

SHORT
COMMUNICATIONS

Two Directions of Reaction between Aminothiophenol and 3-Bromoarylmaleimides

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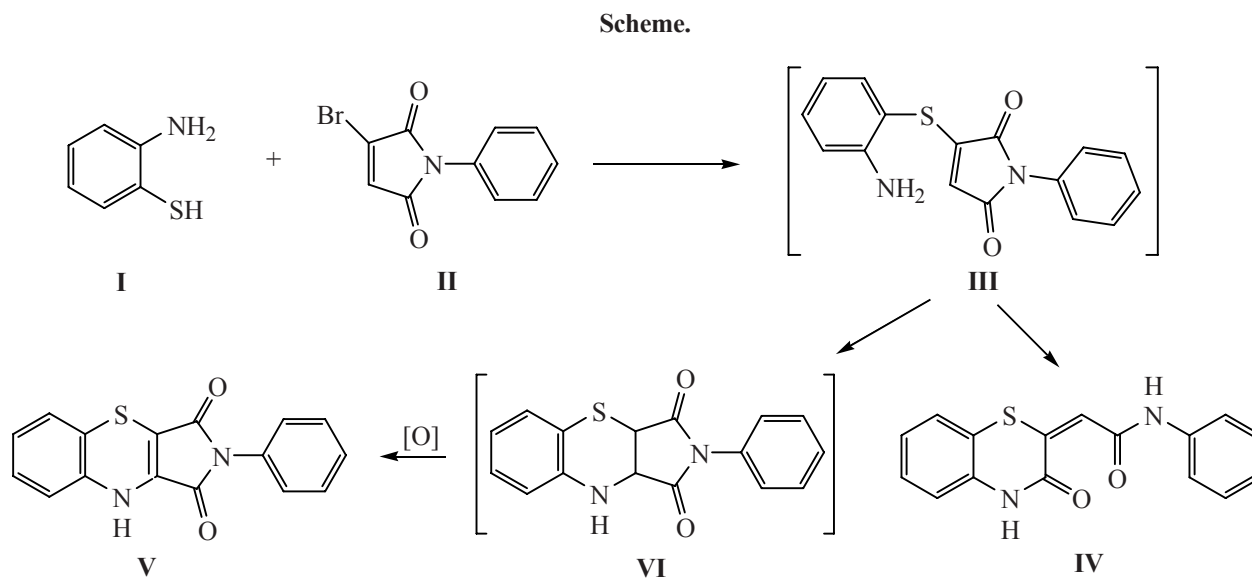
Lately a report was published on the reaction of *o*-phenylenediamine with *N*-arylmaleimides [1] leading through the recyclization of the latter to substituted quinazolinones. We attempted to bring into similar reaction the *o*-aminothiophenol and 3-bromomaleimide.

It was expected that the reaction of aminothiophenol (I) with 3-bromomaleimide II through the stage of S-alkylation followed by recyclization of intermediate III would provide *N*-phenyl-2-(3-oxo-3,4-dihydro-2*H*-1,4-benzothiazin-2-ylidene)acetamide (IV) (see the Scheme).

It was established however that in reaction performed in ethanol and other solvents acetamide IV was the minor product, and the major product unexpectedly proved to be 2-phenyl-1,2,3,9-tetrahydrobenzo[*b*]pyrrolo[1,4]-thiazine-1,3-dione (V) formerly obtained [2] in the reaction

of aminothiophenol and 3,4-dibromomaleimide. The formation of this product apparently occurred by the alternative transformation of the intermediate, 3-(2-amino-phenylsulfanyl)-1-phenyl-2,5-dihydro-1*H*-pyrrole-2,5-dione (III), through the stages of amino group addition to an activated double bond by the Michael type reaction with the subsequent oxidation of compound VI, 2-phenyl-1,2,3,3a,9,9a-hexahydrobenzo[*b*]pyrrolo[3,4-*e*][1,4]-thiazine-1,3-dione.

*N*l-Phenyl-2-(3-oxo-3,4-dihydro-2*H*-1,4-benzothiazin-2-ylidene)acetamide (IV) and 2-phenyl-1,2,3,9-tetrahydrobenzo[*b*]pyrrolo[3,4-*e*][1,4]-thiazine-1,3-dione (V). Equimolar quantities (0.01 mol each) of phenylmaleimide and 2-aminothiophenol were heated in ethanol for 1–2 h. The precipitate was separated,



the reaction products were isolated by column chromatography on aluminum oxide (eluent ethyl acetate).

Compound **IV**. R_f 0.45–0.50, yield 30–35%, mp 323–324°C. ^1H NMR spectrum, δ , ppm: 4.67 s (1H, CH), 7.48 m (9H, H_{arom}), 9.75 br.s (1H, NH), 10.04 br.s (1H, NH). Found, %: C 64.91; H 3.99; N 9.39; S 10.76. $[M]^+$ 296. $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$. Calculated, %: C 64.85; H 4.08; N 9.45; S 10.82. M 296.35.

Compound **V**. R_f 0.75–0.80, yield 50–55%, mp 212°C. ^1H NMR spectrum, δ , ppm: 6.50 br.s (1H, NH), 7.48 m (9H, H_{arom}). Found, %: C 65.11; H 3.97; N 9.33; S 10.62. $[M]^+$ 294. $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$. Calculated, %: C 65.29; H 3.42; N 9.52; S 10.89. M 294.33.

TLC was performed on Merck-254 plates, eluents chloroform, dioxane, methanol, and their mixtures. Development under UV irradiation or in iodine vapor.

^1H NMR spectra were registered on spectrometers Bruker AC (250 and 400 MHz) in $\text{DMSO}-d_6$ relative to TMS. Mass spectra were measured on an instrument LKB 9000, direct admission of the sample into the ion source, ionizing electrons energy 70 eV.

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