Preparation and X-Ray Structure of 4-BrC₆H₄CNSC(Cl)N

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Crystal Structure, 1,2,4-Thiadiazole, Intramolecular Cyclization

The title compound was obtained in 82% yield by the intramolecular cyclization of 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂] in CH₂Cl₂ at 23°C. It crystallizes in the triclinic system, space group Pl, a = 7.957(3) Å, b = 10.864(5) Å, c = 5.625(1) Å, α = 95.94(3)°, β = 97.79(2)°, γ = 100.72(3)°, V = 469.2(3) Å³, and Z = 2. The bond lengths of the planar C₅N₃S ring indicate partial π-delocalization.

Introduction

A variety of synthetic approaches to the 1,2,4-thiadiazole ring system is available [1]. For example, the cyclocondensation of carboxamides RC(NH(R₂))RCNH₂ with Cl₂CSCI produces RCNSC(Cl)N [1]. In this note we report the synthesis and X-ray structure of 5-chloro-1,2,4-thiadiazole (2), which was obtained by the spontaneous intramolecular cyclization of 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂] (1), according to eq. (1).

Results and Discussion

The monothiolated benzamidine 1 was prepared from 4-BrC₆H₄CN₂(SiMe₃)₂ [2,3] and Cl₂CSCI (1:1 molar ratio) cf. synthesis of Ph₃C(SCCl₃)[N(SiMe₃)₂] [4]. The ¹H NMR spectrum of 1 showed resonances for 4-BrC₆H₄ (an AA'XX' pattern centred at δ 8.80 and 7.56) and SiMe₃ groups (δ 0.30) in the intensity ratio 4:18. In addition, a second weak AA'XX' pattern (δ 8.15 and 7.65) attributed to 2 was evident. A solution of 1 in CH₂Cl₂ was kept for 72 h at 23 °C and, after subsequent work-up, the heterocycle 2 was obtained in 82% yield. A small amount of 4-BrC₆H₄C(NH)(NH₂), the hydrolysis product of 1, was also isolated.

The structure of 2 was determined by X-ray crystallography (see Fig. 1). The pertinent bond lengths, bond angles and torsion angles are summarized in Table I. In common with other 1,2,4-thiadiazoles [5-10], the heterocyclic ring in 2 is essentially planar and the bond lengths indicate some π-delocalization. Thus the S-N distance of 1.650(6) Å is significantly shorter than the predicted single bond value of 1.73 Å [11] and the sequence of C-N bond lengths is 1.331(7), 1.380(8) and 1.302(7) Å (cf. single and double bond values of ca. 1.29 and 1.47 Å, respectively [12]). The 4-BrC₆H₄ substituent is coplanar with the heterocyclic ring and there are no significant intermolecular interactions.

Experimental Section

Preparation of 4-BrC₆H₄CNSC(Cl)N (2)

A solution of Cl₂CSCI (0.60 g, 3.22 mmol) in 25 ml of CH₂Cl₂ was added dropwise to 4-BrC₆H₄CN₂(SiMe₃)₂, (1.37 g, 3.30 mmol) in 25 ml of CH₂Cl₂ at 23°C under an atmosphere of N₂. The reaction mixture was stirred for 72h and then solvent and Me₂SiCl were removed by vacuum transfer to give a viscous yellow oil containing a small amount of white powder. The oil was dissolved

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Br\(\text{C}_6\text{H}_4\text{CNSC(Cl)}\text{N})_2\) in CH\(_2\text{Cl}_2\): diethyl ether and the insoluble white solid was removed by filtration. Solvent was removed from the filtrate. Slow evaporation of a diethyl ether solution of the residue gave pale yellow rectangular crystals of 4-BrC\(_6\text{H}_4\text{CNSC(Cl)}\text{N} \) (0.73 g, 82%). M.p. 85°C.

**Analysis for C\(_8\text{H}_4\text{N}_2\text{BrCl}\text{S} \)**

Calcd C 34.87 H 1.46 N 10.17% Found C 35.39 H 1.50 N 9.33%.

\(^1\text{H} \text{NMR} \) (in CDCl\(_3\)): \(\delta 8.15\) and 7.65 (4-BrC\(_6\text{H}_4\text{H}) \text{AA'XX' pattern} \). \(^{13}\text{C} \text{NMR} \) (in CDCl\(_3\)): \(\delta 173.3\) and 171.2 (NC(S)Cl and CN\(_2\)), 132.1, 130.8, 129.6 and 125.6 (C\(_6\text{H}_5\)). The white solid was identified as 4-BrC\(_6\text{H}_4\text{C(NH)(NH}_2\)) (0.10 g, 16%) by EI-MS (\(m/z = 198\) and 200, M\(^+\)).

**X-ray analysis**

The crystal structure of 2 was determined by using a Rigaku AFC6S diffractometer. Experimental details are summarized in Table II*. The structure was solved by the heavy atom method [13] and expanded using Fourier techniques [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions. Scattering factors were taken from Cromer and Waber [15] and allowance was made for anomalous dispersion [16]. All calculations were performed using teXsan [17].

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*Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry No. CSD-406259.