

LETTERS TO THE EDITOR

1-Nitrocyclohexene and 3-Methyl-4-nitro-3-thiolene 1,1-Dioxide in Reactions with Benzoylhydrazine and Its Analogs

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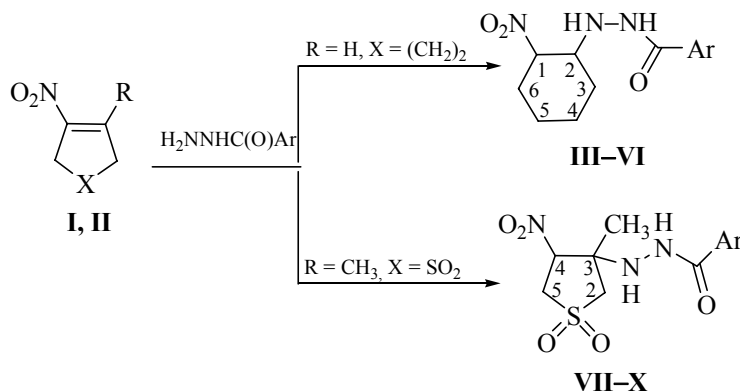
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Reactions of nitroalkenes with hydrazine and its derivatives occur ambiguously: depending on the reaction conditions and reagents nature the products of addition [1–3], transalkenylation [4] or heterocyclization [5, 6] are formed. Aiming at revealing the features of the chemical behavior of carbo- and

heterocyclic nitroalkenes (of the thiolene 1,1-dioxide series) in similar reactions, we studied a reaction of 1-nitrocyclohexene **I** and 3-methyl-4-nitro-3-thiolene 1,1-dioxide **II** with benzoic acid hydrazide and its analogs containing various substituents in the aromatic ring.



The selected *N*-nucleophiles react readily with the nitroalkenes **I**, **II** at room temperature in ethanol medium to give adducts **III–X**. The condensation involving nitrosulfolene **II** completed rapidly (in 1 h). In the case of nitrocyclohexene **I** the keeping for 24 h was required, and the reaction with *p*-chlorobenzoic acid hydrazide required an additional heating.

The structure of compounds **III–X** was established using ^1H NMR and IR spectroscopy. The ^1H NMR spectra contain signals of the protons of all structural fragments of molecules **III–X** and prove its stereo-homogeneity. Thus, methine protons at C^1 and C^2 atoms of cyclohexane ring of compound **III** appear as

multiplets at 4.47 and 3.36 ppm, respectively; hydrazide fragment ($-\text{NHNHCO}-$) protons give rise to singlets at 4.76 and 8.33 ppm, in agreement with the published data for *N*-alkylsubstituted hydrazides [7]. In the spectra of aminonitrosulfolane derivatives **VII–X** the signals of the corresponding proton groups are shifted downfield.

The IR spectra of compounds **III–X** contain absorption bands of the nonconjugated nitro group ($1379\text{--}1386, 1551\text{--}1559\text{ cm}^{-1}$), amide carbonyl ($1624\text{--}1648\text{ cm}^{-1}$), aromatic multiple bonds ($1580\text{--}1602\text{ cm}^{-1}$), and NH groups ($3248\text{--}3312\text{ cm}^{-1}$); in the spectra of hydrazinonitrothiolane 1,1-dioxides there are addi-

tionally absorption bands belonging to sulfonyl group (1126–1129, 1316–1318 cm^{-1}).

The initial 1-nitrocyclohexene **I** and 3-methyl-4-nitro-3-thiolene 1,1-dioxide **II** were obtained by the modified procedures [8] and [9], respectively.

2-(Benzoylhydrazino)-1-nitrocyclohexane (III). Yield 78%, mp 133–136°C (ethanol–water, 1:1). IR spectrum, ν , cm^{-1} : 1381, 1559 (NO_2), 1580 ($\text{C}=\text{C}_{\text{Ar}}$), 1627 ($\text{C}=\text{O}$), 3297, 3312 (NH). ^1H NMR spectrum, δ , ppm: 1.30–1.73 m (6H, C^3H_2 , C^4H_2 , C^5H_2), 1.93–2.05 m (2H, C^6H_2), 3.36 m (1H, C^2H), 4.47 m (1H, C^1H), 4.76 br.s (1H, NH), 7.45 m, 7.53 m, 7.69 m (5H, Ph), 8.33 s (1H, NHCO). Found, %: N 16.19. $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$. Calculated, %: N 15.97.

1-Nitro-2-(*o*-tolylhydrazino)cyclohexane (IV). Yield 44%, mp 122–124°C (ethanol–water, 1:1). IR spectrum, ν , cm^{-1} : 1380, 1559 (NO_2), 1597 ($\text{C}=\text{C}_{\text{Ar}}$), 1624 ($\text{C}=\text{O}$), 3253, 3280 (NH). ^1H NMR spectrum, δ , ppm: 1.31–1.78 m (6H, C^3H_2 , C^4H_2 , C^5H_2), 1.82–2.04 m (2H, C^6H_2), 2.20 s (3H, CH_3), 3.55 m (1H, C^2H), 4.45 m (1H, C^1H), 4.90 br.s (1H, NH), 7.23 m, 7.29 m, (4H, C_6H_4), 7.97 s (1H, NHCO). Found, %: N 15.11. $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_3$. Calculated, %: N 15.16.

2-(*m*-Anisoylhydrazino)-1-nitrocyclohexane (V). Yield 48%, mp 105–107°C (ethanol–water, 1:1). IR spectrum, ν , cm^{-1} : 1382, 1558 (NO_2), 1585 ($\text{C}=\text{C}_{\text{Ar}}$), 1627 ($\text{C}=\text{O}$), 3266, 3297 (NH). ^1H NMR spectrum, δ , ppm: 1.31–1.76 m (6H, C^3H_2 , C^4H_2 , C^5H_2), 1.79–2.04 m (2H, C^6H_2), 3.35 m (1H, C^2H), 3.79 s (3H, OCH_3), 4.46 m (1H, C^1H), 5.04 br.s (1H, NH), 7.07 m, 7.20 m, 7.32 m, (4H, C_6H_4), 8.32 s (1H, NHCO). Found, %: N 14.41. $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_4$. Calculated, %: N 14.33.

1-Nitro-2-(*p*-chlorobenzoylhydrazino)cyclohexane (VI). Yield 19%, mp 132–134°C (ethanol). IR spectrum, ν , cm^{-1} : 1379, 1551 (NO_2), 1594 ($\text{C}=\text{C}_{\text{Ar}}$), 1635 ($\text{C}=\text{O}$), 3248, 3303 (NH). ^1H NMR spectrum, δ , ppm: 1.31–1.73 m (6H, C^3H_2 , C^4H_2 , C^5H_2), 1.80–2.07 m (2H, C^6H_2), 3.35 m (1H, C^2H), 4.46 m (1H, C^1H), 4.70 br.s (1H, NH), 7.45 m, 7.67 m (4H, C_6H_4), 8.38 s (1H, NHCO). Found, %: N 13.68. $\text{C}_{13}\text{H}_{16}\text{ClN}_3\text{O}_3$. Calculated, %: N 14.11.

3-(Benzoylhydrazino)-3-methyl-4-nitrothiolane-1,1-dioxide (VII). Yield 56%, mp 135–137°C (ethanol). IR spectrum, ν , cm^{-1} : 1127, 1317 (SO_2), 1385, 1556 (NO_2), 1580 ($\text{C}=\text{C}_{\text{Ar}}$), 1647 ($\text{C}=\text{O}$), 3294 (NH). ^1H NMR spectrum, δ , ppm: 1.36 s (3H, CH_3), 3.42 m (2H, C^2H_2), 3.87 m, 4.04 m (2H, C^5H_2), 5.32 m (1H, C^4H), 5.55 d (1H, NH), 7.48 m, 7.58 m, 7.82 m

(5H, Ph), 8.53 d (1H, NHCO). Found, %: N 13.27. $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_5\text{S}$. Calculated, %: N 13.41.

3-Methyl-4-nitro-3-(*o*-tolylhydrazino)thiolane-1,1-dioxide (VIII). Yield 49%, mp 115–117°C (ethanol). IR spectrum, ν , cm^{-1} : 1129, 1316 (SO_2), 1386, 1558 (NO_2), 1602 ($\text{C}=\text{C}_{\text{Ar}}$), 1638 ($\text{C}=\text{O}$), 3264, 3290 (NH). ^1H NMR spectrum, δ , ppm: 1.35 s (3H, CH_3), 2.39 s (3H, CH_3), 3.43 m (2H, C^2H_2), 3.83 m, 4.03 m (2H, C^5H_2), 5.33 m (1H, C^4H), 5.52 d (1H, NH), 7.27 m, 7.35 m, 7.41 m (4H, C_6H_4), 8.33 d (1H, NHCO). Found, %: N 12.64. $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_5\text{S}$. Calculated, %: N 12.84.

3-(*m*-Anisoylhydrazino)-3-methyl-4-nitrothiolane-1,1-dioxide (IX). Yield 75%, mp 123–125°C (ethanol). IR spectrum, ν , cm^{-1} : 1126, 1318 (SO_2), 1386, 1558 (NO_2), 1583 ($\text{C}=\text{C}_{\text{Ar}}$), 1648 ($\text{C}=\text{O}$), 3296 (NH). ^1H NMR spectrum, δ , ppm: 1.36 s (3H, CH_3), 3.42 m (2H, C^2H_2), 3.83 s (3H, OCH_3), 3.86 m, 4.03 m (2H, C^5H_2), 5.31 m (1H, C^4H), 5.53 d (1H, NH), 7.12 m, 7.34 m, 7.39 m (4H, C_6H_4), 8.58 (1H, NHCO). Found, %: N 12.37. $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_6\text{S}$. Calculated, %: N 12.24.

3-Methyl-4-nitro-3-(*p*-chlorobenzoylhydrazino)-thiolane 1,1-dioxide (X). Yield 62%, mp 128–130°C (ethanol). IR spectrum, ν , cm^{-1} : 1126, 1317 (SO_2), 1386, 1559 (NO_2), 1596 ($\text{C}=\text{C}_{\text{Ar}}$), 1646 ($\text{C}=\text{O}$), 3289 (NH). ^1H NMR spectrum, δ , ppm: 1.38 s (3H, CH_3), 3.45 m (2H, C^2H_2), 3.90 m, 4.08 m (2H, C^5H_2), 5.35 m (1H, C^4H), 5.55 d (1H, NH), 7.50 m, 7.80 m (4H, C_6H_4), 8.85 d (1H, NHCO). Found, %: N 11.76. $\text{C}_{12}\text{H}_{14}\text{ClN}_3\text{O}_5\text{S}$. Calculated, %: N 12.09.

The ^1H NMR spectra were registered on a Jeol ECX400A spectrometer at operating frequencies 399.78 MHz in CD_3CN using the signals of the residual protonated solvents as reference signals. The IR spectrum was taken on a Shimadzu IR-21 Prestige Fourier-spectrometer from KBr. The elemental analysis was performed on a Eurovector EA3028 analyzer. The reaction progress was monitored by TLC on Silufol UV-254 plates with detection on a chromatoscope.

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