A rearrangement in the reaction of 2-bromomethyl-1,3-thiaselenole with ethanol: synthesis of 2-ethoxy-2,3-dihydro-1,4-thiaselenine

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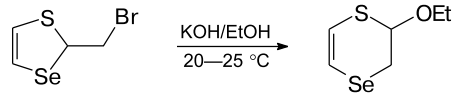
We are carrying out systematic investigations aimed at introduction of novel reagents such as selenium dichloride and dibromide into organic synthesis.[1—10] The reaction of selenium dihalides with divinyl sulfide leads to 2,6-dihalo-1,4-thiaselenanes.[3—6] When kept in chloroform solution at room temperature, 2,6-dihalo-1,4-thiaselenanes undergo spontaneous rearrangement with ring contraction to 5-halo-2-halomethyl-1,3-thiaselenolanes.[3—5] 2-Halomethyl-1,3-thiaselenoles were obtained by dehydrohalogenation reaction of 5-halo-2-halomethyl-1,3-thiaselenolanes in high yields.[3,4,8]

We found that treatment of 2-bromomethyl-1,3-thiaselenole (**1**) with ethanolic KOH at room temperature affords hitherto unknown 2-ethoxy-2,3-dihydro-1,4-thiaselenine (**2**) (yield 40%, not optimized) as a nucleophilic substitution and ring expansion rearrangement product.



1 **2**

It should be mentioned, that no formation of the expected 5-membered heterocycle, 2-ethoxymethyl-1,3-thiaselenole as the reaction product was observed. In addition to compound **2**, polymerization products formed.

The heterocycle **2** was isolated by column chromatography on silica gel (hexane as the eluent) as a light-brown oil. Its structure was established by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy (including two-dimensional correlation spectroscopy) and chromato-mass spectrometry, its composition was proved by data from elemental analysis. The spin-spin coupling constant of selenium with the carbon atom of the CH_2 group (64.1 Hz) indicates this to be a direct constant and the selenium atom to be linked directly with the CH_2-group.

The NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ at 400.13 (^{1}H, HMDS), 100.61 (^{13}C, HMDS) and 76.30 MHz (^{77}Se, Me_2Se). The EI-mass spectrum was recorded on a Shimadzu GCMS-QP5050A instrument with the electron energy of 70 eV.

2-Ethoxy-2,3-dihydro-1,4-thiaselenine (2). Found (%): C, 34.20; H, 5.00; S, 15.55; Se, 37.63. $C_6H_{10}OSSe$. Calculated (%): C, 34.45; H, 4.82; S, 15.33; Se, 37.75. ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$), δ: 1.25 (t, 3 H, CH_3, ^{3}J = 7.0 Hz); 3.07 (dd, 1 H, CH_2Se, ^{2}J = 12.1 Hz, ^{3}J = 5.6 Hz); 3.27 (dd, 1 H, CH_2Se, ^{2}J = 12.1 Hz, ^{3}J = 2.08 Hz); 3.57 (dq, 1 H, OCH_2, ^{2}J = 9.5 Hz, ^{3}J = 7.0 Hz); 3.92 (dq, 1 H, OCH_2, ^{2}J = 9.5 Hz, ^{3}J = 7.0 Hz); 4.94 (dd, 1 H, SCHO, ^{3}J = 2.1 Hz, ^{3}J = 5.6 Hz), 6.38 (d, 1 H, SCH=, ^{3}J = 9.8 Hz); 6.46 (d, 1 H, SeCH=, ^{3}J = 9.8 Hz). ^{13}C NMR spectrum (100.61 MHz, $CDCl_3$), δ: 14.85 (CH_3); 25.23 (CH_2Se, $^{1}J_{Se,C}$ = 64.1 Hz); 64.46 (OCH_2); 76.12 (SCHO); 110.74 (SeCH=, $^{1}J_{SeC}$ = 116.5 Hz); 118.01 (SCH). ^{77}Se NMR spectrum (76.30 MHz, $CDCl_3$) δ: 139 (m, $^{2}J_{\underline{Se},C\underline{H}=}$ = 51.7 Hz, $^{3}J_{\underline{Se}CH=C\underline{H}}$ = 9.4 Hz). Mass spectrum, m/z (I_{rel} (%)): 210 (69) $[M]^{+\cdot}$, 164 (8) $[M - C_2H_6O]^{+\cdot}$, 149 (14) $[C_4H_5OSe]^{+}$, 138 (68) $[C_2H_2SSe]^{+\cdot}$, 129 (49) $[C_6H_9OS]^{+}$, 101 (100) $[C_4H_5OS]^{+}$, 85 (20) $[C_4H_5S]^{+}$, 72 (86) $[C_3H_4S]^{+\cdot}$, 58 (67) $[C_2H_2S]^{+\cdot}$, 45 (70) $[C_2H_5O]^{+}$.

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