Letters to the Editor

Synthesis of 2,6-bis(chloromethyl)-1,4-diselenane

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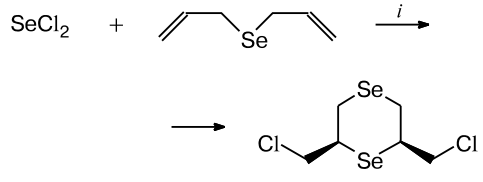
Selenium-containing electrophilic agents play an important role in organic synthesis.[1] Selenium dichloride and dibromide regarded as new efficient electrophilic agents.[2—5]

Selenium dichloride and dibromide are known to react with chalcogenides containing two double bonds.[2—4] Reactions of selenium dihalides with divinyl sulfide[2] and divinyl selenide[3] lead to the Markovnikov addition products: 2,6-dihalo-1,4-thiaselenanes and 2,6-dihalo-1,4-diselenanes, which undergo rearrangement into thermodynamically more stable 1,3-thiaselenolanes and 1,3-diselenolanes. Addition of selenium dihalides to divinyl sulfone leads to new four- and five-membered heterocycles, derivatives of 1,3-thiaselenetane-1,1-dioxides and 1,3-thiaselenolane-1,1-dioxides.[4] There is no reports in the literature on the reaction of selenium halides with allyl selenides.

We for the first time accomplished a reaction of selenium dichloride with diallyl selenide. It was found that this reaction leads to the hitherto unknown 2,6-bis(chloromethyl)-1,4-diselenane (**1**) in 70% yield, the product of anti-Markovnikov addition (Scheme 1).

The reaction was carried out at 0 °C in acetonitrile with the equimolar ratio of reactants. A solution of selenium dichloride, obtained by stirring of the equimolar amounts of selenium and sulfuryl chloride in MeCN, was added dropwise to a solution of diallyl selenide in MeCN at 0 °C, and the reaction mixture was stirred for 4 h. The product **1** was isolated by chromatography on silica gel (elution with hexane). Diallyl selenide was obtained from selenium and allyl bromide.[6]

Scheme 1



1

i. MeCN, 0 °C, 4 h.

The structure of diselenane **1** was established by ^{1}H and ^{13}C NMR spectroscopy (including JMOD) and confirmed by the mass spectrometric and elemental analysis data. The spin-spin coupling constant between the selenium atom and the carbon atom of the CH group (67 Hz) corresponds to the direct coupling constant for the C—Se bond ($^{1}J_{C-Se}$) (see Refs 2—4), that indicates the addition of the selenium atom to the central carbon atom of the allyl fragment. Though, *cis*- and *trans*-isomers can be formed in the reaction, the isolated diselenane **1** is a single

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diastereomer. The signals for the protons of the $SeCH_2$ group, in addition to the geminal spin-spin coupling constant (^2J = 13.3 Hz), have only two vicinal spin-spin coupling constants (^3J = 5.1 and 1.0 Hz), that indicates formation of the *cis*-diastereomer.

In conclusion, the reaction of selenium dichloride with diallyl selenide proceeded chemo-, regio-, and stereoselectively and leads to the new heterocycle **1**, which is promising as an intermediate product for organic synthesis.

2,6-Bis(chloromethyl)-1,4-diselenane (1). Light yellow oil. Found (%): C, 23.49; H, 3.38; Cl, 23.07; Se, 51.31. $C_6H_{10}Cl_2Se_2$. Calculated (%): C, 23.17; H, 3.24; Cl, 22.80; Se, 50.78. ^{1}H NMR, δ: 3.00 (dd, 2 H, $SeCH_2$, ^2J = 13.3 Hz, ^3J = 5.1 Hz); 3.06 (m, 2 H, SeCH); 3.52 (dd, 2 H, $SeCH_2$, ^2J = 13.3 Hz, ^3J = 1.0 Hz); 3.94 (dd, 2 H, $ClCH_2$, ^2J = 10.6 Hz, ^3J = 4.1 Hz); 4.25 (dd, 2 H, $ClCH_2$, ^2J = 10.6 Hz, ^3J = 10.6 Hz). ^{13}C NMR, δ: 20.68 ($SeCH_2$); 30.36 (SeCH, $^1J_{C-Se}$ = 67 Hz); 46.42 ($ClCH_2$). MS, *m*/*z* (I_{rel} (%)): 312 [M^+] (10), 236 (18), 160 (20), 121 (8), 93 (12), 75 (15), 41 (100).

NMR spectra were recorded on a Bruker DPX-400 spectrometer in DMSO-d_6 (400.13 MHz (^{1}H, HMDS) and 100.61 MHz (^{13}C, HMDS)). Mass spectrum was recorded on a Shimadzu GCMS-QP5050A spectrometer (EI, 70 eV).

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