 1,1-addition of dithiols to triple bond (instead of 1,2-addition) proceeds leading to 2-benzyl-1,3-dithiacyclanes, yield up to 40%.



The reasons determining the influence of the substituent on the addition mode are discussed thoroughly. Model experiments showed that in the reactions of 1,2-ethanedithiol induced by  $\text{Pr}_3\text{B} - \text{O}_2$  intermediately 2-propyl-1,3,2-dithiaborolane is formed.

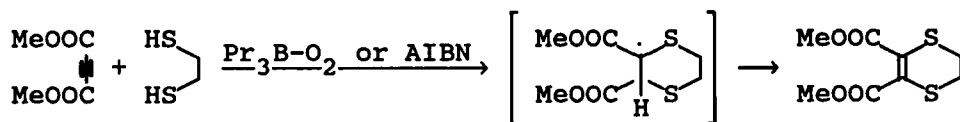
The heterocyclization of disubstituted alkynes with 1,2-ethanedithiol occurs with high regioselectivity; cis/trans ratio achieves ~20:1 for  $\text{R}=\text{CH}_2\text{OAc}$ .



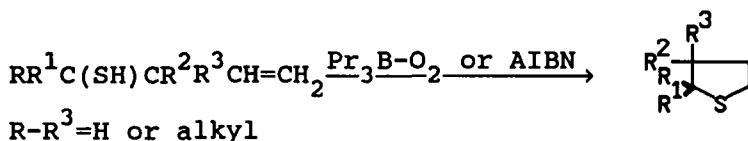
$\text{R}=\text{Pr}, \text{CH}_2\text{Cl}, \text{CH}_2\text{OAc}, \text{Ph}.$

Two consecutive homolytic additions to multiple bonds are supposed: firstly the intermolecular addition to the triple bond and secondly the intramolecular addition to the double bond, and just the second stage is responsible for the observed stereochemistry of the reaction.

The substituents at the triple bond can influence principally on the type of the forming heterocycle. The cycloaddition of dimethyl acetylenedicarboxylate and 1,2-ethanedithiol leads predominantly to corresponding 1,4-dithiin, yield 30%. The most probable reason for the change of the heterocyclization mode is connected with the presence of relatively mobile  $\beta$ -H atom.

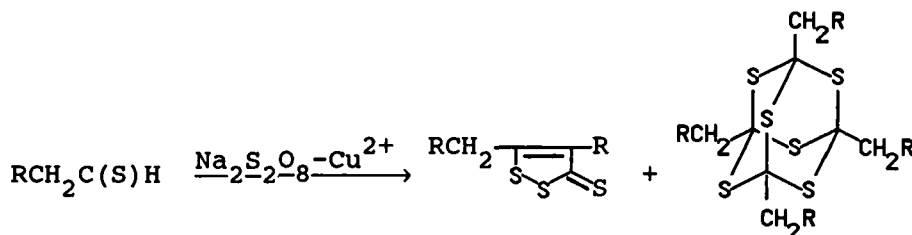


Recently we have elaborated the synthesis of thia-crown ethers based on the discussed reactions of the homolytic heterocyclization. The intramolecular addition of thiyl radicals to multiple bonds in it's "classical" version has been accomplished in the cyclization of homoallylic thiols into various substituted thiolanes, yield 40-80%.



Oxidative and related reactions of dithioic acids and their derivatives provide a convenient path to sulfur-containing aromatic heterocycles.

One-electron oxidation of dithioic acids leads to 1,2-dithiole-3-thiones; as by-product hexathiaadamantanes are formed.

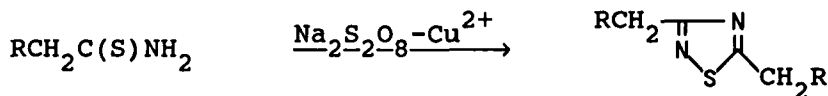


$\text{R}=\text{H}$  or alkyl

yields 30-50%

yield up to 20%

Under the similar conditions alkanethioamides are converted into 1,2,4-thiadiazoles

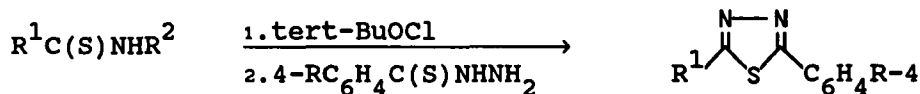


$\text{R}=\text{H}$  or alkyl

yield up to 60%

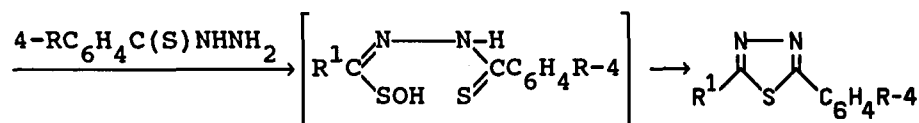
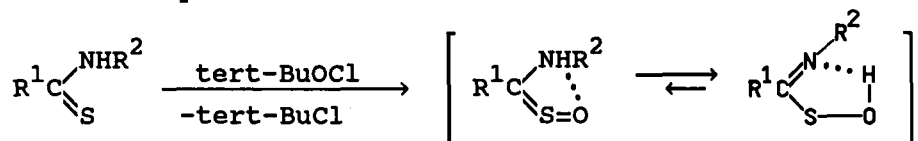
The observed facile transformations of functional groups of dithioic acids and their amides (in contrast to carboxylic acids and their amides) are explained using molecular orbital considerations by the high ability of sulfur atom of thiocarbonyl group to accept the radical and (in the utmost case) electrophile species.

Consecutive reactions of thioamides with tert-butylhypochlorite and then with arenethiohydrazides are established as a facile method for the synthesis of the relatively hard available unsymmetrically substituted 1,3,4-thiadiazoles, yield 40-65%



R=H or MeO;  $\text{R}^1$ =alkyl, Ph, 2-thienyl, 3-pyridyl;  $\text{R}^2$ =H or alkyl.

It has been shown by spectral methods that the activation of thioamides in the interaction with tert-butylhypochlorite is due to oxygen transfer to the sulfur atom. Thioamide-S-oxyde obtained is in equilibrium with  $\alpha$ -iminosulfenic acid and condenses with arenethiohydrazides.



The accomplished investigation result in the developing of the novel facile preparative methods for synthesis of 1,3- and 1,4-dithianes, 1,3- and 1,4-dithiepanes, 1,3-dithiolanes, 1,4-dithiins, thiolanes, thia-crown ethers, 1,2-dithiole-3-thiones, 1,2,4- and 1,3,4-thiadiazoles, hexathiaadamantanes based on the homolytic or oxidative heterocyclization.