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LETTERS
TO THE EDITOR

Synthesis of Dinitrosulfodienes of the Thiolene 1,1-Dioxide Series

I. E. Efremova, S. V. Bortnikov, and V. M. Berestovitskaya

Hertzen Russian State Pedagogical University, St. Petersburg, Russia

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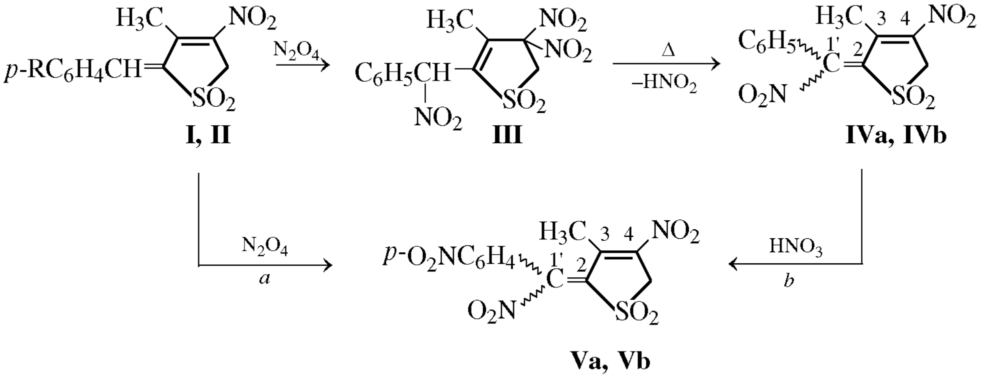
Nitrothiolene-1,1-dioxides are convenient synthons for constructing new types of functionalized thiolene- and thiophene-1,1-dioxides [1–5]. Thus, the *s-trans*-fixed diene system of 2-benzylidene-3-methyl-4-nitro-3-thiolene 1,1-dioxides **I, II**, which was earlier widely used for preparing nucleophilic addition products [6, 7], proved highly effective in nitration reactions. This finding opened the way to the synthesis of original dinitrosulfodienes of the thiolene dioxide series.

The reaction of 2-benzylidene-3-methyl-4-nitro-3-thiolene 1,1-dioxide (**I**) with dinitrogen dioxide proceeds in carbon tetrachloride for 0.5 h at 16–18°C to give trinitrothiolene 1,1-dioxide **III** in 52% yield; short heating (1–2 min) of the latter in methanol (50–60°C) is accompanied by 1,4 elimination of nitrous acid to provide a dinitrosulfodiene as a mixture of geometric isomers **IVa** and **IVb**.



I, II **III** **IVa, IVb** **Va, Vb**

R = H (**I**), NO_2 (**II**); *Z,E* (**a**), *E,E* (**b**).

The reaction of 3-methyl-4-nitro-2-(*p*-nitrobenzylidene)-3-thiolene 1,1-dioxide (**II**) with N_2O_4 proceeds slower (1.5 h) with a larger excess of the nitrating agent (1 : 30) and produces compound **Va, Vb** in 35% yield (method *a*). Compound **Va, Vb** was obtained by independent synthesis via nitration of dinitrosulfodiene **IVa, IVb** with fuming nitric acid (method *b*).

The structure of the products was established on the basis of spectral data. The ^{1}H NMR spectrum of trinitro derivative **III** contains signals of the methyl (2.06 ppm), methylene (4.68 ppm), phenyl (7.46 ppm), and nitromethine (7.04 ppm) protons. The spectrun also contains bands due to the multiple bonds (1610 cm^{-1}) and geminal nitro (1570, 1390 cm^{-1}) and sulfonyl (1345, 1160 cm^{-1}) groups.

The dinitrosulfodienes are yellow crystalline substances. They are formed as mixtures of *Z,E* (**IVa, Va**) and *E,E* (**IVb, Vb**) isomers, whose crystallization or column chromatography gave individual *Z,E* isomers **IVa, Va**.

The geometric isomers were identified by ^1H NMR spectroscopy. Because of the strong through-space deshielding effect of the nitro group proximate to CH_3 the methyl proton signals of *E*,*E* isomers **IVb, Vb** are shifted downfield (2.45, 2.50 ppm) compared with those in the *Z*,*E* isomers (1.85, 1.95 ppm), while the methylene proton signals the *Z*,*E* form (4.55 ppm) are downfield from those of the *E*,*E* form (4.45 ppm). The aromatic proton signals of **IVa, Vb, Va**, and **Vb** appear at 7.30–8.45 ppm.

The IR spectra of compounds **IVa, IVb, Va**, and **Vb** contain bands of the multiple bonds (1610–1590 cm^{-1}) and sulfonyl (1345–1310, 1170–1140 cm^{-1}) and conjugated nitro groups (1540–1520, 1380–1340 cm^{-1}).

2-Benzylidene-3-methyl-4-nitro-3-thiolene 1,1-dioxides I, II were prepared as described in [5].

3-Methyl-4,4-dinitro-2-[nitro(phenyl)methyl]-2-thiolene 1,1-dioxide (III). Yield 52%, mp 105–106°C (decomp.). Found, %: C 40.57, 40.58; H 3.34, 3.33; N 11.92, 11.91. $C_{12}H_{12}N_3O_8S$. Calculated, %: C 40.34; H 3.08; N 11.76.

3-Methyl-4-nitro-2-[nitro(phenyl)methylene]-3-thiolene 1,1-dioxide IVa, IVb. Yield 92%, mp 130–135°C (for a 1:2 *Z,E*:*E,E* mixture). *Z,E* isomer **IVa**: mp 155–158°C (from benzene). Found, %: C 46.74, 46.73; H 3.37, 3.45; N 9.05, 9.08. $C_{12}H_{10}N_2O_6S$. Calculated, %: C 46.45; H 3.23; N 9.03.

3-Methyl-4-nitro-2-[nitro(phenyl)methylene]-3-thiolene 1,1-dioxide Va, Vb. Yield 35 (method *a*) and 97% (method *b*), mp 169–170°C (for a 2:3 *Z,E*: *E,E* mixture). *Z,E* isomer **Va**: mp 172–174°C (from acetone–chloroform, 1:1). Found, %: C 40.65; H 2.62; N 11.88. $C_{12}H_9N_3O_8S$. Calculated, %: C 40.56; H 2.50; N 11.80.

The IR spectra were recorded on an IR-75 spectrometer in KBr. The ^1H NMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz), internal reference HMDS, solvent $CDCl_3$ (**III, IVa, IVb**) and CD_3CN (**Va, Vb**).

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