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THIOLENE 1,1-DIOXIDES. SYNTHESIS OF AZIDO- AND AMINONITROSULFODIENES

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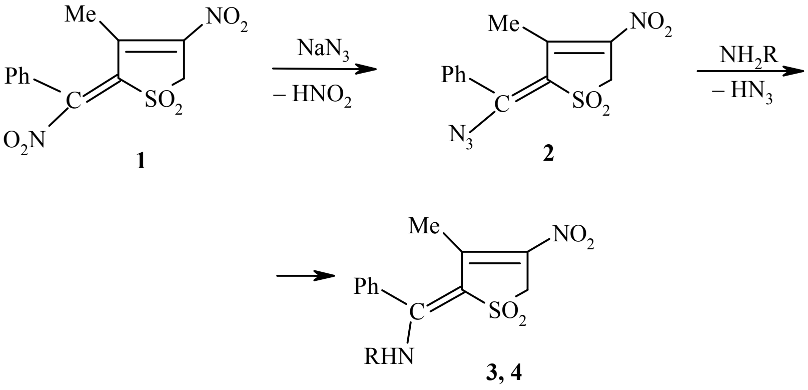
Dinitrothiolene 1,1-dioxides [1] containing the *s-trans*-fixed 1,4-dinitro-1,3-diene system hold interest as key synthones for the preparation of functionally substituted heterocyclic nitrosulfodienes. Dinitrodienes are capable of reacting with nucleophiles through an electron transfer pathway as well as Ad_N and S_NVin reactions [2, 3].



3 R = Ph, **4** R = NHPh

We have shown that the reaction of dinitrosulfodiene **1** with sodium azide in acetic acid at room temperature proceeds chemo-, regio-, and stereoselectively to give the product of nucleophilic vinyl substitution of the exocyclic nitro group, namely, *Z,E*-2-(1-azido-1-phenyl)methylene-3-methyl-4-nitro-3-thiolene 1,1-dioxide (**2**) in yields above 50%. The reaction of **2** with aniline and phenylhydrazine proceed through an analogous S_NVin pathway to give nitroenamines **3** and **4**.

We note that **3** and **4** could not be obtained directly from dinitrothiolene 1,1-dioxide **1**. This failure is probably related to the high oxidizing capacity of this dioxide and its high tendency to oxidize amines.

Azido- and aminonitrosulfodienes **2-4** are stable crystalline compounds, which are colorless in the crystalline state but appear yellow in polar solvents. The structure of **2-4** was assigned by analyzing their spectral data in comparison with the indices of **1** [1] and a model analog, namely, 4-anilino-1-nitro-2,3-diphenyl-1,3-butadiene [4]

Heterocyclic nitroenamines **3** and **4** hold interest as compounds with potential biological activity [5, 6].

The IR spectra were taken on a Specord IR-75 spectrometer. The ^{1}H NMR spectra were taken for solutions in $CDCl_3$ on a Bruker AC-200 spectrometer at 200 MHz with HMDS as the internal standard.

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2-(1-Azido-1-phenyl)methylene-3-methyl-4-nitro-3-thiolene 1,1-Dioxide (2) was obtained in 51% yield; mp 162-165°C (dec., from acetic acid). IR spectrum, ν, cm^{-1}: 1635 (C=C), 1520, 1330 (NO_2), 1330, 1130 (SO_2), 2130 (N_3). ^1H NMR spectrum, δ, ppm: 2.02 (3H, s, CH_3); 4.52 (2H, s, CH_2); 7.40-8.05 (5H, m, Ph). Found, %: C 47.14, 47.14; H 3.51, 3.54; N 18.35, 18.30. $C_{12}H_{10}N_4O_4S$. Calculated, %: C 47.06; H 3.27; N 18.30.

2-(1-Anilino-1-phenyl)methylene-3-methyl-4-nitro-3-thiolene 1,1-Dioxide (3) was obtained in 25% yield; mp 157-158°C (ethanol). IR spectrum, ν, cm^{-1}: 1610 (C=C), 1550, 1320 (NO_2), 1320, 1140 (SO_2), 3330 (NH). ^1H NMR spectrum, δ, ppm: 1.90 (3H, s, CH_3); 4.75 (2H, s, CH_2); 6.90, 7.20, 7.93, 7.80, 8.15 (11H, m, Ph, NH). Found, %: C 60.80, 60.78; H 4.67, 4.65; N 7.99, 8.02. $C_{18}H_{16}N_2O_4S$. Calculated, %: C 60.67; H 4.49; N 7.87.

3-Methyl-4-nitro-2-(1-phenyl-1-phenylhydrazino)methylene-3-thiolene 1,1-Dioxide (40 was obtained in 24% yield; mp 110-111°C (ethanol). IR spectrum, ν, cm^{-1}: 1600 (C=C), 1555, 1320 (NO_2), 1320, 1140 (SO_2), 3330 (NH). ^1H NMR spectrum, δ, ppm: 2.00 (3H, s, CH_3); 4.48 (2H, s, CH_2); 6.80, 7.00, 7.25, 7.48, 7.70, 8.00 (12H, m, Ph, NH). Found, %: C 58.20, 58.24; H 4.51, 4.54; N 11.35, 11.30. $C_{18}H_{17}N_3O_4S$. Calculated, %: C 58.22; H 4.58; N 11.32.

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