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REACTION OF 2-PYRIDYLSELENENYL BROMIDE WITH DIVINYL SELENIDE

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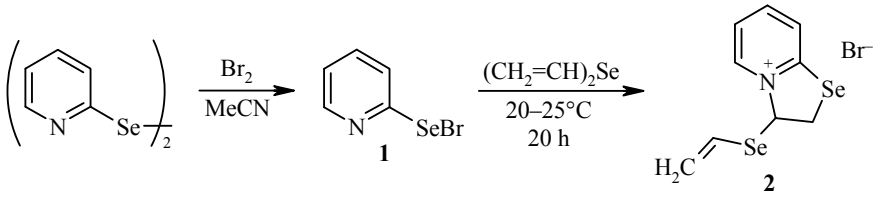
The pyridine ring is an important pharmaceutical scaffold, and pyridine derivatives exhibit various biological activities [1]. Many alkaloids with annelated structures contain the pyridine ring [1].

In this paper, we elaborate on novel approaches to annelation of chalcogen-containing rings [2–6]. One of the important intermediates that can serve for the annelation of chalcogen-containing rings to the pyridine cycle is 2-pyridylselenenyl halides [7, 8]. Although 2-pyridylselenenyl chloride was used in annelation reactions [7, 8], 2-pyridylselenenyl bromide was not. It was reported that 2-pyridineselenenyl bromide reacted with styrene in methanol to give the solvoadduct – 1-methoxy-1-phenyl-2-(2-pyridylselanyl)ethane – in quantitative yield [9]. Annelation products were not formed in this reaction.

We found that the reaction of 2-pyridylselenenyl bromide (**1**) with divinyl selenide [10, 11] led to a previously unknown annelated heterocycle, 3-(vinylselanyl)-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridin-4-ium bromide (**2**). The reaction was carried out in acetonitrile at room temperature for 20 h. The yield of heterocycle **2** is 98% based on consumed bromide **1** (the conversion is 20%).



It is noteworthy that bromide **1** is a special organylselenenyl halide, which exhibits low solubility in common solvents. Its solubility is lower than that of 2-pyridylselenenyl chloride [7, 8]. The best solvents to dissolve bromide **1** are alcohols and aprotic bipolar solvents (DMSO, DMF, HMPA, MeCN); however, its

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solubility is low even in these solvents. The main part of bromide **1** stays as a solid during the reaction and remains unconverted. The use of methanol as solvent increased the solubility of bromide **1**;, however, when we carried out the reaction of bromide **1** with divinyl selenide in methanol, the formation of heterocycle **2** was not observed. Raising the temperature of the reaction increased the solubility of bromide **1** but caused formation of by-products. When the reaction was carried out at room temperature for 40 h (instead of 20 h), the obtained product **2** was contaminated with some impurities.

Thus, the annelation of the dihydro-1,3-selenazole ring to pyridine, which is based on the reaction of 2-pyridylselenenyl bromide with divinyl selenide, was accomplished for the first time. The use of divinyl selenide permitted us to obtain the annelated product containing the reactive vinylselanyl group.

^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on a Bruker DPX-400 spectrometer (400, 100 and 76 MHz, respectively) in D_2O; external standards were HMDS (for ^{1}H and ^{13}C NMR spectra) and Me_2Se (δ 0.0 ppm, for ^{77}Se NMR pectrum). Divinyl selenide is ready accessible from elemental selenium and acetylene [10, 11]. Elemental analysis was performed on a Thermo Finnigan EA 1112 Elemental Analyzer. Melting point was determined on a Boetius hot stage apparatus (PHMK 05 VEB Wägetechnik Rapido). Bis(2-pyridyl) diselenide was obtained from 2-bromopyridine and selenium [12].

3-(Vinylselanyl)-2,3-dihydro[1,3]selenazolo[3,2-*a*]pyridin-4-ium Bromide (2). A solution of bromine (80 mg, 0.5 mmol) in acetonitrile (2 ml) was added dropwise to a cooled (an ice bath) solution of bis(2-pyridyl) diselenide (157 mg, 0.5 mmol) in MeCN (4 ml). The mixture was stirred for 1 h on the ice bath and for1 h at room temperature. A solution of divinyl selenide (133 mg, 1.0 mmol) in MeCN (2 ml) was added to the obtained suspension of bromide **1**, and the mixture was stirred for 20 h at room temperature. The precipitate was filtered off to give unconsumed bromide **1** (190 mg, 20% conversion). The solvent and divinyl selenide were distilled off from the filtrate. The residue was washed with hexane and dried in vacuum. Yield 73 mg (19.7%, 98% based on consumed bromide **1**). Yellowish powder, mp 166-169 ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.87 (1H, dd, ^{2}J = 11.7, ^{3}J = 5.6) and 4.27 (1H, dd, ^{2}J = 11.7, ^{3}J = 7.0, $SeCH_2$); 5.67 (1H, d, ^{3}J = 16.7) and 5.88 (1H, d, ^{3}J = 9.1, $=CH_2$); 6.64 (1H, dd, ^{3}J = 7.0, ^{3}J = 5.6, $N^{+}CHSe$); 6.82 (1H, dd, ^{3}J = 9.1, ^{3}J = 16.7, SeCH=); 7.57-7.62 (1H, m, H Ar); 7.96-7.99 (1H, m, H Ar); 8.02-8.08 (1H, m, H Ar); 8.80-8.84 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 31.5 ($SeCH_2$); 71.2 (SeCH); 120.9 ($=CH_2$); 123.8 (C Ar); 127.6 (SeCH=); 128.8 (C Ar); 142.6 (C Ar); 144.0 (C Ar); 157.9 (C Ar). ^{77}Se NMR spectrum, δ, ppm (*J*, Hz): 407 ($^{2}J_{Se–H}$ = 9.5, $^{2}J_{Se–H}$ = 15.9, $SeCH_2$); 474 ($^{2}J_{Se–H}$ = 13.5, $^{2}J_{Se–H}$ = 16.7, CHSeCH=). Found, %: C 29.56; H 2.91; N 3.58; Br 21.32; Se 43.02. $C_9H_{10}NBrSe_2$. Calculated, %: C 29.22; H 2.72; N 3.79; Br 21.60; Se 42.68.

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