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REACTION OF 1,2,3-SELENADIAZOLES WITH BORANES

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The complex formation of 1,2,3-selenadiazoles with boron trifluoride etherate and phenyldichloroborane has been studied. The molecular structure of the5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazole has been confirmed by X-ray analysis.

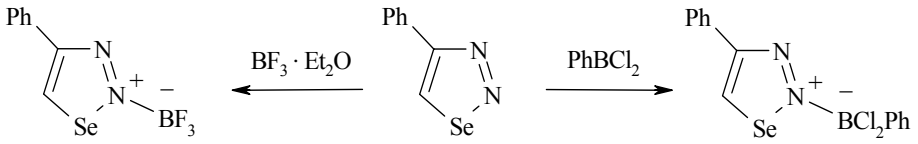
Keywords: boranes, 1,2,3-selenadiazoles, complexes, molecular structure.

The great interest of many investigators in 1,2,3-selenadiazole and its derivatives is due to the fact that this compound plays a significant role in resolving many theoretical and practical questions in organic chemistry [1]. Compounds containing a selenadiazole ring show an aromatic character and, very importantly, lose molecules of nitrogen and selenium with ring opening to give both acyclic series and also novel heterocyclic products [2, 3]. Hence they are promising subjects for the study of the mechanisms of certain reactions and the synthesis of many practically interesting compounds [4]. In the thermolysis reactions of selenadiazoles with elemental sulfur and selenium polysulfur and polyselenium cyclic systems are formed [5-7]. Various selanylethylenes can be prepared by treatment of selenadiazoles with nucleophilic agents such as butyl lithium, trialkylphosphites, mercaptans, disulfides etc. [8].

There is particular interest in an investigation of the molecular structure of 1,2,3-selenadiazoles because few structures have been confirmed by X-ray analysis according to literature data [9-12].

The aim of this work is to study the reaction of 1,2,3-selenadiazoles with boron trifluoride etherate and with phenyldichloroborane.

Formation of complexes with electron-deficient compounds is possible because the selenium atom has unshared electron pairs. The reaction of boron trifluoride etherate and phenyldichloroborane with an equimolar amount of 4-phenyl-1,2,3-selenadiazole (**1**) in dry benzene gives the stable complexes **2** and **3** in almost quantitative yield. Both complexes are crystalline materials, sensitive to moisture. ^{11}B NMR spectroscopic data shows that the boron atom in the complexes is tetracoordinated.



2 **1** **3**

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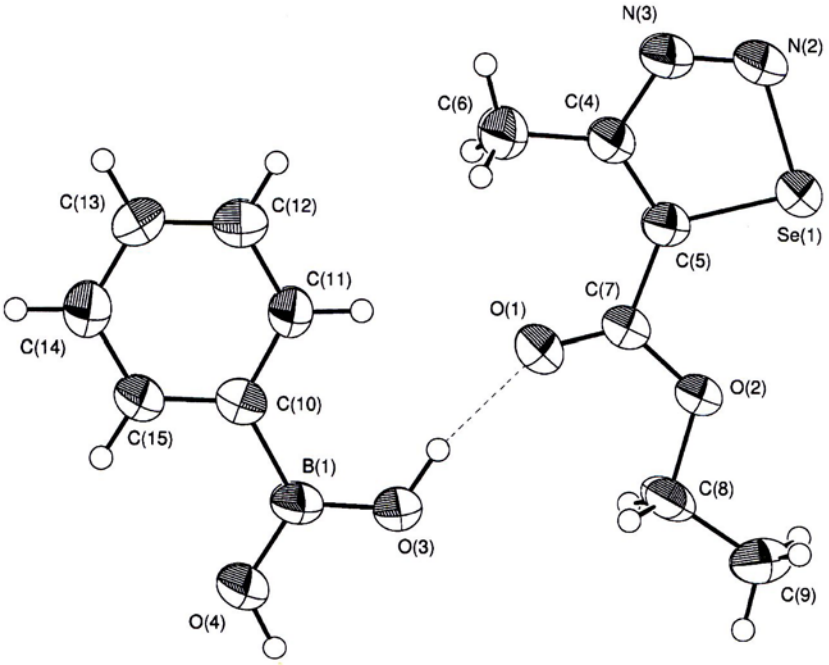

Fig. 1. Molecular structure of the H-complex of compound **4** with phenylboric acid.

A mixture of products is formed in the reaction of 5-etoxycarbonyl-4-methyl-1,2,3-selenadiazole (**4**) with boron trifluoride etherate. However, complex formation of compound **4** with phenyldichloroborane occurs smoothly to form the single product **5**. As a result of crystallization of the complex **5** from hexane the phenyldichloroborane undergoes hydrolysis to phenylboric acid. The structure of the mixed crystal **6** was studied by X-ray analysis.

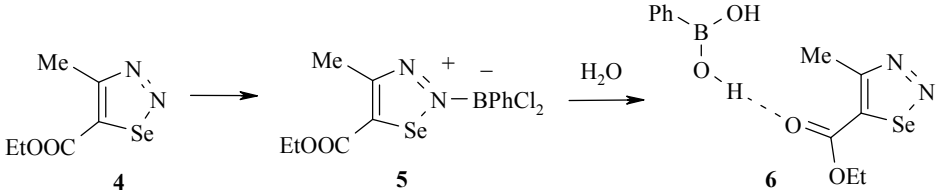

TABLE 1. Basic Interatomic Distances (*l*) and Valence Angles (ω) in Structure **6**

Bond	*l*, Å	Angle	ω, deg
Se(1)–N(2)	1.860(3)	N(2)–Se(1)–C(5)	86.2(2)
Se(1)–C(5)	1.834(4)	Se(1)–N(2)–N(3)	111.2(2)
N(2)–N(3)	1.273(4)	N(2)–N(3)–C(4)	118.2(3)
N(3)–C(4)	1.366(5)	N(3)–C(4)–C(5)	113.9(3)
C(4)–C(5)	1.369(5)	C(4)–C(5)–Se(1)	110.5(3)
C(4)–C(6)	1.469(5)	O(3)–B(1)–C(10)	117.6(3)
C(5)–C(7)	1.482(5)	O(3)–B(1)–C(10)	123.5(3)
C(7)–O(1)	1.200(4)	O(4)–B(1)–C(10)	118.9(4)
C(7)–O(2)	1.337(4)		
B(1)–O(3)	1.378(5)		
B(1)–O(4)	1.346(5)		
B(1)–C(10)	1.564(5)		

The molecular structure, atom numbering and thermal vibration ellipsoids for **6** is given in Fig. 1. The length of the hydrogen bond between the hydroxyl H atom in the phenylboric acid and the carbonyl oxygen atom in the selenadiazole is 2.790(4) Å. The unit cell contains two molecules of 5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazole **4** and two molecules of phenylboric acid (Z = 2). The basic bond lengths and valence angles for structure **6** are given in Table 1.

The C(5)–Se(1) bond length is 1.834(4) Å which is less than the N(2)–Se(1) (1.860(3) Å) and the C(5)–Se(1)–N(2) angle is 86.2(2)°. According to the X-ray analysis of other selenadiazoles [9-13] the C–Se bond is also shorter than the N–Se. The N(2)–N(3) and C(4)–C(5) bonds are lengthened when compared with standard values for N=N and C=C bonds [14] and this confirms the aromatic character of the selenadiazole ring.

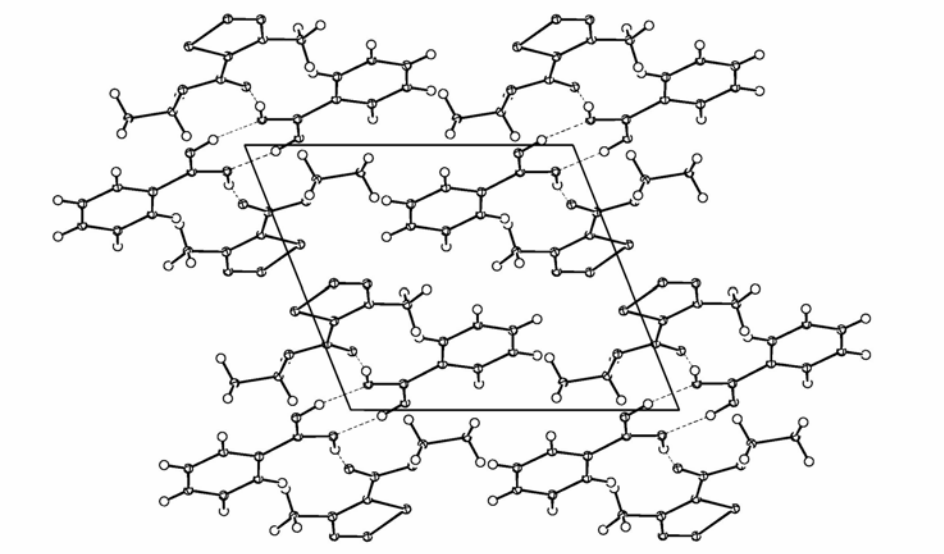

Fig. 2. Molecular packing in the crystal structure of compound **6.**

Figure 2 shows the projection of the packing of the molecules in the crystalline structure of **6** in the crystallographic [1 0 0] direction. Besides the hydrogen bond discussed before for structure **6** it also possesses an O(4)–H···O(3) hydrogen bond (Table 2). The lengths of the hydrogen bonds are somewhat longer than the mean statistical value of 2.72 Å for an OH···O type bond [15]. The crystal structure forms centrosymmetric associates of four molecules *via* hydrogen bonding.

TABLE 2. Hydrogen Bond Parameters in the Crystal Structure **6**

D–H···A bond	H-bond length D···A, Å	D···A distance, Å	D–H···A, angle, deg.	Atom A position
O(3)–H···O(1)	2.867(3)	2.03	148	x, y, z
O(4)–H···O(3)	2.790(3)	1.90	167	$2–x, –y, –z$

EXPERIMENTAL

^{1}H, ^{13}C, ^{11}B, and ^{77}Se NMR spectra were measured on a Varian Mercury-200 instrument (200, 50, 64, and 39.7 MHz respectively) using DMSO-d_6 as solvent with TMS internal standard and BF_3·etherate (^{11}B) and SeO_2 (^{77}Se) external standards.

X-Ray analysis was carried out on monocrystals of **6** grown from hexane. The **6** crystals are assigned a triclinic symmetry with the crystal lattice parameters: a = 7.4666(3), b = 10.0980(3), c = 11.1689(4) Å, α = 107.750(2), β = 98.402(2), γ = 107.905(2)°, V = 735.97(5) Å^3, $F(000)$ = 344, μ = 2.563 mm^{-1}, d_{calc} = 1.539 g/cm^{-3}, Z = 2, space group $P\bar{1}$.

The intensities of 3389 independent reflections were measured on a Nonius KappaCCD automatic diffractometer (molybdenum radiation with λ = 0.71073 Å, graphite monochromator) to $2\theta_{max}$ = 55°. In the calculations 2106 reflections with $I > 2\sigma$ (I) were used. The structure was solved by method [16]. Refinement was carried out by least squares analysis in the full matrix anisotropic approximation using the SHELXL program package [17]. The final difference factor was R = 0.0441.

Complex Formation of 1,2,3-selenadiazole with Boranes (General Method). A mixture of equimolar amounts of the selenadiazole and borane was dissolved in dry benzene and stirred at room temperature for 1 h. The complexes **2, 3, 5** precipitated from the reaction mixture after several days. The precipitate was then filtered off and recrystallized from a mixture of benzene and hexane (1 : 5).

Complex of 4-Phenyl-1,2,3-selenadiazole with Boron Trifluoride (2). Mp 69-70°C. ^{1}H NMR spectrum, δ, ppm: 7.42-7.52 (3H, m), 8.03-8.08 (2H, m), 9.38 (1H, s). ^{13}C NMR spectrum, δ, ppm: 127.3, 128.1, 128.4, 132.5, 135.0, 137.4. ^{1}B NMR spectrum, δ, ppm: -4.78. Found, %: C 34.74; H 2.22; N 10.11. $C_8H_6BF_3N_2Se$. Calculated, %: 34.70; H 2.18; N 10.12.

Complex of 4-Phenyl-1,2,3-selenadiazole with Phenyldichloroborane (3). Mp 91-92°C. ^{1}H NMR spectrum, δ, ppm: 7.42-7.60 (6H, m), 8.03-8.07 (2H, m), 8.23-8.27 (2H, m), 9.39 (1H, s). ^{13}C NMR spectrum, δ, ppm: 127.7, 128.0, 128.9, 129.1, 132.0, 132.7, 135.6, 137.0, 166.8. ^{11}B NMR spectrum, δ, ppm: 29.48. ^{77}Se NMR spectrum, δ, ppm: 1569.9. Found, %: C 45.74; H 3.08; N 7.70. $C_{14}H_{11}BCl_2N_2Se$. Calculated, %: C 45.70; H 3.01; N 7.61.

Complex of 5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazole with Phenyldichloroborane (5). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.34 (3H, t, J = 4.0), 3.02 (3H, s), 4.35 (2H, q, J = 4.0), 7.43-7.73 (5H, m). ^{13}C NMR spectrum, δ, ppm: 14.1, 24.9, 62.6, 127.9, 131.0, 131.1, 132.5, 135.6, 162.3. ^{11}B NMR spectrum, δ, ppm: 29.60. ^{77}Se NMR spectrum, δ, ppm: 1574.6. Found, %: C 38.10; H 3.41; N 7.36. $C_{12}H_{13}BCl_2N_2O_2Se$. Calculated, %: C 38.14; H 3.47; N 7.41.

Preparation of the H-complex of 5-ethoxycarbonyl-4-phenyl-1,2,3-selenadiazole (4) with Phenylboric Acid (6). Complex **5** was dissolved in hexane at room temperature and left to crystallize at 5°C. After 2 days crystals of compound **6** were obtained. The spectroscopic data for compound **4**, appearing in the H-complex, has been reported in [18].

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