

SHORT
COMMUNICATIONS

Reaction of Selenium Dihalides with Allyl Benzyl Ether

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Received July 10, 2014

DOI: 10.1134/S1070428014120227

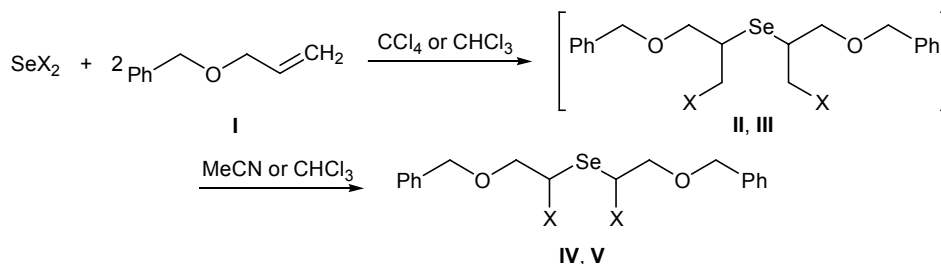
In recent time the chemistry of selenium dihalides has been extensively developed. Selenium dihalides have been shown to be efficient and selective reagents in the synthesis of organoselenium compounds. Although neither selenium dichloride nor selenium dibromide can be isolated in the pure state [1], these reagents can be generated *in situ* and involved in various transformations [2–14].

We perform systematic studies on reactions of selenium dichloride and dibromide with unsaturated compounds [5–14]. The reaction of selenium dihalides with vinyl ethers gave the corresponding Markovnikov adducts, bis(2-halo-2-organyloxyethyl) selenides, in high yield [8, 9].

The double C=C bond in vinyl chalcogenides is conjugated with the lone electron pair on the chalcogen atom, which largely determines chemical behavior of that bond. No such conjugation exists in the molecules of allyl chalcogenides. The reactions of selenium dichloride and dibromide with diallyl ether, diallyl sulfide, and diallyl selenide led to the formation of six-membered heterocycles, 3,5-bis(halomethyl)-1,4-chalcogenaselenanes, whose structure corresponds to the anti-Markovnikov addition [10–12]. The reactions of selenium dihalides with divinyl and diallyl tellurides involved halogenation of the tellurium atom [13, 14].

In continuation of our studies on reactions of selenium dihalides with unsaturated chalcogenides [5–14], the present communication reports on the reaction of selenium dichloride and dibromide with allyl benzyl ether (**I**). The reactions were carried out in carbon tetrachloride or chloroform at room temperature, and the products were the corresponding anti-Markovnikov adducts, bis(3-benzyloxy-1-halopropan-2-yl)selenes **II** and **III**, which underwent gradual rearrangement into thermodynamically more stable Markovnikov adducts **IV** and **V**. Conditions ensuring selective formation of compounds **IV** and **V** in high yield were found.

Selenides **II** and **III** are kinetically controlled products whose fraction in the mixture with Markovnikov adducts **IV** and **V** in the initial period was more than 90% (according to the NMR). The fraction of **II** (**III**) decreased while the fraction of **IV** (**V**) increased as the reaction progressed. The rearrangement in polar solvents (chloroform, acetonitrile) was faster than in carbon tetrachloride. The reaction of SeX₂ with ether **I** in carbon tetrachloride was more selective, whereas in chloroform a small amount of by-products (about 5%) was formed. Therefore, it is advisable to carry out the reaction in CCl₄, while the isomerization of the anti-Markovnikov adducts gives better results in chloro-



II, IV, X = Br; **III, V**, X = Cl.

form or acetonitrile. We thus succeeded in isolating selenides **IV** and **V** in 90–92% yield.

The rearrangement of bromide **II** was faster than that of chloride **III**. In the reaction of SeCl_2 with ether **I** in CCl_4 at room temperature, the ratio of compounds **III** and **V** was 9:1 in 18 h. In the reaction with selenium dibromide under analogous conditions, the corresponding Markovnikov adduct was the major product (ratio **II:IV** 2:3). Presumably, the isomerization involves intermediate formation of seleniranium cations [9].

The structure of selenides **II–V** was confirmed by ^1H and ^{13}C NMR spectra and elemental analyses (**IV**, **V**). In the ^{13}C NMR spectra of **IV** and **V** the coupling constant between ^{77}Se and CH_2 carbon nucleus was about 69 Hz, which is typical of direct coupling ($^1J_{\text{Se-C}}$). This indicates that the selenium atom adds to the terminal carbon atom of the allyl group. Each selenide **II–V** was a mixture of two diastereoisomers (*d,l* and *meso*) at a ratio of 1:1.

Thus, we have developed an efficient procedure for the synthesis of compounds **IV** and **V** which attract interest as intermediate products in fine organic synthesis.

Bis(1-benzyloxy-3-bromopropan-2-yl)selane (II) was identified by NMR in a mixture with compound **IV**. ^1H NMR spectrum, δ , ppm: 3.20–3.25 m (2H, CHSe), 3.70–3.78 m (4H, CH_2Br), 3.90–3.96 m (4H, CH_2O), 4.51 s (4H, CH_2Ph), 7.24–7.26 m (10H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 34.12 (CH_2Br), 41.11 (CHSe), 41.81 (CHSe), 70.95 (CH_2O), 73.37 (CH_2O); 127.51, 127.66, 128.31, 137.64 (C_{arom}).

Bis(1-benzyloxy-3-chloropropan-2-yl)selane (III) was identified by NMR in a mixture with compound **V**. ^1H NMR spectrum, δ , ppm: 3.24–3.27 m (2H, CHSe), 3.76–3.79 m (4H, CH_2Cl), 3.79–3.94 m (4H, CH_2O), 4.56 s (4H, CH_2Ph), 7.30–7.37 m (10H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 41.59 (CHSe), 41.92 (CHSe), 45.93 (CH_2Cl), 70.31 (CH_2O), 73.33 (CH_2O); 127.56, 127.71, 128.38, 138.03 (C_{arom}).

Bis(3-benzyloxy-2-bromopropan-1-yl)selane (IV). A solution of 0.32 g (2 mmol) of bromine in 10 mL of carbon tetrachloride was added dropwise under stirring at room temperature to a mixture of 0.158 g (2 mmol) of elemental selenium and 6 mL of carbon tetrachloride, and the mixture was stirred until selenium dissolved completely (10–15 min). The resulting solution of selenium dibromide was added dropwise under stirring over a period of 3 h at room

temperature to a solution of 0.59 g (4 mmol) of allyl benzyl ether (**I**) in 14 mL of carbon tetrachloride. The mixture was stirred for 18 h and filtered, the solvent was distilled off from the filtrate on a rotary evaporator, and the residue was analyzed by NMR. It contained compounds **II** and **IV** at a ratio of 2:3. The product mixture was heated for 8 h in 30 mL of boiling chloroform, the solvent was distilled off on a rotary evaporator, and the residue was dried under reduced pressure. Yield 0.98 g (92%), purity >95%, yellowish oily substance. ^1H NMR spectrum, δ , ppm: 3.15–3.31 m (4H, CH_2Se), 3.76–3.87 m (4H, CH_2O), 4.28 m (2H, CHBr), 4.58 s (4H, CH_2Ph), 7.29–7.37 m (10H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 29.97 (CH_2Se , $^1J_{\text{C-Se}} = 69$ Hz), 30.01 (CH_2Se , $^1J_{\text{C-Se}} = 69$ Hz), 51.16 (CHBr), 72.42 (CH_2O), 73.25 (CH_2O), 127.35, 127.56, 128.24, 138.01. Found, %: C 45.02; H 4.71; Br 30.05; Se 14.42. $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{O}_2\text{Se}$. Calculated, %: C 44.89; H 4.52; Br 29.86; Se 14.75.

Bis(3-benzyloxy-2-chloropropan-1-yl)selane (V) was synthesized in a similar way from selenium dichloride (prepared by reaction of elemental selenium with sulfur chloride [2–6]) and ether **I**. Yield 90%. ^1H NMR spectrum, δ , ppm: 3.04–3.07 m (2H, CH_2Se), 3.16–3.21 m (2H, CH_2Se), 3.67–3.79 m (4H, CH_2O), 4.23 m (2H, CHCl), 4.60 s (4H, CH_2Ph), 7.31–7.48 m (10H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 29.57 (CH_2Se , $^1J_{\text{C-Se}} = 69$ Hz), 59.56 (CHCl), 72.42 (CH_2O), 73.38 (CH_2O), 127.56, 127.71, 128.44, 137.56. Found, %: C 53.52; H 5.26; Cl 16.12; Se 17.91. $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{O}_2\text{Se}$. Calculated, %: C 53.83; H 5.42; Cl 15.89; Se 17.69.

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz for ^1H and ^{13}C , respectively, using CDCl_3 as solvent and hexamethyldisiloxane as reference.

This study was performed under financial support by the Russian Scientific Foundation (project no. 14-13-01085). The main results were obtained using the facilities of the Baikal Joint Analytic Center, Siberian Branch, Russian Academy of Sciences.

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