β-Aminoselenenation of alkenes with arylselenenamides in the presence of sulfamic acid

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In the present study, we suggested a new method of the synthesis of β-aminoalkyl aryl selenides by the reaction of electrophilic selenenation of alkenes with phenylselenenamide **1** in the presence of $HOSO_2NH_2$.

We have shown earlier that the reaction of arylselenenamides with unsaturated compounds in the presence of phosphorus(V) or sulfur(IV) oxohalides results in the corresponding β-halogenalkyl aryl selenides in high yields.[1,2] Also, the possibility of a reaction of arylsulfenamides with olefins in the presence of sulfamic acid resulting in substituted aminoalkyl aryl sulfides was found.[3]

It is of note that the Gabriel reaction of nucleophilic substitution of the amino group for halogen successfully used for the preparation of β-aminoalkyl sulfides[4] is inapplicable in the case of selenium-containing analogs. The other known method for obtaining β-aminoalkyl aryl selenides (in the form of NBoc derivatives)[5] with olefins as the starting compounds requires preliminary aziridination of the alkenes, the use of indium iodide, and the inert atmosphere.

We used cyclohexene and hex-1-ene in our experiments. The reaction of phenylselenenamide **1** (see Ref. 3) with hex-1-ene occurs regioselectively with the formation of 2-amino-1-phenylselenohexane (**2**). *trans*-Amino selenide **3** was obtained from cyclohexene (Scheme 1).

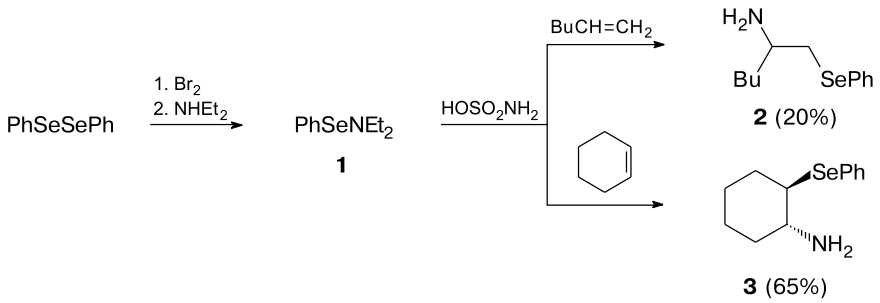
The structures of the obtained products were established by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum of amino selenide **2**, a half-width of the signals for the protons HCSe and HCN is ~25 Hz, which unambiguously indicated *trans*-diequatorial orientation of the substituents and the axial positions of the corresponding protons of the cyclohexane moiety. In the two-dimensional correlation spectrum $^{13}C—^1H$ HMBC of compound **3**, intense cross-peaks corresponding to the $C(1')—H_a(1)$ and $C(1')—H_b(1)$ (^3J) couplings are present. Besides, in the ^{13}C NMR spectrum of amino selenide **3** satellite peaks were observed corresponding to the ^{77}Se and ^{13}C coupling with $J = 65$ Hz.

Thus, we suggested a convenient method for the synthesis of primary alkylamines containing arylseleno group in the β-position.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument in $CDCl_3$ at 400.13 and 100.61 MHz, respectively. IR spectra were obtained on a UR-20 instrument for suspensions in Nujol. Elemental analysis was performed on an Elementar Variocube CHN-analyzer. Diethyl phenylselenenamide (**1**) was synthesized from diphenyl diselenide according to the known procedure.[2]

Addition of phenylselenenamide to alkenes (general procedure). To a boiling suspension of sulfamic acid (11 mmol) in dry nitromethane (5 mL), a solution of an alkene (6.6 mmol) and phenylselenenamide **1** (2.2 mmol) in $MeNO_2$ (10 mL) was added, the reaction mixture was refluxed to complete disappearance of the starting selenenamide (TLC monitoring). Then the solution was filtered and the solvent was evaporated. The obtained yellow oil was dissolved in 5% HCl (20 mL) and refluxed for 4 h. Activated carbon was added and the mixture was refluxed for 30 min. The

Scheme 1



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hot solution was filtered, a solution of NaOH was added to pH ≥ 9, the mixture was extracted with diethyl ether (2×25 mL). After removal of the solvent *in vacuo*, compounds **2** and **3** were obtained in a form of amber-colored oils.

2-Amino-1-phenylselenohexane (2). Yield 0.06 g (20%). IR, ν/cm^{-1}: 3375, 3360 (NH_2). ^{1}H NMR, δ: 0.89 (t, 3 H, Me, J = 7.3 Hz); 1.32 (m, 4 H, CH_2); 1.50 (2 H, HC(3)); 1.63 (br.s, 2 H, NH_2); 2.78 (dd, 1 H, HCSe, J_1 = 8.5 Hz, J_2 = 12.4 Hz); 2.89 (m, 1 H, HCN); 3.12 (dd, 1 H, HCSe, J_1 = 5.2 Hz, J_2 = 12.4 Hz); 7.26 (m, 3 H, Ph); 7.54 (m, 2 H, Ph). ^{13}C NMR, δ: 14.0, 22.7, 28.5, 37.3, 37.8 (CSe), 50.9 (CN), 126.9, 129.0, 132.8, 135.3.

***trans*-2-Amino-1-phenylselenocyclohexane (3).** Yield 0.37 g (65%). Found (%): C, 56.62; H, 6.60; N, 5.50. $C_{12}H_{17}NSe$. Calculated (%): C, 56.69; H, 6.74; N, 5.51. IR, ν/cm^{-1}: 3380, 3360 (NH_2). ^{1}H NMR, δ: 1.20 (m, 3 H, HC(5), HC(4)); 1.47 (m, 1 H, HC(4)); 1.67 (m, 2 H, HC(6), HC(3)); 1.84 (br.s, 2 H, NH_2); 2.00 (d, 1 H, HC(6), J_1 = 13.0); 2.15 (dt, 1 H, HC(3), J_1 = 4.0 Hz, J_2 = 13.0 Hz); 2.60 (ddd, 1 H, HCSe, J_1 = 4.0 Hz, J_2 = 10.1 Hz, J_3 = 12.0 Hz); 2.81 (dt, 1 H, HCN, J_1 = 4.0 Hz, J_2 = 10.1 Hz); 7.25 (m, 3 H, Ph); 7.58 (m, 2 H, Ph). ^{13}C NMR, δ: 25.1, 27.2, 34.3, 33.8, 54.3 (CSe), 54.4 (CN), 127.7, 127.9, 128.9, 135.8.

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