Regioselective dehydrobromination reaction of 5-bromo-2-bromomethyl-1,3-thiaselenolane 1,1-dioxide

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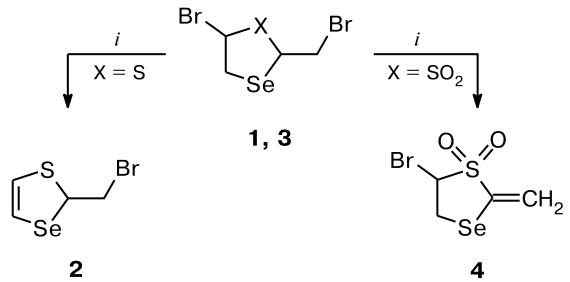
We are intensively studying chemical properties of new reagents, selenium dichloride[1—13] and dibromide,[10—20] in order to synthesize the earlier unknown or poorly available heterocyclic compounds.[3—19] The reaction of selenium dibromide with divinyl sulfide in chloroform leads to 5-bromo-2-bromomethyl-1,3-thiaselenolane (**1**).[13,14] On standing in chloroform at room temperature, compound **1** undergoes spontaneous dehydrobromination to be converted to 2-bromomethyl-1,3-thiaselenole (**2**).[13,14] The dehydrobromination reaction also occurs during chromatography of compound **1** on silica gel and upon the action of pyridine in benzene solution.[13] The process proceeds with high regioselectivity: the dehydrobromination results in the only formation of endocyclic double bond.

The reaction of selenium dibromide with divinyl sulfone in acetonitrile leads to 2,4-bis(bromomethyl)-1,3-thiaselenetane 1,1-dioxide and 5-bromo-2-bromomethyl-1,3-thiaselenolane 1,1-dioxide (**3**).[18] We found that compound **3** upon chromatography on silica gel undergoes dehydrobromination to be converted to 5-bromo-2-methylidene-1,3-thiaselenolane 1,1-dioxide (**4**) in 90% yield. Similar reaction is observed upon the action of pyridine on compound **3** in benzene at room temperature (the yield of product **4** was 82%).

Scheme 1



i. Silica gel or pyridine.
X = S (**1**, **2**), SO_2 (**3**, **4**)

The reaction was performed at room temperature by addition of a solution of pyridine in benzene to a solution of equimolar amount of compound **3** in benzene, then the mixture was stirred for 48 h. The reaction resulted in the formation of product **4** and precipitation of pyridine hydrobromide, which was filtered off. In another case, a solution of compound **3** in benzene was deposited on silica gel (NM Kieselgel 60, 70—230 mesh) and after 48 h compound **4** was washed off with benzene.

The structure of compound **4** was inferred from the ^1H, ^{13}C, and ^{77}Se NMR, including method of two-dimensional correlation spectroscopy, mass spectrometry, and confirmed by the elemental analysis data.

Dehydrobromination of compound **3** is characterized by high regioselectivity and proceeds under exceptionally mild conditions. Depending on the presence of either sulfide, or sulfone group in the molecule (compounds **1** and **3**), dehydrobromination takes different directions to form either thiaselenol **2**, or thiaselenolane **4**. At present, we study the reasons for such a behavior, as well as chemical properties of compounds **1—4**.

Thiaselenolane *S*,*S*-dioxide **4** is the earlier unknown heterocycle containing activated double bond and bromine atom capable of nucleophilic substitution. It can find its application as intermediate product in the synthesis of new organochalcogene compounds.

5-Bromo-2-methylidene-1,3-thiaselenolane 1,1-dioxide (4), colorless crystals, m.p. 76—77 °C. Found (%): C, 17.21; H, 1.97; Br, 28.87. $C_4H_5O_2BrSSe$. Calculated (%): C, 17.41; H, 1.82; Br, 28.95. IR, ν/cm^{-1}: 1153, 1332 (SO_2); 1595 (C=CH_2). ^1H NMR ($CDCl_3$), δ: 3.42 (dd, 1 H, $SeCH_2$, ^2J = 10.9 Hz, ^3J = 8.3 Hz); 3.64 (dd, 1 H, $SeCH_2$, ^2J = 10.9 Hz, ^3J = 5.3 Hz); 4.98 (dd, 1 H, $BrCHSO_2$, ^3J = 5.3 Hz, ^3J = 8.3 Hz); 6.02 (d, 1 H, =CH_2, ^2J = 3.2 Hz); 6.61 (d, 1 H, =CH_2, ^2J = 3.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 22.02 ($SeCH_2$, $^1J_{SeC}$ = 52.0 Hz); 55.20 ($BrCHSO_2$); 119.73 (=CH_2); 132.14 ($SeCSO_2$). ^{77}Se NMR ($CDCl_3$), δ: 288 ($^2J_{SeH}$ = = 18.2 Hz, $^2J_{SeH}$ = 13.2 Hz). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 276 $[M]^{+\cdot}$ (38), 108 (42), 106 (100), 104 (94), 102 (38), 80 (14), 48 (14).

NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 (^1H, HMDS), 100.61 (^{13}C, HMDS) and 76.30 MHz (^{77}Se, Me_2Se). The mass spectrum was obtained on a Shimadzu GCMS-QP5050A instrument.

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