Chemistry of Heterocyclic Compounds, Vol. 38, No. 8, 2002

LETTERS TO THE EDITOR

HALO- AND PROTOTROPIC TRANSFORMATIONS IN BROMONITROTHIOLENE 1,1-DIOXIDES

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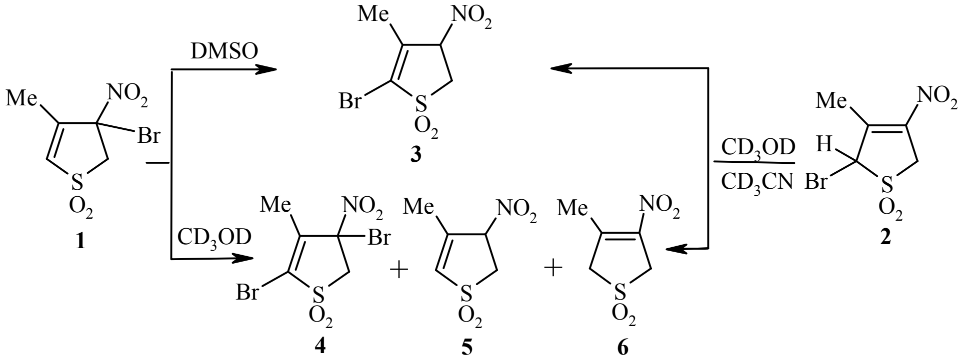
Keywords: halonitrothiolene dioxides, prototropy, halotropy, heterocycles, sulfonyl group.

In previous work [1, 2], we showed that the introduction of a nitro group into the heterocycle in 4-nitro-2-thiolene dioxide and 4-nitro-3-thiolene dioxide significantly activates the prototropic allyl–vinyl isomerization, which proceeds under mild conditions by the action of polar solvents at room temperature.

Bromonitrothiolene 1,1-dioxides **1** and **2** obtained in our laboratory by brominating sodium 3-methyl-1,1-dioxo-2-thiolenyl-4-nitronates proved even more labile compounds [3].

An irreversible bromine shift occurs upon dissolving **1** in DMSO-d$_6$ to give a structural isomer, namely, 2-bromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide **4** and isomeric nitrothiolene 1,1-dioxides **5** and **6**.



In the case of 2-bromo-3-methyl-4-nitro-3-thiolene 1,1-dioxide **2**, the isomerization to give **3** and conversion to **4-6** proceed in solution in methanol or acetonitrile and also in the absence of solvent at room temperature. The disproportionation reaction predominates. These reactions were monitored by ^{1}H NMR spectroscopy. Dioxides **3** and **4** were preparatively isolated. The sequence of these transformations may be represented by the following scheme:

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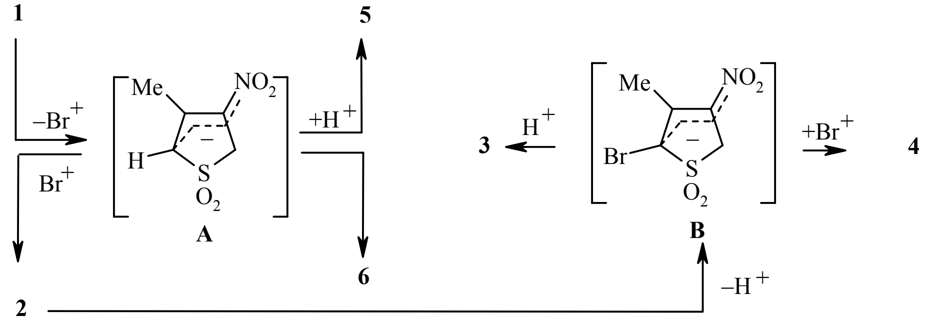

The formation of resonance-stabilized heterocyclic nitroallylic anions **A** and **B** as stable intermediates is probably the driving force for these reactions, markedly facilitating the loss of positive halogen and deprotonation.

Thus, we are the first to observe a characteristic tendency of bromonitrothiolene dioxides to undergo a cascade of transformations under mild conditions, including halotropy, prototropy, and disproportionation. The examples of similar reactions in the literature relate to compounds not containing a nitro group and require vigorous conditions in the presence of alkali metal amides, *n*-butyllithium, or lithium diisopropylamide [4-6].

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

2-Bromo-3-methyl-4-nitro-2-thiolene 1,1-Dioxide (3), mp 160-161°C ($CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 2.12 (3H, s, CH_3); 3.86, 4.05 (2H, q, $J = 15$, CH_2); 5.63 (1H, q, $J_{AX} = 3$, $J_{BX} = 7$, CH); IR spectrum in KBr pellets, ν, cm^{-1}: 1570, 1360 (NO_2), 1370, 1160 (SO_2). Found, %: C 23.44; H 2.51; N 5.51. $C_5H_6BrNO_4S$. Calculated, %: C 23.40; H 2.34; N 5.47.

2,4-Dibromo-3-methyl-4-nitro-2-thiolene 1,1-Dioxide (4), mp 99-100°C (CCl_4). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 2.21 (3H, s, CH_3); 4.22, 4.63 (2H, q, $J = 15$, CH_2). IR spectrum in KBr pellet, ν, cm^{-1}: 1580, 1350 (NO_2), 1350, 1155 (SO_2). Found, %: C 18.27; H 1.84; N 4.31. $C_5H_5Br_2NO_4S$. Calculated, %: C 17.91; H 1.49; N 4.18.

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