

SHORT  
COMMUNICATIONS

## Synthesis of 4-(1-Adamantyl)-1,3-dithiol-2-thione from 4-(1-Adamantyl)-1,2,3-thiadiazole

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Received February 22, 2008

DOI: 10.1134/S1070428008070269

Derivatives of 1,3-dithiol-2-thione find application as biologically active substances and initial compounds for the synthesis of organic metals [1]. The majority of adamantyl-substituted compounds in their turn possess biological action [2]. Of adamantyl-substituted 1,3-dithiol-2-thiones only 4,5-diadamantyl-1,3-dithiol-2-thione is known obtained by reduction of 3,4-di(1-adamantyl)-1,2-dithiete with  $\text{LiEt}_3\text{BH}$  followed by treating with hydrogen sulfide [3].

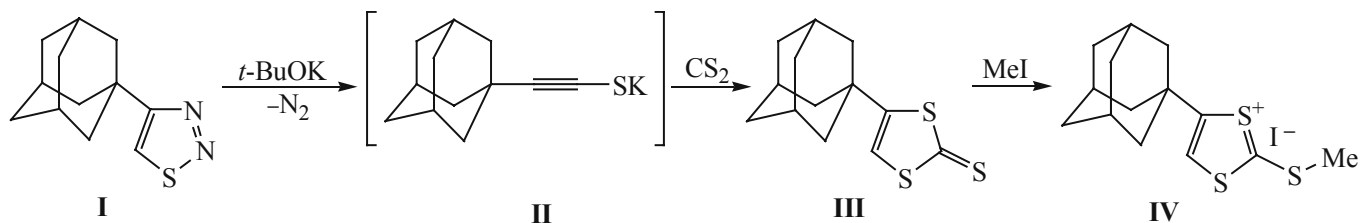
We developed a new preparation method for previously unknown 4-adamantyl-1,3-dithiol-2-thione from the available 4-(1-adamantyl)-1,2,3-thiadiazole. The initial 4-(1-adamantyl)-1,2,3-thiadiazole we recently obtained from 1-adamantyl methyl ketone through the formation of the corresponding ethoxycarbonyl-hydrazone followed by the treatment with the thionyl chloride [4].

4-(1-Adamantyl)-1,2,3-thiadiazole (**I**) under the action of a strong base like potassium *tert*-butylate in anhydrous THF easily decomposed with nitrogen liberation and the formation of potassium 2-(1-adamantyl)-ethynethiolate (**II**) [4]. At the subsequent treatment of the reaction mixture with excess hydrogen sulfide we obtained 4-(1-adamantyl)-1,3-dithiol-2-thione (**III**).

The structure of 4-(1-adamantyl)-1,3-dithiol-2-thione (**III**) was proved by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and mass spectra,

and also by chemical reactions. In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1,3-dithiol-2-thione **III** the proton and  $^{13}\text{C}$  signals both by the chemical shifts and multiplicity resemble the analogous spectra of 4,5-diadamantyl-1,3-dithiol-2-thione [3]. The proton signal  $\text{H}^5$  of dithiol ring appeared as a singlet at 7.07 ppm in agreement with the known data for the 4-substituted 1,3-dithiol-2-thiones [5]. In the mass spectrum of 1,3-dithiol-2-thione **III** the molecular ion peak was detected whose isotope composition was consistent with the calculated one and confirmed the presence in the molecule of three sulfur atoms. The main direction of the molecular ion fragmentation for 1,3-dithiol-2-thione **III** was the rupture of the adamantane–heterocycle bond and the formation of a stable adamantyl ion, although the elimination from the molecular ion of the alkyl radical  $\text{C}_4\text{H}_9$  was also observed as was characteristic of adamantane and its derivatives [6].

The formation of dithiolium salts is characteristic of 1,3-dithiol-2-thiones [1]. In the same manner the treatment with excess methyl iodide converted 4-(1-adamantyl)-1,3-dithiol-2-thione (**III**) into 4-(1-adamantyl)-2-methylsulfanyl-1,3-dithiolium iodide (**IV**). The structure of dithiolium iodide **IV** was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and mass spectra. For instance, in contrast to the  $^1\text{H}$  NMR spectrum of initial 1,3-dithiol-2-thione **III** in the



spectrum of dithiolium iodide **IV** appeared a singlet from the protons of the MeS group at 2.13 ppm, and the singlet of the H<sup>5</sup> proton of the dithiol ring shifted upfield by 0.5 ppm under the effect of the positive charge. In the <sup>13</sup>C NMR spectrum of dithiolium iodide **IV** the <sup>13</sup>C signal of the thiomethyl group was observed at 24.02 ppm. In the mass spectrum of dithiolium iodide **IV** the molecular ion was not found but strong peaks were observed from the products of the salt dissociation: methyl iodide and 4-(1-adamantyl)-1,3-dithiol-2-thione (**III**). The rest of ions corresponded to the fragmentation of ions of methyl iodide and 4-(1-adamantyl)-1,3-dithiol-2-thione (**III**).

**4-(1-Adamantyl)-1,3-dithiol-2-thione (III).** To a solution of 0.5 g (2.22 mmol) of thiadiazole **I** in 25 ml of anhydrous THF was added at room temperature 0.28 g (2.5 mmol) of potassium *tert*-butylate. The reaction mixture was stirred for 5 min till the end of gas evolution, and therewith a precipitate of potassium thiolate **II** settled from the solution. Then a solution of 0.2 g (2.6 mmol) of hydrogen sulfide in 15 ml of anhydrous THF was added. The reaction mixture was stirred for 2 h and then poured into 150 ml of water and extracted with chloroform (3×15 ml). The combined extracts were dried with anhydrous sodium sulfate, filtered, boiled with activated carbon, filtered, and evaporated. On recrystallization from ethanol we obtained 0.5 g (61%) of chromatographically pure 1,3-dithiol-2-thione **III** (eluent ethyl acetate–hexane, 1:10; hexane–acetone–ether, 5:2:1). Yellow plate crystals, mp 176–177°C. <sup>1</sup>H NMR spectrum, (DMSO-*d*<sub>6</sub>), δ, ppm: 1.76 br.s (3CH<sub>2</sub>, Ad), 1.87 s (3CH<sub>2</sub>, Ad), 2.07 s (3CH, Ad), 7.07 s (H<sup>5</sup>, Ht). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), ppm: 28.09 (CH, Ad), 35.56 + 43.22 (CH<sub>2</sub>, Ad), 38.60 (C<sup>1</sup>, Ad), 119.38 (C<sup>5</sup>, Ht), 160.04 (C<sup>4</sup>, Ht), 212.98 (C<sup>2</sup>, Ht). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 268 (100) [M]<sup>+</sup>, 211 (8) [M – C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 174 (6), 149 (7), 135 (39) [Ad]<sup>+</sup>, 115 (9), 91 (24), 77 (22), 53 (13), 41 (33). Found, %: C 58.43, 58.26; H 5.85, 5.74. C<sub>13</sub>H<sub>16</sub>S<sub>3</sub>. Calculated, %: C 58.16; H 6.01. *M* 268.45.

**4-(1-Adamantyl)-2-methylsulfanyl-1,3-dithiolium iodide (IV).** A mixture of 0.2 g (0.7 mmol) of 1,3-dithiol-2-thione **III** and 10 ml of methyl iodide was boiled for 5 h, then the reaction mixture was cooled to room temperature. The precipitate separated on cooling was filtered off, washed with ethyl ether, and dried to obtain 0.15 g (50%) of chromatographically pure dithiolium iodide **IV** (eluent ethyl acetate–hexane, 1:10; hexane–

acetone–ether, 5:2:1). Bright red needle crystals, mp 196–197°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 1.71 κ (3CH<sub>2</sub>, Ad), 1.85 s (3CH<sub>2</sub>, Ad), 2.06 s (3CH, Ad), 2.13 s (CH<sub>3</sub>S), 6.59 s (H<sup>5</sup>, Ht). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 24.02 (CH<sub>3</sub>S), 28.19 (CH, Ad), 35.39 + 43.95 (CH<sub>2</sub>, Ad), 39.83 (C<sup>1</sup>, Ad), 132.40 (C<sup>5</sup>, Ht), 168.05 (C<sup>4</sup>, Ht), 201.79 (C<sup>2</sup>, Ht). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 268 (90) [M – CH<sub>3</sub>I]<sup>+</sup>, 211 (9) [M – CH<sub>3</sub>I – C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 174 (6), 149 (12), 142 (54) [CH<sub>3</sub>I]<sup>+</sup>, 135 (60) [Ad]<sup>+</sup>, 127 (73) [I]<sup>+</sup>, 115 (13), 97 (21), 91 (51), 77 (55), 71 (15), 65 (24), 53 (30), 45 (42), 39 (100). Found, %: C 40.69, 40.55; H 4.95, 4.77. C<sub>14</sub>H<sub>19</sub>IS<sub>3</sub>. Calculated, %: C 40.97; H 4.67. *M* 410.39.

Melting points were measured on a Boëtius heating block. <sup>1</sup>H and <sup>13</sup>C NMR spectra were registered on a spectrometer Bruker AMX-400 (400 and 100 MHz respectively), as internal references served the signals of residual protons (<sup>1</sup>H) and carbon atoms (<sup>13</sup>C) of the deuterated solvents. Mass spectra were measured on a mass spectrometer Finnigan INCOS MAT 95 with a direct sample admission into the ion source, ionizing electrons energy 70 eV, and ionization chamber temperature 200°C. The reaction progress was monitored by TLC on Silica Gel 60 F<sub>254</sub> plates, development under UV irradiation and in iodine vapor. All solvents used in the study were purified and dried by standard procedures.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 08-03-00383-a).

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