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LETTERS TO THE EDITOR

Mercaptobenzotellurazoles, New Chalcogen-Containing Heterocycles

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Nitrogen heterocycles occupy one of the leading positions in organic chemistry due to a wide spectrum of their biological activity and versatile applications in different fields of human life [1–3]. Organotellurium compounds also possess useful properties. The increasing interest in them is caused by the fact that some compounds from this class have found practical application as catalysts in a number of organic reactions, accelerators of rubber curing, inhibitors of corrosion of metals and alloys, they are used as insecticides, fungicides, components of special photomaterials, drugs in photodynamic therapy, etc. [4, 5].

The goal of the present study was to develop preparative methods of synthesis of 2-mercaptobenzotellurazole and 6-methyl-2-mercaptobenzotellurazole.

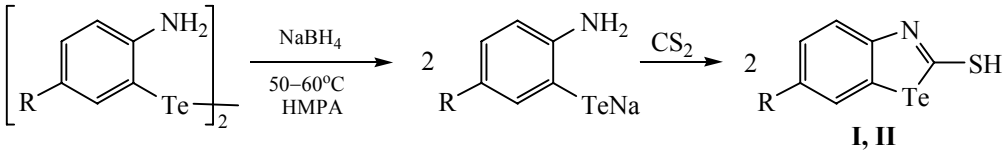
The synthesis of 2-mercaptobenzimidazole, -oxazole, and -thiazole was reported [6, 7], but there are no data in the literature on the synthesis of 2-mercaptobenzotellurazole. The known methods of synthesis of 2-mercaptobenzimidazole, -oxazole, and -thiazole using carbon disulfide or potassium xanthogenate in ethanol as the solvent cannot be applied to the synthesis of 2-mercaptobenzotellurazoles in view of a large number of side reactions and very low yields of the target compounds.

For the synthesis of 2-mercaptobenzotellurazoles **I** and **II** we have used the one-pot two-step reaction of the corresponding 2,2-diaminodiphenylditellurides with sodium borohydride and carbon disulfide in hexamethylphosporamide (HMPA); in this case, the use of CS_2 and $NaBH_4$ is not complicated by numerous side reactions providing an opportunity to obtain the target compounds in satisfactory yields (Scheme 1).

In the first step, sodium borohydride was added until steady decolorization of the reaction mixture occurred, and then carbon disulfide was charged. The yields of compounds **I** and **II** were 64% and 65%, respectively. According to ^1H NMR and IR spectroscopy and to the presence of a cross peak in the ^1H–^{15}N HMBC spectrum, compounds **I** and **II** exist in the thione form.

The mass spectrum of 2-mercaptobenzotellurazole is characterized by the most intense peak of the ion

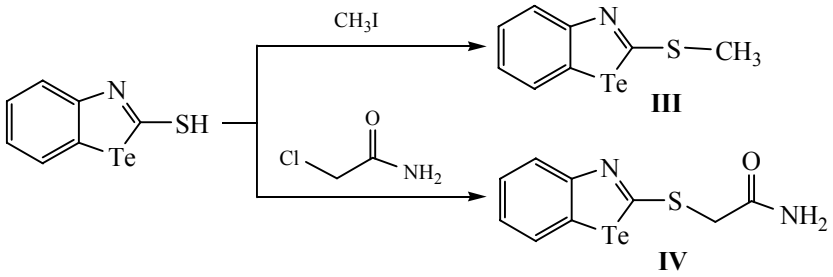
Scheme 1.



I, II

R = H (**I**), CH_3 (**II**).

Scheme 2.



with *m/z* 135 corresponding to elimination of tellurium atom and by the absence of the molecular ion peak. By the reaction of compound **I** with methyl iodide and α-chloroacetamide 2-methylmercaptobenzotellurazole **III**, and 2-acetamidomercaptobenzotellurazole **IV** were obtained in good yields (Scheme 2).

2-Mercaptobenzotellurazole (I). To the solution of 2.2 g (5 mmol) of the corresponding 2,2-diaminodiphenylditelluride [2, 3] in 25–30 mL of HMPA heated in an argon atmosphere to 40–50°C 1.33 g (0.035 mol) of sodium borohydride was added in small portions till steady decolorization occurred of the mixture. Then 7 mL (0.11 mol) of carbon disulfide was added, the mixture was stirred for 1 h at 50–60°C, filtered, to the filtrate ice water (150 mL) was added, the formed precipitate was filtered, washed with water to neutral pH, dried, and crystallized from dioxane. Yield 1.7 g (3 mmol) (64%). Yellow crystalline compound, mp 208–210°C. IR spectrum, ν, cm^{-1}: 3105 (NH), 3080–3030 (CH_{Ar}), 1630–1575 (Ar), 1525–1475, 1465–1440, 1315 (C=S). ^1H NMR spectrum, δ_H, ppm: 7.10 d.d (1H, CH(6), ^3J 7.9 Hz, ^4J 1.5 Hz), 7.30 d.d (1H, CH^5, ^3J 7.0 Hz, ^4J 1.3 Hz), 7.36 d.d (1H, CH^4, ^3J 8.1 Hz, ^4J 1.1 Hz), 7.74 d.d (1H, CH^7, ^3J 7.8 Hz, ^4J 0.9 Hz), 13.36 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 114.73 (C^4), 120.78 (C^8), 123.86 (C^5), 127.21 (C^7), 132.14 (C^6), 146.64 (C^9), 195.41 (C^2), ^{15}N NMR spectrum, δ_N: 199.40 ppm. ^{125}Te NMR spectrum, δ_{Te}: 990.15 ppm. Mass spectrum, *m/z* (I_{rel}, %): 161(11), 135 (100), 108(12), 91(7), 82(3), 76(30), 63(8), 50(13), 39 (4), 27(2). Found, %: C 32.08; H 1.98; N 5.33; S 12.23; Te 49.50. C_7H_5NSTe. Calculated, %: C 31.99; H 1.90; N 5.33; S 12.19; Te 48,59.

6-Methyl-2-mercaptobenzotellurazole (II) was prepared similarly. Yield 1.7 g (3 mmol, 65%). Yellow-orange crystals, mp 188–190°C. IR spectrum, ν, cm^{-1}: 3105 (NH), 3080–3030 (CH_{arom}), 2975-2950, 2885–2860 (CH_3), 1630–1575 (Ar), 1525-1475, 1465–1440, 1315 (C=S). ^1H NMR spectrum, δ_H, ppm: 2.26 s (3H, CH_3), 7.11 d.d (1H, CH^5, ^3J 8.2, ^4J 1.5 Hz), 7.36 d (1H, CH^4, ^3J 8.2 Hz), 7.54 d (1H, CH^7, ^4J 1.5 Hz), 13.33 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.65 (C^{11}), 120.92 (C^8), 144.74 (C^9), 114.48 (C^4), 132.14 (C^7), 128.26 (C^5), 133.32 (C^6), 194.59 (C^2). Found, %: C 34.71; H 2.54; N 5.06; S 11.56; Te 49.50. C_8H_7NSTe. Calculated, %: C 34.70; H 2.53; N 5.06; S 11.57; Te 46.13.

2-Methylmercaptobenzotellurazole (III) was obtained according to [4]. To the solution of 1.0 g (3.8 mmol) of compound **I** in 30 mL of ethanol containing 7.5 mmol of NaOH 0.26 mL (4.8 mmol) of methyl iodide was added. The obtained yellow mixture was stirred for 1 h at room temperature and kept for 5 h. The formed precipitate was filtered, washed with water to neutral pH, dried, and crystallized from isopropanol. Yield 0.58 g (2.1 mmol, 58 %). White crystals, mp 115–117°C. IR spectrum, cm^{-1}: 3067–3043 (CH_{arom}), 2900–2811 (CH_3), 1613–1574, 1549–1420. ^1H NMR spectrum, δ_H, ppm: 2.67 s (3H, CH_3), 7.07–7.10 m (1H, CH^4, 7.34–7.37 m (1H, CH^7, 7.37–7.82 m (1H, CH^5, 7.94 c (1H, CH^6). ^{13}C NMR spectrum, δ_C, ppm: 17.07 (C^{11}), 123.30 (C^5), 123.60 (C^4), 126.56 (C^6), 123.59 (C^7), 133.16 (C^8), 160.29 (C^9), 168.64 (C^2). ^{15}N NMR spectrum, δ_N: 173.73 ppm. ^{125}Te NMR spectrum, δ_{Te}: 986.05 ppm. Found, % C 34.71; H 2.55; N 5.06; S 11.58. C_8H_7NSTe. Calculated, % C 34.70; H 2.53; N 5.06; S 11.57.

2-Acetamidomercaptobenzotellurazole (IV) was obtained according to [4]. To the solution of sodium ethoxide prepared from 0.08 g Na (3.8 mmol) and 25 mL of anhydrous ethanol, 1 g (3.8 mmol) of compound **I** was added in small portions at stirring. To the obtained mixture the solution of 0.33 g (3.5 mmol) of α-chloroacetamide in 15 mL of anhydrous ethanol was added, the mixture was stirred for 2 h at room temperature, filtered, the filtrate was diluted with cold water, the formed precipitate was dried and crystallized from ethanol. Yield 0.93 g (3.5 mmol,

77%). White crystals, mp 188–190°C. IR spectrum, cm^{-1}: 3174 (NH), 3047–3000 (CH_{arom}), 2950–2900 (CH_3), 1659 (C=O), 1621–1576, 1452–1426 (Ar), 1370 (C=S). ^1H NMR spectrum, δ_H, ppm: 3.95 s (2H, CH_2), 7.09 m (1H, CH^5, 7.24 s and 7.67 s (NH_2), 7.35 m (1H, CH^6), 7.80 m (1H, CH^4), 7.97 m (1H, CH^7). ^{13}C NMR spectrum, δ_C, ppm: 37.31 (C^{11}), 123.53 (C^5), 123.66 (C^4), 126.50 (C^6), 131.92 (C^7), 133.87 (C^8), 159.66 (C^9), 166.50 (C^{12}), 169.13 (C^2). ^{15}N NMR spectrum, δ_N: 109.14 ppm. ^{125}Te NMR spectrum, δ_{Te}: 1001.50 ppm. Found, %: C 32.50; H 2.52; N 8.76; S 10.02; Te 39.89. $C_9H_8N_2OSTe$. Calculated, %: C 33.80; H 2.52; N 8.76; S 10.01; Te 39.92.

^1H, ^{13}C, ^{15}N and ^{125}Te NMR spectra were registered on Avance 600 (Bruker) and Avance 400 (Bruker) instruments from 20% solutions in DMSO-d_6. Chemical shifts are given with respect to residual proton and carbon signals of the solvent, 2.49 ppm and 39.5 ppm. IR spectra were taken on Bruker VERTEX-70 instrument in KBr in the range 400–4000 cm^{-1}. Chromatomass spectrometry analysis was performed on a Maestro 7820A instrument with mass-selective detector Agilent 5975 (AligentTechnologies) in electron impact mode with ionizing electrons energy 70 eV, equipped with capillary column HP-5ms. L = 30 m, d = 0.25 mm, isothermal mode at 45°C and in temperature programming regime from 45 to 250°C, heating rate 15 deg/min, time of analysis 30 min, carrier gas helium. Melting points were determined in the apparatus in open capillaries.

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