Short Note

4-Bromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole)

Timofey N. Chmovzh 1,2, Daria A. Alekhina 1, Timofey A. Kudryashev 1 and Oleg A. Rakitin 1,*

1 N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospekt, 119991 Moscow, Russia; tim1661@yandex.ru (T.N.C.); alekhinadariaalex@gmail.com (D.A.A.); tp12345678@yandex.ru (T.A.K.)
2 Nanotechnology Education and Research Center, South Ural State University, 76 Lenina Avenue, 454080 Chelyabinsk, Russia
* Correspondence: orakitin@ioc.ac.ru; Tel.: +7-499-1355327

Abstract: Bromoderivatives of benzofused 1,2,5-thiadiazoles are important precursors for the synthesis of dyes, which are widely used to design effective photovoltaic materials. In this study, 4-bromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole was selectively obtained from the bromination of benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole. 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: benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazoles; bromination; 4-bromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole); synthesis

1. Introduction

Benzofused 1,2,5-thiadiazoles play an important role as electron-withdrawing building blocks in the synthesis of organic dyes which have various applications in optoelectronics [1–3]. The addition of another electron-acceptor thiadiazole ring to the 2,1,3-benzothiadiazole heterocyclic system leads to the formation of 1H,5H-benzo[1,2-c:4,5-c′]bis([1,2,5]thiadiazoles (BBTs) which have a stronger electron-withdrawing character [4,5] and provide a variety of donor-acceptor materials with a small bandgap [6,7]. Unexpectedly, its benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole isomers (iso-BBTs), differing only in the order of atoms in the five-membered rings, have been practically unstudied as building blocks. This is because 4-bromo- 1 and 4,8-dibromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazoles 2, which could serve as efficient intermediates for photovoltaic materials, have never been isolated in pure state or characterized. These compounds have only been identified in an inseparable mixture of benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole 3 and its mono-bromo 1 and bis-bromo 2 derivatives obtained by the nitrosation of 2,5-diaminobenzene-1,4-dithiol 3 in hydrobromic acid [8]. Herein, we report the selective synthesis of 4-bromobenzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole 1 by the reaction of benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole 3 with bromine.

2. Results and Discussion

To synthesize bromoderivatives of benzo[1,2-d:4,5-d′]bis([1,2,3]thiadiazole) Fachetti et al. studied the nitrosation of 2,5-diaminobenzene-1,4-dithiol in hydrobromic acid [8]. As a result of this reaction, a mixture of three compounds was formed—tricycle 3, its 4-mono- 1 and 4,8-bis-bromo 2 derivatives, although the authors failed to isolate and characterize individual compounds (Scheme 1).
To selectively obtain bromoderivatives of benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole, we chose the reaction of unsubstituted tricycle 3 [9] with brominating reagents N-bromosuccinimide (NBS) and bromine (Scheme 2). It was shown that NBS does not react with tricycle 3 in CHCl₃ and DMF, either at room temperature or when heated at 61 and 100 °C, respectively; starting compound 3 was fully recovered from the reaction mixtures (Entries 1–4, Table 1). Heating compound 3 with excess bromine in HBr at 80 °C for 12 h resulted in a single mono-brominated product (compound 2) in moderate yield (60%, Entry 5). Increasing the reaction temperature to 110 °C resulted in the same product, 1, in a lower yield, probably due to partial decomposition of the final compound (Entry 6).

Table 1. Bromination of benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole 3.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>Solvent</th>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Yield of 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBS</td>
<td>CHCl₃</td>
<td>25</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>NBS</td>
<td>DMF</td>
<td>25</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>NBS</td>
<td>CHCl₃</td>
<td>61</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>NBS</td>
<td>DMF</td>
<td>110</td>
<td>24</td>
<td>0</td>
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<tr>
<td>5</td>
<td>Br₂</td>
<td>HBr</td>
<td>80</td>
<td>12</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Br₂</td>
<td>HBr</td>
<td>110</td>
<td>12</td>
<td>45</td>
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</tbody>
</table>

The structure of 4-bromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 was confirmed by means of elemental analysis, high-resolution mass spectrometry, ¹H-, ¹³C-NMR, IR, UV spectroscopy and mass-spectrometry.

Mono-bromoderivatives of benzo fused thiadiazoles are rare and difficult-to-prepare compounds, and they are important precursors for the synthesis of unsymmetrical disubstituted benzothiadiazoles [10]. Thus, the 4-bromobenzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 synthesized by us can be widely explored for the preparation of previously inaccessible various photovoltaic material, such as dye-sensitized solar cells (DSSCs), organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), etc.

3. Materials and Methods

Benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole 1 [9] was prepared according to the published method. 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 was 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 CDCl₃ solution, with TMS as the standard. The IR spectrum was measured with a Bruker “Alpha-T” instrument (Santa Barbara, CA, USA) in KBr pellets.
The high-resolution MS spectrum was measured on a Bruker micrTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Solution UV–Visible absorption spectra were recorded using an OKB Spektr SF-2000 UV/Vis/NIR spectrophotometer (St. Petersburg, Russia) controlled with SF-2000 software (St. Petersburg, Russia). The sample was measured in a 1 cm quartz cell at room temperature with 7.6 × 10⁻⁶ mol/mL concentration in CH₂Cl₂.

Synthesis of 4-bromobenzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole 1. (Supplementary Materials).

Bromine (0.5 mL, 20 mmol) was added to a solution of benzo[1,2-d:4,5-d']bis[1,2,3]thiadiazole 3 (250 mg, 1.28 mmol) in HBr (10 mL). The mixture was stirred at 80 °C for 12 h. On completion, the reaction mixture was poured into ice (50 g) and the organic layer was extracted with EtOAc (3 × 35 mL), dried over MgSO₄ and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent CH₂Cl₂). Yield: 211 mg (60%), yellow solid, R₂ = 0.3 (CH₂Cl₂). Mp > 250 °C. IR spectrum, ν, cm⁻¹: 3083, 2925, 1393, 1289, 1190, 886, 796, 558. ¹H-NMR (ppm): δ 9.27 (s). UV-Vis spectra (in CH₂Cl₂), λmax: 240 nm (ε = 1,3702 M⁻¹ cm⁻¹). ¹³C-NMR (ppm): δ 156.5, 156.2, 143.2, 140.6, 113.2, 107.5. HRMS (ESI-TOF), m/z: calcd for C₁₂H₁₀BrN₄S₂Ag [M+Ag]⁺, 378.7871, found, 378.7870. MS (EI, 70 eV), m/z (1, %): 274 ([M + 2]⁺, 70), 273 ([M⁺], 6), 272([M − 1]⁺, 65), 244 (10), 218 (73), 149 (98), 137 (97), 93 (98), 69 (100), 61 (55), 44(50), 32 (53), 18 (96). Anal. calcd. for C₂₈H₂₆N₆O₂ (271.8899): C, 64.25; H, 0.37; N, 20.51. Found: C, 63.83; H, 0.30; N, 20.45%.

Supplementary Materials: The following supporting information can be downloaded at: copies of ¹H-, ¹³C-NMR, IR, HRMS, UV–Vis and mass-spectra for compound 1.

Author Contributions: Conceptualization, O.A.R. and T.N.C.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, investigation, D.A.A. and T.A.K.; resources, O.A.R.; data curation, O.A.R.; writing—original draft preparation, O.A.R.; writing—review and editing, O.A.R.; visualization, O.A.R.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of compounds 1–3 are available from the authors.

References
2. Rakitin, O.A. Recent developments in the synthesis of 1,2,5-thiadiazoles and 2,1,3-benzothiadiazoles. Synthesis 2019, 51, 4338–4347. [CrossRef]
3. Rakitin, O.A. Fused 1,2,5-thia- and 1,2,5-selenadiazoles: Synthesis and application in materials chemistry. Tetrahedron Lett. 2020, 61, 152230. [CrossRef]
