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LETTERS TO THE EDITOR

Perspective Approach to the Synthesis of 4,5-Dimercapto-1,3-oxazole Derivatives

S. B. Babii, V. S. Zyabrev, and B. S. Drach

Institute of Bioorganic and Coal Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

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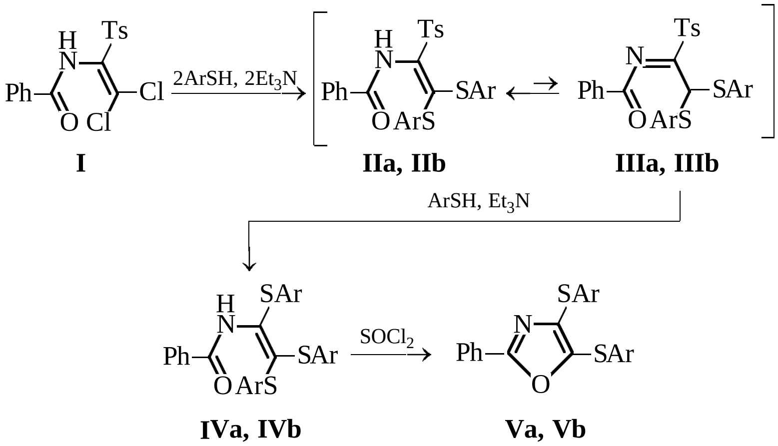
In the course of a systematic study of new transformations of α-sulfonyl-substituted enamides we found that the available reagent **I** [1] reacts in an unusual way with an excess of thiphenols in the presence of triethylamine. The intermediate products of this reaction are, probably, functionalized enamides **II** which are in equilibrium with the corresponding *N*-acylimine tautomers **III**. The latter may well react with thiophenol in mild conditions with elimination of a tosyl residue to give new sulfur-containing enamides **IV** which readily cyclize under the action of thionyl chloride.



Ar = 4-ClC$_6$H$_4$ (**a**), 4-MeC$_6$H$_4$ (**b**).

The structure of cyclization products **V** was proved by spectral methods. The field of application of the convenient synthetic approach to previously hardly available 4,5-dimercapto-1,3-oxazole derivatives (cf. [2]) will be considered at a later time.

***N*-[1,2,2-Tri(arylthio)ethenyl]benzamides IVa, IVb.** Triethylamine, 0.03 mol, and 0.01 mol of enamide **I** [3] were added to a solution of 0.03 mol of *p*-chlorothiophenol or *p*-thiocresol in 50 ml of ethanol. The mixture was stirred at 20–25°C for 24 h, the precipitate was filtered off and recrystallized from ethanol. Compound **IVa**. Yield 87%, mp 150–151°C. IR spectrum (CH_2Cl_2), ν, cm^{-1}: 1685 (C=O), 3390 (N–H). Found, %: Cl 18.40; S 16.75. $C_{27}H_{18}Cl_3NOS_3$. Calculated, %: Cl 18.50; S 16.73. Compound **IVb**. Yield 85%, mp 84–85°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (3H, Me), 2.30 s (3H, Me), 2.33 s (3H, Me), 7.00–7.44 m (17H, Ar–H; 1H, NH). Found, %: N 2.72; S 18.67. $C_{30}H_{27}NOS_3$. Calculated, %: N 2.73; S 18.72.

4,5-Bis(arylthio)-2-phenyl-1,3-oxazoles Va, Vb. A solution of 0.001 mol of enamide **IVa** or **IVb** in 6 ml of thionyl chloride was heated under reflux for 1.5 h, excess thionyl chloride was removed in a

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vacuum, and the residue was crystallized from ethanol. Compound **Va**. Yield 42%, mp 121–122°C. IR spectrum (CH_2Cl_2): in the ranges 1600–2000 and 3200–3600 cm^{-1} no bands are observed. Found, %: C 58.50; H 2.99; Cl 16.45; S 14.87. $C_{21}H_{13}Cl_2NOS_2$. Calculated, %: C 58.61; H 3.04; Cl 16.48; S 14.90. Compound **Vb**. Yield 37%, mp 106–107°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (6H, 2Me), 7.05–7.45 m (11H, Ar–H), 8.00–8.04 m (2H, Ar–H). Found, %: N 3.65; S 16.03. $C_{23}H_{19}NOS_2$. Calculated, %: N 3.60; S 16.46.

The IR spectra were obtained on a Specord IR-71 instrument, solvent CH_2Cl_2. The ^1H NMR spectra were measured on a Varian Gemini spectrometer (200 MHz), internal reference TMS, solvent $CDCl_3$.

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