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*On the 100th anniversary of V.V. Perekalin*

# The Interaction of 3-Methyl-4-nitro-3-thiolene-1,1-dioxide with Aliphatic Amines

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**Abstract**—The reactions of 3-methyl-4-nitro-3-thiolene-1,1-dioxide with highly basic amines (p$K_a$ of $HB^+$ = 8.97–13.27), morpholine, piperazine, piperidine, cyclohexylamine, diphenylguanidine, and guanidine, proceed via deprotonation of methylene group at the $C^2$ atom of sulfolene ring with formation of ammonium thiolene nitronates. The products were characterized by IR, UV, and NMR ($^1H$, $^{13}C$, 2D) spectroscopy methods.

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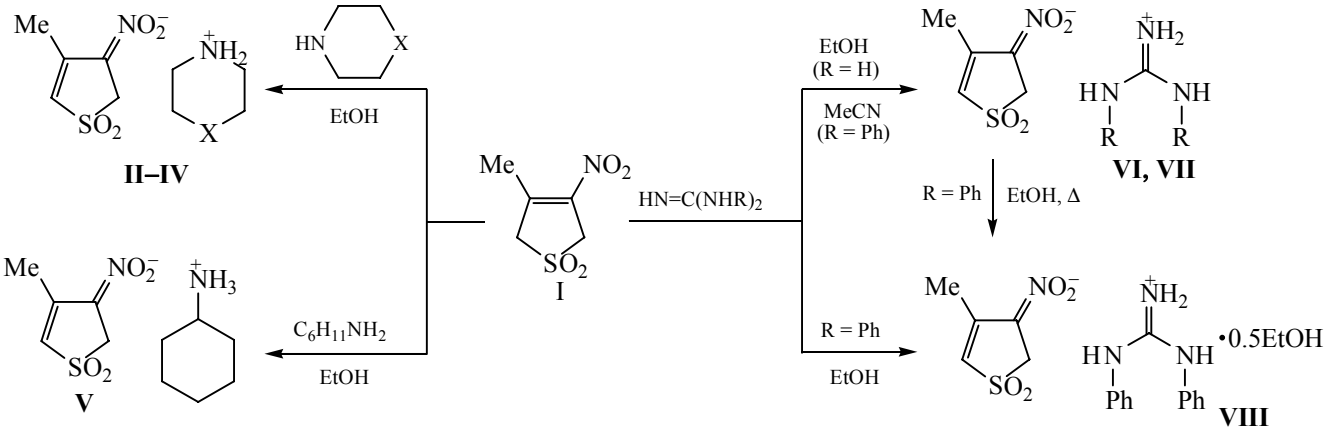
Heterocyclic nitroalkenes (4-nitrotiolene-1,1-dioxides) are promising starting materials for synthesis of heterocyclic and diene derivatives [1] which are difficult to be obtained by other methods. Furthermore, they are suitable model compounds for investigation of some theoretical aspects of organic chemistry [2], for example, oxime–nitrone tautomerism [3, 4], allyl–vinyl isomerization [5], and halotropic transformations [6, 7].

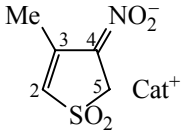
The reactions involving *N*-nucleophiles [1, 2], their pathway depending on the reagents nature, play an important part in the chemistry of nitrothiolene dioxides. In the case of arylamines and hydrazine derivatives of low basicity, the nucleophilic addition products are formed [1, 8]. Formed by this way hydrazine aza-adducts can undergo sulfolane ring opening to give (2-nitro-ethylsulfonyl)propanone hydrazones [9]. In reactions of $\Delta^2$- and $\Delta^3$-nitrosulfolenes with highly basic reagents (alkoxides and secondary aliphatic amines), the CH-acidic properties of nitrothiolene dioxide system come into play, leading to formation of thiolene nitronates [1, 6, 10]. However, the available information about formation of 4-nitrothiolene-1,1-dioxide salts in the reactions with highly basic aliphatic amines is insufficient. To fill the gap, we devoted this paper to extend the range of nitrogenous bases capable to form corresponding thiolene nitronates, and to characterize the products by spectral methods.

We investigated the interactions of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I** with highly basic (p$K_a$ of $HB^+$ 8.97–13.27 [11]) amines differing in structure and basicity: cyclohexylamine (p$K_a$ $HB^+$ 10.57), morpholine (p$K_a$ $HB^+$ 8.97), piperazine (p$K_a$ $HB^+$ 9.90),




X = O (**II**), NH (**III**), $CH_2$ (**IV**); R = H (**VI**), Ph (**VII**).

Yields, melting points, and spectral data of thiolene nitronates **II–VIII**




| Comp. no. | Cat$^+$ | Yield, % | mp, °C | $^1$H NMR spectrum, δ, ppm, DMSO-$d_6$ | | | | Electronic spectrum, in EtOH | | IR spectrum, ν, cm$^{-1}$, in KBr | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $CH_3$ | $CH_2$ | =CH | Kat$^+$ | λ, nm | ε | $NO_2^-$, $SO_2$ | C=C, C=N$^+$ | NH$^+$ |
| **II** | Morpholinium | 46 | 127–129 | 2.25 | 3.85 | 5.87 | 3.03, 3.73 | 327 | 10700 | 1384, 1280, 1239, 1158, 1084 | 1605, 1518 | 2732–2201 |
| **III** | Piperazinium | 58 | 133–134 | 2.26 | 3.86 | 5.89 | 3.03 | 327 | 10700 | 1388, 1247, 1220, 1166, 1078 | 1622, 1535, 1514 | 2609–2170 |
| **IV** | Piperidinium | 90 | 100–103 | 2.22 | 3.87 | 5.91 | 1.50, 1.60, 2.96 | 326 | 19100 | 1384, 1274, 1238, 1167, 1087 | 1603, 1514 | 2759–2360 |
| **V**[a] | Cyclohexulammonium | 75 | 105–107 | 2.24 | 3.81 | 5.76 | 1.26, 1.71, 1.88, 3.14 | 326 | 17800 | 1384, 1298, 1233, 1159, 1090 | 1605, 1527 | – |
| **VI** | Guanidinium | 51 | 100–101 | 2.25 | 3.85 | 5.89 | 7.14 | 326 | 11800 | 1385, 1281, 1242, 1170, 1089 | 1659, 1533 | 3425–3045 |
| **VII**[b] | *N*,*N*-Diphenylguanidinium | 98 | 63–67 | 2.33 | 3.99 | 5.90 | 7.26, 7.32, 7.43 | 322 | 15800 | 1385, 1287, 1244, 1167, 1089 | 1676, 1597, 1534 | 3372 |
| **VIII**[c] | *N*,*N*-Diphenylguanidinium (·0.5EtOH) | 48 | 103–105 | 2.34 | 4.01 | 5.91 | 7.27, 7.32, 7.43 | 324 | 15100 | 1386, 1284, 1228, 1165, 1086 | 1645, 1596, 1538 | 3178–2756 |

[a] IR spectrum was recorded in $CHCl_3$. [b] $^1$H NMR spectrum was recorded in $CDCl_3$. [c] The signals of ethanol appeared at 1.19 (t, $CH_3$) and 3.95 ppm (q, $CH_2$).

piperidine (p$K_a$ HB$^+$ 11.12), guanidine (p$K_a$ HB$^+$ 13.27), and diphenylguanidine (p$K_a$ HB$^+$ 10.12). The equimolar mixture of the reagents in ethanol or acetonitrile was incubated at room temperature for 1 h. As a result, crystalline thiolene nitronates **II–VIII** were obtained with yields of 46–98%.

In the case of the nitrosulfolene **I** reaction with *N*,*N*'-diphenylguanidine in ethanol, the resulting nitronate was isolated in the form of solvate **VIII** (nitronate:solvent = 1:0.5). Noteworthily, formation of solvates (with THF and dioxane) was previously described in the cases of some nitrosulfolene derivatives [4, 12]. In the studied case, diphenylguanidinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate **VII** was obtained in its pure form when the reaction was performed in acetonitrile; however, crystallization of the salt **VII** from ethanol resulted in the solvate **VIII**.

Ammonium 1,1-dioxo-3-methyl-2-thiolene-4-nitronates **II–VI**, **VIII** were stable colorless or pale yellow crystalline substances (see table).

Physico-chemical characteristics of the newly prepared thiolene nitronates **II–VIII** corresponded to the assumed salt structure. Electronic spectra of the obtained salts contained an absorption band at $\lambda_{max}$ of 322–327 nm (ε = 10700–19100) assigned to thiolene nitronate anion [10]. The IR spectra of **II–VIII** contained the absorption bands of ionized nitro group (1384–1388, 1220–1298, 1158–1170, and 1078–1090 cm$^{-1}$), of C=C and C=N$^+$ double bonds (1596–1676 and 1514–1538 cm$^{-1}$), and of ammonium groups (2170–2759 cm$^{-1}$). In the spectra of guanidinium salts **VI–VIII** the absorption of NH groups was observed in the range of 2756–3425 cm$^{-1}$, in accordance with the published data [13]. In the spectra of thiolenenitronates **II–VIII**, the absorption bands of sulfonyl group and those of ionized nitro group overlapped [6].

The structure of **II–VIII** was confirmed by $^1$H NMR spectroscopy data (never described before). Along with the signals of ammonium cation, the $^1$H NMR spectra contained three singlet signals assigned

to olefin (5.76–5.91 ppm), methylene (3.81–4.01 ppm), and methyl (2.22–2.34 ppm) protons (see table).

The electron density distribution in the thiolene nitronate anion affected the carbon atoms chemical shifts in the $^{13}C$ NMR spectrum of salt **VII**, the spectrum interpretation was performed basing on the results of $^{1}H$–$^{13}C$ HMQC experiment. A downfield signal at 122.64 ppm (which correlated with the olefinic $C^2H$ proton singlet at 5.90 ppm) was assigned to $C^2$. The signals at 146.43 and 113.98 ppm were assigned to $C^3$ and $C^4$ $sp^2$-hybrid atoms of heterocyclic anion, respectively. The signal at 18.15 ppm was assigned to carbon atom of the methyl group. A set of signals at 125.30, 127.99, 130.42, 134.58, and 154.59 ppm was assigned to thirteen carbon atoms of diphenylguanidinium cation [14, 15].

To conclude, the interaction of 3-methyl-4-nitro-3-thiolene-1,1-dioxide with highly basic amines ($pK_a$ $HB^+$ of 8.97–13.27) proceeded selectively via deprotonation of allyl methylene group of the heterocycle to give ammonium 1,1-dioxo-3-methyl-2-thiolene-4-nitronates.

## EXPERIMENTAL

The $^{1}H$, $^{13}C$–{$^{1}H$}, and $^{1}H$–$^{13}C$ HMQC NMR spectra were recorded with Jeol ECX400A spectrometer [399.78 ($^{1}H$), 100.525 ($^{13}C$) MHz] in chloroform-$d_1$ and DMSO-$d_6$ solutions; the residual signals of non-deuterated solvents were used as internal standards. The IR spectra were recorded with Shimadzu IRPrestige-21 Fourier spectrometer in chloroform solution ($c \sim 40$ mg $ml^{-1}$) or in KBr pellets. The electronic absorption spectra were recorded with Shimadzu UV2401PC spectrophotometer in quartz cuvettes ($l = 0.1$ cm, $c = 1.0\times10^{-3}$ mol $l^{-1}$ in ethanol). Elemental analysis was performed with Eurovector EA 3000 (CHN Dual mode) analyzer.

3-Methyl-4-nitro-3-thiolene-1,1-dioxide **I** was prepared as described in [16].

**Morpholinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate (II).** A solution of 0.18 g (0.18 ml, 2 mmol) of morpholine in 10 ml of ethanol was added to 0.35 g (2 mmol) of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I**. The reaction mixture was stirred at room temperature for 1 h. The appeared white precipitate was filtered off, washed with ethanol, and dried in air. Yield 0.43 g (46%), mp 127–129ºC. Found, %: C 40.73; H 6.19; N 10.78. $C_9H_{16}N_2O_5S$. Calculated, %: C 40.90; H 6.10; N 10.60.

**Piperazinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate (III)** was prepared similarly to **II**. Yield 58%, mp 133–134ºC. Found, %: C 41.13; H 6.37; N 15.78. $C_9H_{17}N_3O_4S$. Calculated, %: C 41.05; H 6.51; N 15.96.

**Piperidinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate (IV)** was prepared similarly to **II**. Yield 90%, mp 100–103ºC. Found, %: C 46.13; H 7.019; N 10.78. $C_{10}H_{18}N_2O_4S$. Calculated, %: C 45.79; H 6.92; N 10.68.

**Cyclohexylammonium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate (V).** A solution of 0.20 g (0.23 ml, 2 mmol) of cyclohexylamine in 10 ml of ethanol was added to 0.35 g (2 mmol) of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I**. The reaction mixture was stirred at room temperature for 1 h, and then concentrated in a Petri dish. The resulting pale yellow precipitate was washed with diethyl ether and dried in air. Yield 0.41 g (75%), mp 105–107°C. Found, %: C 47.63; H 7.35; N 10.78. $C_{11}H_{20}N_2O_4S$. Calculated, %: C 47.46; H 7.24; N 10.28.

**Guanidinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate(VI).** A solution of 0.11 g (2 mmol) of potassium hydroxide in 2 ml of water was added to a solution of 0.22 g (1 mmol) of guanidinium sulfate in 3 ml of water. The resulting solution was added to a suspension of 0.35 g (2 mmol) of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I** in 10 ml of ethanol. The reaction mixture was stirred at room temperature for 1 h. The formed precipitate was filtered off. The mother liquor was evaporated in a Petri dish. The resulting pale yellow precipitate was washed with diethyl ether and dried in air. Yield 0.24 g (51%), mp 100–101°C. Found, %: C 30.25; H 5.19; N 23.28. $C_6H_{12}N_4O_4S$. Calculated, %: C 30.51; H 5.08; N 23.73.

***N*,*N*'-Diphenylguanidinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate (VII).** A suspension of 0.42 g (2 mmol) of *N*,*N*'-diphenylguanidine in 10 ml of acetonitrile was added to 0.35 g (2 mmol) of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I**. The reaction mixture was stirred at room temperature for 1 h and then concentrated in a Petri dish. The resulting pale yellow precipitate was washed with acetonitrile and dried in air. Yield 0.8 g (98%), mp 63–67°C. Found N, %: 14.21. $C_{18}H_{20}N_4O_4S$. Calculated N, %: 14.43.

***N*,*N*'-Diphenylguanidinium 1,1-dioxo-3-methyl-2-thiolene-4-nitronate ethanol solvate (VIII).** *a.* A suspension of 0.42 g (2 mmol) of *N*,*N*'-diphenyl-

guanidine in 10 ml of ethanol was added to 0.35 g (2 mmol) of 3-methyl-4-nitro-3-thiolene-1,1-dioxide **I**. The reaction mixture was stirred at room temperature for 1 h. The formed white precipitate was filtered off, washed with ethanol, and dried in air. Yield 0.39 g (48%), mp 103–105°C (ethanol). Found, %: C 55.59; H 5.94; N 13.19. $C_{18}H_{20}N_4O_4S{\cdot}0.5C_2H_5OH$. Calculated, %: C 55.47; H 5.60; N 13.63.

*b. N,N'*-Diphenylguanidinium 1,1-dioxo-3-methyl-2-thiolenyl-4-nitronate **VII** was recrystallized from ethanol. The crystals of ethanol solvate **VIII** were obtained, mp 99–102°C. Melting point of the mixture of compounds obtained via the methods *a* and *b* was not depressed. Found N, %: 13.19. $C_{18}H_{20}N_4O_4S{\cdot}0.5C_2H_5OH$. Calculated N, %: 13.63.

Physico-chemical studies were performed in the Center for Collective Use in Herzen State Pedagogical University of Russia.

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