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REACTION OF 1,2,3-SELENADIAZOLES WITH PHOSPHINES

P. Arsenyan, K. Oberte, K. Rubina, S. Belyakov, and E. Lukevics

Nucleophilic attack of tributyl- and triphenylphosphines on 4-phenyl- and 5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazoles leads to the quantitative formation of selenophosphoranes and substituted acetylenes. The molecular structure of 4-phenyl-1,2,3-selenadiazole was confirmed by X-ray crystallography.

Keywords: selenadiazole, selenium, phosphine, crystal structure, nucleophilic attack.

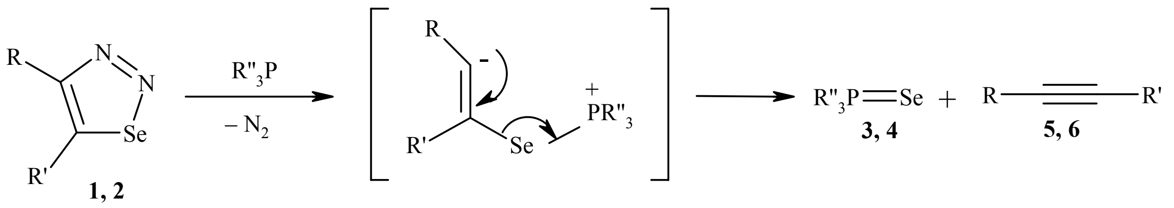
1,2,3-Selenadiazole and its derivatives play an important role in the solution of many theoretical and practical questions in organic chemistry [1] which explains the great interest of researchers in these compounds. Compounds containing the selenadiazole ring show aromatic character, but they have a considerable tendency to eliminate molecules of nitrogen and selenium with ring opening with formation of both acyclic compounds and new heterocycles [2, 3], therefore they are promising materials for the investigation of the mechanism of some reactions and for the synthesis of many compounds interesting in a practical sense [4].

A number of methods for the preparation of selenophosphoranes have been described in the literature. Boiling of triphenylphosphine with metallic selenium in THF gave triphenylselenophosphorane in 66% yield [5], while use of toluene increased the yield to 88% [6]. When selenium black was used in boiling toluene for 6 h the yield increased to 100% [7]. Selenophosphorane was also formed by keeping triphenylphosphine and tetrachloroselenotungsten (WCl_4Se) in toluene for 2 days [8]. Benzhydrylidenetriphenylphosphorane underwent an exchange reaction with metallic selenium to give selenophosphorane in 71% yield [9, 10]. Triphenylselenophosphorane was formed on heating triphenyl(phenyl-*p*-tolylmethylene)-λ^5-phosphorane with selenium in toluene at 85°C for 4 h [11].

In this work a method is developed for the preparation of selenophosphoranes from 4-phenyl- and 5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazoles.

4-Phenyl-1,2,3-selenadiazole (**1**) reacted with tributylphosphine in benzene at room temperature. In the first stage the Se–N bond is broken as a result of nucleophilic attack by tributylphosphine. Elimination of a molecule of nitrogen follows. A molecule of phenylacetylene is released from the intermediate and tributylselenophosporane (**3**) is produced. When triphenylphosphine is used, triphenylselenophosphorane (**4**) is formed in quantitative yield only after boiling for one hour. In the case of 5-ethoxycarbonyl-4-methyl-1,2,3-selenadiazole (**2**) selenophosphoranes **3** and **4** are formed in 100% yield. Ethyl but-2-ynecarboxylate (**6**) was isolated from the reaction mixtures in 92% yield.

Latvian Institute of Organic Synthesis, Riga, LV -1006; e-mail: pavel.arsenyan@lycos.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, 599-603, April 2004. Original article submitted October 7, 2003.



1, **5** R = Ph, R' = H; **2**, **6** R = Me, R' = COOEt; **3** R'' = Bu; **4** R'' = Ph

When trimethyl- or triethyl phosphite was used the reaction stopped at the first stage to give selenophosphates [12]. Destruction of the selenadiazole ring with phosphines is an alternative method for the preparation of substituted acetylenes under mild conditions.

The molecular structure of compound **1** was determined by X-ray diffractometry (Fig. 1).

In the crystalline state the molecule of selenadiazole **1** is practically planar with a torsion angle C(5)–C(4)–C(6)–C(7) of 178.6°. The C(5)–Se(1) bond (1.814 A) is shorter than the N(2)–Se(1) bond (1.878 A), and the C(5)–Se(1)–N(2) angle equals to 86.41° (Tables 1 and 2). There are 8 independent molecules in the unit cell.

TABLE 1. Bond Lengths and Intermolecular Contacts (*l*) in Compound **1**

Bond	*l*, Å	Bond	*l*, Å
Se(1)–C(5)	1.814(3)	Se(1)–N(2)	1.878(3)
C(6)–C(7)	1.405(4)	C(6)–C(11)	1.391(4)
C(6)–C(4)	1.472(5)	C(5)–C(4)	1.355(4)
C(7)–C(8)	1.371(4)	C(11)–C(10)	1.389(4)
N(3)–C(4)	1.387(4)	N(3)–N(2)	1.265(4)
C(8)–C(9)	1.391(5)	C(9)–C(10)	1.367(5)
C(5)–H(5)	1.07(3)	C(7)–H(7)	0.990(3)
C(11)–H(11)	0.96(3)	C(8)–H(8)	1.04(4)
C(9)–H(9)	1.03(4)	C(10)–H(10)	1.10(3)
Contact	*l* contact, Å	Contact	*l* contact, Å
Se(1)···Se(1)	3.8062(8)	Se(1)···N(2)	3.379(3)
Se(1)···Se(1)	3.6294(8)	N(2)···H(5)	2.59(3)

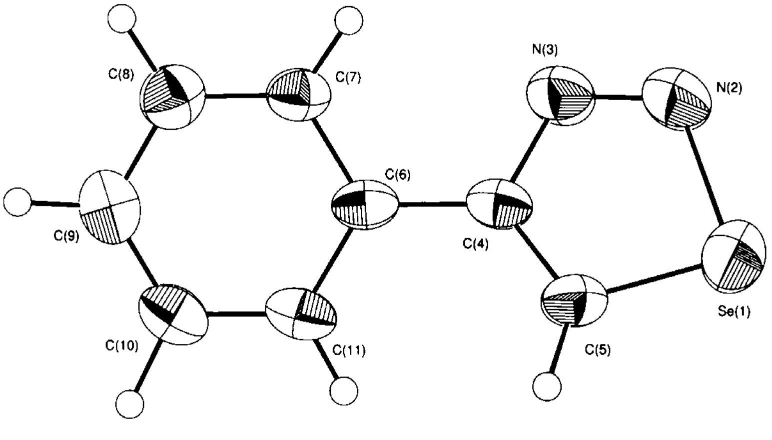


Fig. 1. Molecular structure of 4-phenyl-1,2,3-selenadiazole (**1**).

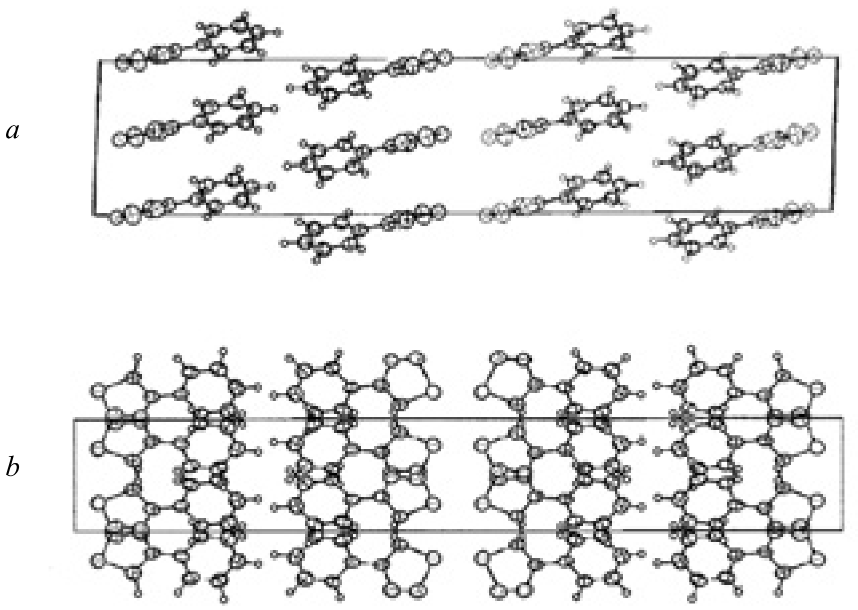


Fig. 2. Crystal Packing of Compound **1**: Projections Along the *Y* (*a*) and *Z* (*b*) Axes.

TABLE 2. Torsion Angles (τ) in Compound **1**

Angle	τ, deg.	Angle	τ, deg.
C(5)–Se(1)–N(2)	86.41(12)	C(7)–C(6)–C(11)	118.4(3)
C(7)–C(6)–C(4)	120.6(2)	C(11)–C(6)–C(4)	121.0(3)
Se(1)–C(5)–C(4)	111.0(2)	C(6)–C(7)–C(8)	120.1(3)
C(6)–C(11)–C(10)	120.8(3)	C(4)–N(3)–N(2)	117.3(3)
C(7)–C(8)–C(9)	120.9(3)	C(8)–C(9)–C(10)	119.7(3)
C(11)–C(10)–C(9)	120.2(3)	C(6)–C(4)–C(5)	126.4(3)
C(6)–C(4)–N(3)	119.3(2)	C(5)–C(4)–N(3)	114.3(3)
Se(1)–N(2)–N(3)	110.9(2)	Se(1)–C(5)–H(5)	122.(2)
C(4)–C(5)–H(5)	126.(2)	C(6)–C(7)–H(7)	115.(2)
C(8)–C(7)–H(7)	125.(2)	C(6)–C(11)–H(11)	121.(2)
C(10)–C(11)–H(11)	119.(2)	C(7)–C(8)–H(8)	121.(2)
C(9)–C(8)–H(8)	118.(2)	C(8)–C(9)–H(9)	115.(2)
C(10)–C(9)–H(9)	125.(2)	C(11)–C(10)–H(10)	116.0(14)
C(9)–C(10)–H(10)	123.7(13)		

There are intermolecular contacts between selenium atoms of neighbouring molecules of selenadiazole **1** crystal within the limits of 3.63-3.81 Å, which is less than the sum of the van der Waals radii [13]. In addition to Se(1)···Se(1) contacts there are Se(1)···N(2) and N(2)···H(5) contacts of 3.38 Å and 2.59(3) Å respectively.

EXPERIMENTAL

For the X-ray Structural Analysis 1961 reflections were measured with a Nonius KappaCCD diffractomer using molybdenum radiation, MoKα (0.7103 Å). Monocrystals of compound **1** (mp 76-77°C) grown from acetone–water (60:40) were monoclinic with unit cell parameters: a = 36.833(2), b = 5.7406(2), c = 7.3839(4) Å; β = 92.975(2)°; V = 1559.44(13) Å^3; D_x = 1.781 g/cm^3; μ = 4.74 cm^{-1}; coefficient of absorption

4.74 mm^{-1}; space group $P2_{1/a}$; $Z = 8$. In the calculations 1114 independent reflections with $|F| > 2\sigma_F$ were used for 124 refined parameters. The final residual factor was 0.057. Calculations were carried out using a suite of programs [14-16].

Selenophosphoranes 3, 4 (General Method). Mixture of equimolar amounts of 1,2,3-selenadiazole and phosphine was dissolved in benzene and stirred for 1 h (it was necessary to boil the mixture for triphenylphosphine). The reaction mixture was evaporated and selenophosphoranes separated in quantitative yield from the substituted acetylenes by crystallization from hexane. The structure of the products was confirmed by mass and NMR spectra [6, 8].

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