

SHORT  
COMMUNICATIONS

Dedicated to Professor G.I.Koldobskii on occasion of his 70th anniversary

## 2-Halo-2,4-dinitrothiolen-1,1-dioxides in Reaction with Pyridine

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It was formerly demonstrated by an example of 2,2,4-trinitro-3-thiolen-1,1-dioxides [1–3] that trinitro derivatives of thiolen-1,1-dioxide were quite easily available and stable compounds. A wide range of their synthetic opportunities [2–6] is due to a good compromise between the properties of aliphatic trinitromethyl compounds [7], nitroalkenes [8], and sulfolenes [9]. In particular these compounds of high electron-acceptor qualities actively react with pyridine and its substituted derivatives with  $\text{HNO}_2$  elimination affording stable molecular complexes of 2,4-dinitrothiophene-1,1-dioxide with the above mentioned heterocycles [2, 5, 6].

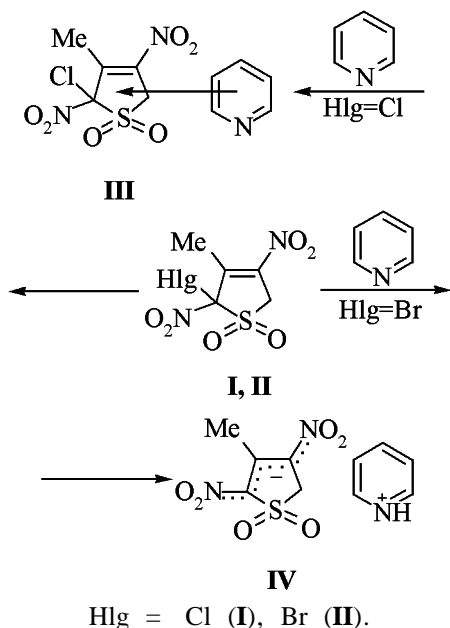
2-Halo-3-methyl-2,4-dinitrothiolenedioxides (**I**, **II**) [10] which we prepared are structural analogs of 3-methyl-2,2,4-trinitro-3-thiolen-1,1-dioxide [1] and as the latter actively react with pyridine at room temperature in ethanol solution. However the replace-

ment of halogen for a nitro group notably affects the course of reaction and the structure of the final products. With chloro compound **I** the electron transfer from a donor to an acceptor is finished at the stage of forming molecular complex **III**.

With bromo-containing analog **II** this process is followed by cleavage of bromine cation and stops at formation of pyridinium thiolenylnitronate (**IV**); apparently higher lability of bromine as compared to chlorine and a formation of a resonance-stabilized heterocyclic dinitroanion are the factors ensuring the successful realization of this reaction. Molecular complex **III** is a crystalline red-brown substance soluble in DMSO, unstable to heating. The complex character of this compound is evidenced by the presence in its electronic spectrum of a charge transfer band at  $\lambda_{\text{max}} \sim 410$  nm ( $\epsilon$  3500), located in similar region as the corresponding band ( $\lambda_{\text{max}} \sim 440$  nm,  $\epsilon \sim 2500$ ) of the analogous complexes that has been detected spectrally in reactions of 3-methyl-2,2,4-trinitro-3-thiolen-1,1-dioxide with alcohols and esters [6].

Pyridinium 3-methyl-4(2)-nitro-1,1-dioxothiolenyl-2(4)-nitronate (**IV**) is an orange crystalline compound soluble in water and DMSO, unstable to heating. Its electron absorption spectrum in water is characterized by an absorption band at  $\lambda_{\text{max}} \sim 370$  nm ( $\epsilon \sim 8000$ ) corresponding to thiolenylnitronate anion of the respective potassium salt ( $\lambda_{\text{max}} \sim 379$  nm,  $\epsilon \sim 81000$  l·mol<sup>-1</sup>·cm<sup>-1</sup>). <sup>1</sup>H NMR spectrum of compound **IV** registered in D<sub>2</sub>O contains proton signals of methyl group ( $\delta$  CH<sub>3</sub> 2.20 ppm), methylene group ( $\delta$  CH<sub>2</sub> 4.35 ppm), of protons from the heterocyclic anion and pyridinium cation (7.20–9.00 ppm). We failed to detect the signals of NH<sup>+</sup> in D<sub>2</sub>O and DMSO-*d*<sub>6</sub>.

2-Halo-3-methyl-2,4-dinitrothiolen-1,1-dioxides **I** and **II** were prepared by procedure [10].



**Molecular complex of 3-methyl-2,4-dinitro-2-chloro-3-thiolene-1,1-dioxide with pyridine (III).** Yield 35%, mp 190–195°C (after repeated washing with ethanol). Found, %: C 35.20, 35.27;  $\Delta$  3.33, 3.32; N 12.10, 12.15.  $C_{10}H_{10}ClN_3O_6S$ . Calculated, %: C 35.76;  $\Delta$  2.98; N 12.51.

**Pyridinium 3-methyl-4(2)-nitro-1,1-dioxothiolenyl-2(4)-nitronate (IV).** Yield 59%, mp 152–154°C (after repeated washing with ethanol). Found, %: N 13.93, 13.94.  $C_{10}H_{11}N_3O_6S$ . Calculated, %: N 13.95.

$^1H$  NMR spectra were registered on spectrometer Bruker Ac-200 (200 MHz), internal reference HMDS. Electron absorption spectra were recorded on SF-46 instrument.

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