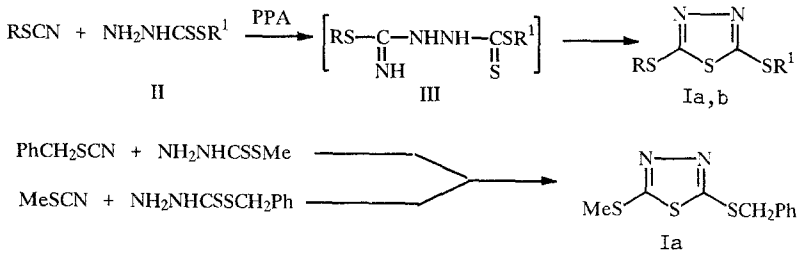
A NEW VARIANT OF THE DITHIOCARBAZATE METHOD OF SYNTHESIS OF ASYMMETRIC DITHIOETHERS OF 2,5-DIMERCAPTO-1,3,4-THIADIAZOLE

S. Sh. Shukurov, M. A. Kukaniev, V. M. Bobogaribov, and S. S. Sabirov

One of the methods for the synthesis of asymmetric dithioethers of 2,5-dimercapto-1,3,4-thiadiazole I is the dithiocarbazate method. Esters of dithiocarbazic acid form monoethers of 2,5-dimercapto-1,3,4-thiadiazole with carbon disulfide, which convert into diethers I by alkylation [1].

We found that in a polyphosphoric acid (PPA) medium compounds II can be converted into diethers I by reaction with thiocyanic esters. It is assumed that the reaction proceeds through the stage of addition of a nitrile group of the thiocyanic ester to the hydrazine fragment of compound II with subsequent cyclization of the intermediate III into diether I. We tested the two possible variants of the preparation of diether Ia by the above method.



Ia R = Me, R^1 = $PhCH_2$; Ib R = Ph, R^1 = $PhCH_2$

Compounds Ia, b were characterized by their conversion into the corresponding disulfones.

Thus, an equimolar mixture of 0.01 mole of thiocyanic acid esters (R = CH_3; $CH_2C_6H_5$; C_6H_5) and 0.01 mole of dithiocarbazic acid ester was heated with 10-15 g of PPA for 3-4 h at 95-100°C. The reaction mixture was diluted with 100-120 ml of water. The aqueous layer was decanted, and to the remaining oil 25-30 ml of glacial acetic acid and 10 ml of a 35% hydrogen peroxide were added. The solution was heated for 3-4 h to 50-60°C, and after 12-24 h was diluted with 70-80 ml of water. The disulfones of diethers Ia, b that separated out were filtered off and recrystallized from aqueous dioxane (1:1).

Sulfone of diether Ia, yield 53%, 72%, mp 124°C (according to the data in [2], mp 105°C).

Sulfone of compounds Ib, yield 41%, mp 138-140°C (according to the data in [2], mp 138°C).

The elemental analysis data of sulfones of compounds Ia, b correspond to the calculated values.

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V. I. Nikitin Institute of Chemistry, Academy of Sciences of the Republic of Tadzhikistan, Dushanbe 734063. Abuali ibn Sino Tadzhik State Medicinal University, Dushanbe 734003. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1145-1146, August, 1993. Original article submitted June 30, 1993.

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