

SHORT  
COMMUNICATIONS

## Unusual Reaction of 1,3-Thiazole-2-thiones with *N*-(*O*-Nitrophenyl)-*C*-substituted Nitrile Imines

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Compounds containing a C=S bond are highly reactive in 1,3-dipolar cycloaddition. Reactions of versatile thiocarbonyl compounds with nitrile imines give rise to substituted thiadiazoles [1–3].

Reactions of 1,3-thiazole-2-thiones with various *C,N*-disubstituted nitrile imines generated *in situ* by treating appropriate hydrazonoyl chlorides with triethylamine proceed along the common route of [3+2]cycloaddition affording in most cases stable spiro compounds **III**.

However if in the benzene ring of nitrile imine a nitro group is located in the *ortho*-position to nitrogen [4, 5] the reaction occurs in uncommon way furnishing acyclic compounds **V** as the main product. Yet with an exocyclic C=S bond such nitrile imines react to form stable spiro compounds [6].

We presume that spiro compound **A** arising in the first stage is unstable and suffers further transformations. The

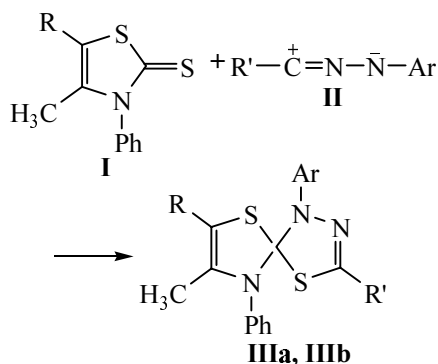
decomposition probably starts by the rupture of the C–S bond in the thiazole ring providing a bipolar ion **B**. The bipolar ion undergoes stabilization by migration of the *o*-nitrophenyl moiety to the sulfur atom.

The structure of compounds **IIIb** and **Va** obtained was proved by X-ray diffraction analysis.

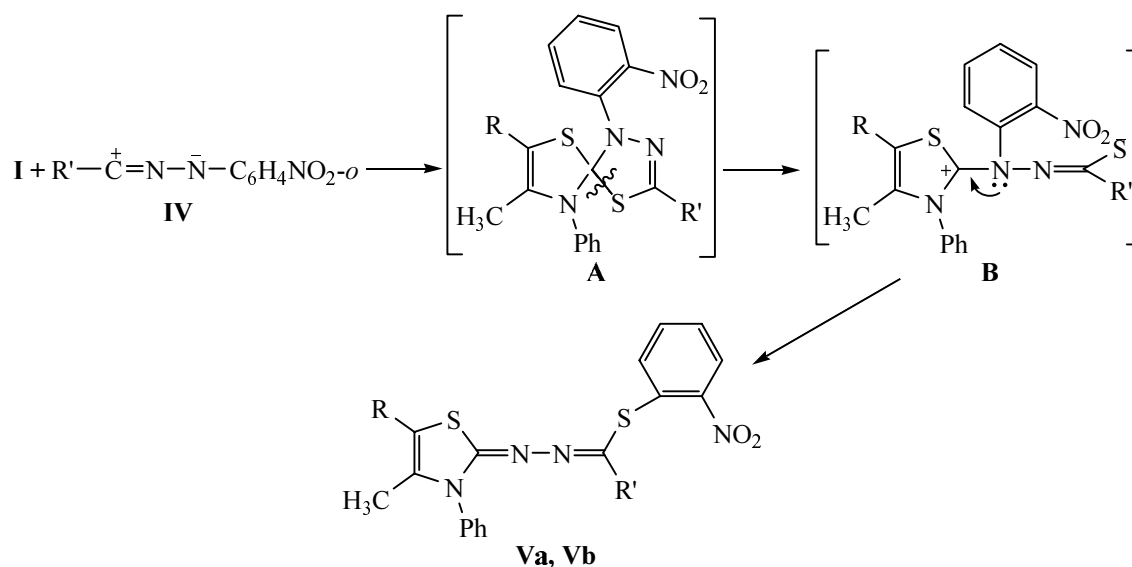
Initial 1,3-thiazole-2-thiones were prepared by treatment of ethyl  $\alpha$ -chloroacetoacetate or 3-chloroacetylacetone with ammonium *N*-phenyldithiocarbamates [7].

**Reaction of 1,3-thiazole-2-thione with hydrazonoyl chlorides.** To a mixture of 0.004 mol of 1,3-thiazole-2-thione (**I**) and 0.004 mol of an appropriate hydrazonoyl chloride **II** or **IV** in 15–20 ml of dichloromethane was added 20 ml of 2-propanol and 1 ml (0.007 mol) of triethylamine. The reaction mixture was left overnight at room temperature. Then the solution was concentrated, the separated precipitate was filtered off, washed with 50% 2-propanol, and recrystallized from acetone or acetonitrile.

**3-Acetyl-7-methyl-8-methoxycarbonyl-1-(4-nitrophenyl)-6-phenyl-4,9-dithia-1,2,6-triazaspiro[4.4]nona-2,7-diene (IIIa).** Yield 78%, mp 168–170°C (from acetonitrile). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.05 s (3H, CH<sub>3</sub>), 2.29 s [3H, CH<sub>3</sub>C(O)], 3.73 s [3H, CH<sub>3</sub>OC(O)], 6.65–8.33 m (9H, Ar). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 14.31 (CH<sub>3</sub>), 24.38 [CH<sub>3</sub>C(O)], 51.22 [CH<sub>3</sub>OC(O)], 114.35 (C<sup>5</sup>), 117.99 (C<sup>8</sup>), 145.67 (C<sup>7</sup>), 146.93 (C<sup>3</sup>), 163.01 [CH<sub>3</sub>OC(O)], 190.73 [CH<sub>3</sub>C(O)], 125.26, 129.70, 130.02, 135.74, 143.53, 145.14 (Ar). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 471 (100) [ $M$ ]<sup>+</sup>, 266 (30) [C<sub>12</sub>H<sub>12</sub>NO<sub>2</sub>S<sub>2</sub>]<sup>+</sup>. Found, %: C 53.43; H 4.03; N 11.70. C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>5</sub>S<sub>2</sub>. Calculated, %: C 53.61; H 3.86; N 11.91.



R = CH<sub>3</sub>OC(O), R' = CH<sub>3</sub>C(O), Ar = C<sub>6</sub>H<sub>4</sub>NO<sub>2-p</sub> (**a**); R = CH<sub>3</sub>C(O), R' = C<sub>2</sub>H<sub>5</sub>OC(O), Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>3-p</sub> (**b**).



R = C<sub>2</sub>H<sub>5</sub>OC(O), R' = CH<sub>3</sub>C(O) (a); R = CH<sub>3</sub>C(O), R' = C<sub>2</sub>H<sub>5</sub>OC(O) (b).

**8-Acetyl-7-methyl-1-(4-methylphenyl)-6-phenyl-3-ethoxycarbonyl-4,9-dithia-1,2,6-triazaspiro[4.4]nona-2,7-diene (IIIb).** Yield 75%, mp 170–172°C (from acetone). <sup>1</sup>H NMR spectrum, δ, ppm: 1.25 t [3H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 2.05 s (3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 2.25 s (3H, CH<sub>3</sub>), 2.35 s [3H, CH<sub>3</sub>C(O)], 4.20 q [2H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 7.10–7.45 m (9H, Ar). <sup>13</sup>C NMR spectrum, δ, ppm: 13.81 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 15.51 (CH<sub>3</sub>), 20.25 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 29.54 [CH<sub>3</sub>C(O)], 61.72 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 109.33 (C<sup>5</sup>), 113.30 (C<sup>8</sup>), 137.42 (C<sup>7</sup>), 144.12 (C<sup>3</sup>), 158.97 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 188.56 [CH<sub>3</sub>C(O)], 117.89, 129.24, 129.50, 132.24, 133.15, 135.35 (Ar). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 453 (30) [M]<sup>+</sup>, 249 (30) [C<sub>12</sub>H<sub>11</sub>NOS<sub>2</sub>]<sup>+</sup>, 250 (10) [C<sub>12</sub>H<sub>12</sub>NOS<sub>2</sub>]<sup>+</sup>, 204 (5) [C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>. Found, %: C 61.88; H 5.02; N 10.24. C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>5</sub>S<sub>2</sub>. Calculated, %: C 61.59; H 4.68; N 10.26.

**1-[Acetyl(2-nitrophenylthio)methylene]-2-[4-methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazole-2(3*H*)-ylidene]hydrazine (Va).** Yield 70%, mp 153–155°C (from acetonitrile). <sup>1</sup>H NMR spectrum, δ, ppm: 1.36 t [3H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 2.23 s (3H, CH<sub>3</sub>), 2.52 s [3H, CH<sub>3</sub>C(O)], 4.31 q [2H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 7.04–7.94 m (9H, Ar). <sup>13</sup>C NMR spectrum, δ, ppm: 13.76 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 14.12 (CH<sub>3</sub>), 26.12 [CH<sub>3</sub>C(O)], 61.17 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 106.25 (C<sup>5</sup>), 146.51 (C<sup>4</sup>), 147.45 (C<sup>2</sup>), 160.81 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 172.38 (N=C–S), 193.79 [CH<sub>3</sub>C(O)], 125.40, 126.84, 127.68, 129.41, 130.65, 131.81, 133.02, 134.86, 146.93 (Ar). Found, %: C 54.99; H 4.41; N 11.58. C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub>S<sub>2</sub>. Calculated, %: C 54.53; H 4.16; N 11.56.

**1-[2-(Nitrophenylthio)ethoxycarbonylmethylene]-2-[5-acetyl-4-methyl-3-phenyl-1,3-thiazole-2(3*H*)-ylidene]hydrazine (Vb).** Yield 98%, mp 167–167.5°C (from acetonitrile). <sup>1</sup>H NMR spectrum, δ, ppm: 1.10 t [3H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 2.25 s (3H, CH<sub>3</sub>), 2.46 s [3H, CH<sub>3</sub>C(O)], 4.04 q [2H, CH<sub>3</sub>CH<sub>2</sub>OC(O)], 7.19–8.01 m (9H, Ar). <sup>13</sup>C NMR spectrum, δ, ppm: 13.56 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 14.63 (CH<sub>3</sub>), 26.58 [CH<sub>3</sub>C(O)], 61.76 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 117.32 (C<sup>5</sup>), 142.89 (C<sup>4</sup>), 148.50 (C<sup>2</sup>), 161.34 [CH<sub>3</sub>CH<sub>2</sub>OC(O)], 171.28 (N=C–S), 189.25 [CH<sub>3</sub>C(O)], 125.45, 127.98, 128.32, 129.04, 129.56, 132.97, 133.43, 135.18, 145.51 (Ar). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 485 (100) [M]<sup>+</sup>, 231 (10) [C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>OS]<sup>+</sup>. Found, %: C 54.72; H 4.41; N 11.43. C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub>S<sub>2</sub>. Calculated, %: C 54.53; H 4.16; N 11.56.

<sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra were registered on spectrometer Bruker AM-500 from 20% solutions of compounds in DMSO-*d*<sub>6</sub>. Mass spectra were measured on a mass spectrometer MKh-1321, vaporizer temperature 120°C, ionizing chamber temperature 200°C, ionizing electrons energy 70 eV. The reaction progress was monitored by TLC on Silufol UV-254 plates, development under UV irradiation.

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