


Short Note

7-Bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one

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Abstract: New heterocyclic systems containing 1,2,5-chalcogenadiazoles are of great interest for the creation of organic photovoltaic materials and biologically active compounds. In this communication, 3,6-dibromopyridazine-4,5-diamine was investigated in reaction with selenium dioxide in order to obtain 4,7-dibromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazine. We found that 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one, the first representative of the new heterocyclic system, was isolated as a hydrolysis product of the corresponding 4,7-dibromoderivative. The structure of the newly synthesized compound was established by means of elemental analysis, high-resolution mass spectrometry, ¹H, ¹³C NMR, IR and UV spectroscopy, and mass spectrometry.

Keywords: [1,2,5]selenadiazolo[3,4-*d*]pyridazines; selenium dioxide; 3,6-dibromopyridazine-4,5-diamine; ring closure



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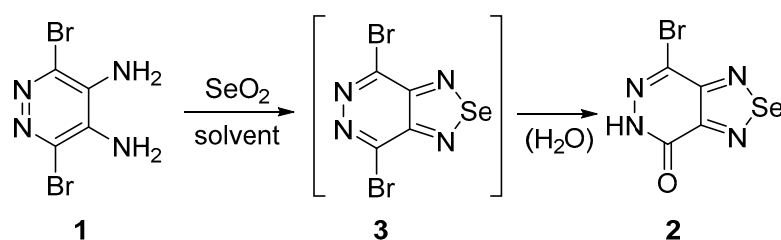
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1. Introduction

Ortho-Diamine moiety in benzene or heterocyclic rings is often used for the construction of fused 1,2,5-chalcogeno (thia, seleno, telluro) diazoles [1–4], which are of great interest as various photovoltaic materials, i.e., organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), and others [5–10]. 4,7-Dibromo derivatives of these heterocyclic systems are the most convenient precursors for the synthesis of photoactive materials [11]. Recently, we synthesized one of the interesting precursors for fused 1,2,5-chalcogenadiazolopyridazines—3,6-dibromopyridazine-4,5-diamine **1** [12]. Herein, we report on the study of the reaction between 3,6-dibromopyridazine-4,5-diamine **1** and selenium dioxide and the synthesis of 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2**, the first representative of a new heterocyclic system.

2. Results and Discussion

As a rule, cyclization of aromatic and heteroaromatic *ortho*-diamines was carried out with selenium dioxide in ethanol, less often in water, acetic acid, and MeCN [1]. It was found that the treatment of 3,6-dibromopyridazine-4,5-diamine **1** with SeO₂ in EtOH under reflux after 1 h led to the formation of 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2** in good yield (Table 1, Entry 1). Apparently the isolation of this product is the result of hydrolysis of the initially formed 4,7-dibromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazine **3** (Scheme 1). The ease of hydrolysis of 4,7-dibromo[1,2,5]chalcogenadiazolo[3,4-*d*]pyridazines into a monohydroxy derivative has been previously described for its closest analogue—thiadiazopyridazine [13]. Unfortunately, replacing ethanol with dry acetonitrile and using magnesium sulfate or molecular sieves as dehydrating agents did not change the result of the reaction; compound **2** was isolated in all cases with approximately the same yield (Table 1, Entries 2–4).



Scheme 1. Synthesis of 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2**.

Table 1. Reaction of 3,6-dibromopyridazine-4,5-diamine **1** with SeO₂.

Entry	Solvent	Dehydrating Agent	Temperature, °C	Time, h	Yield of 2 , %
1	EtOH	-	78	1	75
2	MeCN	-	81	1	77
3	MeCN	MgSO ₄	81	1	76
4	MeCN	Molecular sieves	81	1	75

The structure of 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2** was confirmed by means of elemental analysis, high-resolution mass spectrometry, ¹H, ¹³C NMR, UV and IR spectroscopy, and mass spectrometry. Compared with the starting amine **1**, in the weak field of the ¹H NMR spectrum of compound **2**, one singlet ($\delta_{\text{H}} = 12.88$ ppm) is observed, corresponding to the proton of the NH group of the pyridazine ring. This confirms both the fact of the closure of the selenadiazole ring from diamine **1** and the absence of the second bromine atom in the pyridazine ring. The ¹³C NMR spectrum shows a signal from the carbonyl amide group ($\delta_{\text{C}} = 157.6$ ppm), as well as three signals from the carbons of the pyridazine ring with chemical shifts δ_{C} 126.6, 153.0, and 155.3 ppm.

In conclusion, it was shown that the reaction of 3,6-dibromopyridazine-4,5-diamine **1** with selenium dioxide gave 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2** apparently as a hydrolysis product of the intermediate 4,7-dibromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazine **3**. This result led to the formation of a new heterocyclic system and opened up possibilities to its further functionalization to obtain compounds with useful physical properties.

3. Materials and Methods

3,6-Dibromopyridazine-4,5-diamine **1** was prepared according to the published method [12]. The solvents and reagents were purchased from commercial sources and used as received. Elemental analysis was performed on a 2400 Elemental Analyzer (Perkin Elmer Inc., Waltham, MA, USA). The melting point was determined on a Kofler hot-stage apparatus and is uncorrected. ¹H and ¹³C-NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in DMSO-*d*₆ solution, with TMS as the standard. MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). IR spectrum was measured with a Bruker "Alpha-T" instrument in KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). The measurement was performed in a positive ion mode (interface capillary voltage—4500 V) or in a negative ion mode (3200 V); the mass range was from *m/z* 50 to *m/z* 3000 Da; external or internal calibration was performed with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The interface temperature was set at 180 °C. Solution UV–visible absorption spectra were recorded using a OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer controlled with SF-2000 software. All

samples were measured in a 1 cm quartz cell at room temperature with 1×10^{-4} mol/mL concentration in DMSO.

Synthesis of 7-bromo-[1,2,5]selenadiazolo[3,4-*d*]pyridazin-4(5*H*)-one **2** (Supplementary Materials).

A mixture of 3,6-dibromopyridazine-4,5-diamine **1** (100 mg, 0.37 mmol) and SeO₂ (49 mg, 0.45 mmol) in CH₃CN (8.0 mL) was refluxed with stirring for 1 hour, cooled to room temperature. The CH₃CN was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent: EtOAc–CH₂Cl₂, 1:5, *v/v*). Yield 79 mg (77%), yellow solid, mp = >250 °C, R_f = 0.3 (EtOAc–CH₂Cl₂, 1:10, *v/v*). ¹H NMR (ppm): δ 12.88 (s, 1H, NH). ¹³C NMR (ppm): δ 157.6 (C=O), 155.3 (C(Br)–C=N), 153.0 (C–Br), 126.6 (C(O)–C=N). HRMS (ESI-TOF), *m/z*: calcd for C₄H⁷⁹BrN₄OSe [M + Na]⁺, 302.8387, found, 302.8386. MS (EI, 70 eV), *m/z* (*I*, %): 283 ([M + 3]⁺, 4), 282 ([M + 2]⁺, 35), 281 ([M + 1]⁺, 10), 280 ([M]⁺, 41), 279 ([M – 1]⁺, 6), 278 ([M – 2]⁺, 12), 277 ([M – 3]⁺, 5), 225 (8), 97 (30), 80 (50), 57 (80), 43 (100). IR spectrum, ν , cm⁻¹: 3181, 3090, 2926, 2887 (NH), 1681 (C=O), 1495, 1386, 1364, 1342, 1284, 1146, 1040, 960, 771, 755, 706, 625, 548, 504, 444. UV–Vis spectrum (in DMSO), λ_{\max} : 254 nm ($\epsilon = 7426 \text{ M}^{-1} \text{ cm}^{-1}$), 301 nm ($\epsilon = 6185 \text{ M}^{-1} \text{ cm}^{-1}$), 360 nm ($\epsilon = 6209 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. calcd. for C₄HBrN₄OSe (279.94): C, 17.16; H, 0.36; N, 20.01. Found: C, 17.28; H, 0.39; N, 19.83.

Supplementary Materials: The following are available online: copies of ¹H, ¹³C-NMR, IR, UV and mass spectra for compound **2**.

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