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> LETTERS TO THE EDITOR

Heterocycles' Ring-Opening in Reactions of 3-Methyl-4-nitro-3-thiolene-1,1-dioxide with Substituted Hydrazines

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4-Nitro-3-thiolene-1,1-dioxides are the active heterocyclic sulfonitroalkenes able to interact with nucleophiles by the addition, vinyl substitution or salt formation pathways. The direction and effectiveness of these processes are determined by the nature of the substituents in the sulfolene ring, the reagents nature, and the reaction conditions [1, 2]. Thus, the addition of arylamines to the multiple bond of 3-methyl-4-nitro-3thiolene-1,1-dioxide I proceeds in refluxing ethanol. More active nucleophiles, aroylhydrazines, react at room temperature to give corresponding Michael adducts [3]. Tightening of the reaction conditions of nitrothiolene dioxide I with benzoylhydrazine at equimolar ratio in refluxing ethanol unexpectedly results in the formation of the novel open-chain structure, (2-nitroethylsulfonyl)propanone benzoylhydrazone II. The reactions of nitrosulfolene I with the more basic substituted hydrazines, semicarbazide and phenylhydrazine, give rise to similar linear nitroalkylsulfones III and IV even at room temperature.



These results suggest that the reaction of 4-nitro-3thiolene-1,1-dioxide I with the substituted hydrazines proceeds via a tandem process scheme, including the Ad_N stage followed by the sulfolane ring opening in the intermediate adducts at the C^3-C^4 bond. The studyed reaction is the first example of the sulfolane ring opening in so mild conditions, which is certainly connected with the active participation of the nitro group in this process. Indeed, the similar in character transformations accompanied by the C=C bond rupture are observed quite frequently in a series of acyclic aryl- and heterylnitroethenes. For example, the reaction of 2-(indol-3-yl)-1-nitroethene with phenylhydrazine proceeds with the removal of nitromethane to form the corresponding hydrazone [4]. A similar process accompanied with the removal of acetylnitromethane occurs in the reaction of 1-acetyl-2-(*p*-dimethylamino-phenyl)-1-nitroethene with hydrazine [5].

The structure of the synthesized products was confirmed by the spectral methods. In the IR spectra of (2-nitroethylsulfonyl)propanone hydrazones **II–IV** there are the absorption bands of the non-conjugated nitro (1550–1560, 1370–1390 cm⁻¹), sulfonyl (1300–1320, 1120–1140 cm⁻¹), NH groups (3210–3530 cm⁻¹) and C=N bond (1600–1630 cm⁻¹). In addition, the spectra of benzoylhydrazone **II** and semicarbazone **III** contain the amide bands at 1660, 1520 and 1710, 1570 cm⁻¹, respectively. The ¹H NMR spectra of the linear sulfones **II–IV** contain the singlets of methyl (1.90–2.10 ppm) and methylene (4.13–4.33 ppm) protons of the propanone hydrazone fragment. The

methylene protons of nitroethyl moieties are manifested as two triplets at 3.83–3.93 and 4.93–4.98 ppm with the spin-spin coupling constant ${}^{3}J_{\text{HH}}$ 6.41 Hz, which is typical for the vicinal protons with a free rotation around the σ -bonds [6]. The NH-protons resonate as a singlet in the weak field (9.21–10.77 ppm).

In the ¹³C NMR spectra of hydrazones **III** and **IV** there are the signals in the weak field at 134.37–137.90 ppm corresponding to the azomethine carbon atoms, as well as the signals at 68.79, 68.70 ppm, which are characteristic of the primary carbon atoms bonded with the nitro groups [6]. The assignment of the signals of $C^{2'}$ and C^{1} (62.00, 61.83 ppm) and $C^{1'}$ (48.50, 48.61 ppm) was made on the basis of the ¹H–¹³C HMQC experiment.

The starting 3-methyl-4-nitro-3-thiolene 1,1-dioxide I was obtained by a modified method [7].

(2-Nitroethylsulfonyl)propanone benzoylhydrazone (II). Yield 21%, mp 154–156°C (ethanol). IR spectrum, v, cm⁻¹: 1310, 1120 (SO₂), 1555, 1370 (NO₂), 1620 (C=N), 1660, 1520 (C(O)NH), 3335 (NH). ¹H NMR spectrum, δ , ppm (*J*, Hz): 2.10 s (3H, CH₃), 3.93 t (2H, C¹H₂), 4.33 s (2H, C¹H₂), 4.98 t (2H, C²H₂, ³*J* 6.41), 7.44 m, 7.50 m, 7.81 m (5H, Ph), 10.77 s (1H, NH). Found, %: C 46.34; H 5.01; N 13.20. C₁₂H₁₅N₃O₅S. Calculated, %: C 46.00; H 4.83; N 13.41.

(2-Nitroethylsulfonyl)propanone semicarbazone (III). Yield 80%, mp 128–131°C (ethanol). IR spectrum, v, cm⁻¹: 1300, 1140 (SO₂), 1550, 1390 (NO₂), 1630 (C=N), 1710, 1570 [C(O)NH], 3530, 3410, 3210 (NH). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.90 s (3H, CH₃), 3.83 t (2H, C¹H₂, ³*J* 6.41), 4.13 s (2H, C¹H₂), 4.93 t (2H, C²H₂, ³*J* 6.41), 6.39 br. s (2H, NH₂), 9.44 s (1H, NH). ¹³C NMR spectrum, δ_{C} , ppm: 61.83 (C¹), 137.90 (C²), 17.35 (CH₃), 48.61 (C^{1'}), 68.70 (C^{2'}), 157.35 (C=O). Found, %: C 28.30; H 4.83; N 22.48. C₆H₁₂N₄O₅S. Calculated, %: C 28.57; H 4.80; N 22.22.

(2-Nitroethylsulfonyl)propanone phenylhydrazone (IV). Yield 44%, mp 125–127°C (ethanol). IR spectrum, v, cm⁻¹: 1320, 1130 (SO₂), 1560, 1390 (NO₂), 1600 (C=N), 3360 (NH). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.98 s (3H, CH₃), 3.88 t (2H, C¹H₂, ³*J* 6.41), 4.23 s (2H, C¹H₂), 4.98 t (2H, C²H₂, ³*J* 6.41), 6.72 m, 7.08 m, 7.15 m (5H, Ph), 9.21 s (1H, NH). ¹³C NMR spectrum, δ_{C} , ppm: 62.00 (C¹), 134.37 (C²), 17.41 (CH₃), 48.50 (C¹), 68.79 (C^{2'}), 113.20, 119.76, 129.40, 146.07 (C₆H₅). Found, %: C 46.63; H 5.52; N 14.79. C₁₁H₁₅N₃O₄S. Calculated, %: C 46.31; H 5.30; N 14.73.

The ¹H, ¹³C–{¹H}, ¹H–¹³C HMQC NMR spectra were recorded on a Jeol ECX400A spectrometer operating at 399.78 (¹H) and 100.525 MHz (¹³C) in (CD₃)₂SO, using the residual signals of the nondeuterated solvent as an internal standard. The IR spectra were obtained on a Shimadzu IR-21 Prestige Fourier spectrometer (KBr). The elemental analysis was performed on an Eurovector EA3028 analyzer.

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