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SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
B.A. Trofimov on his 70th anniversary

Reaction of Selenium Dichloride with Divinyl Selenide

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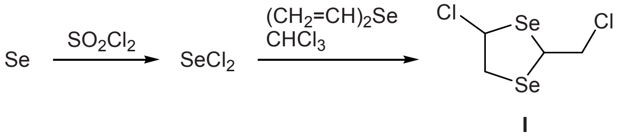
Selenium dichloride is a promising reagent for organic synthesis. However, prior to our studies [1–3] it was not used for the preparation of organoselenium compounds. By addition of selenium halides to diethynylsilanes we obtained previously unknown heterocyclic compounds [4–8]. It is known that the selenium atom in divinyl selenide stabilizes the positive charge on the neighboring carbon atom. Therefore, electrophilic reagents add selectively at the terminal carbon atom of the vinyl group [9]. The reaction of selenium dichloride with divinyl selenide was expected to produce a six-membered heterocyclic compound, 2,6-dichloro-1,4-diselenane.

We have found that selenium dichloride reacts with divinyl selenide to give previously unknown five-membered heterocyclic compound, 4-chloro-2-chloromethyl-1,3-diselenolane (**I**) with high selectivity (yield 80%). No six-membered 2,6-dichloro-1,4-diselenane was detected in the reaction mixture. The reaction was carried out in chloroform at 0–5°C, and the product was purified by chromatography on silica gel. Compound **I** was isolated as a mixture of diastereoisomers at a ratio of 4:1.



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Presumably, in this case the formation of five-membered ring is more favorable than the formation of six-membered ring. Selenium dichloride adds at the β-carbons atom of the vinyl groups, and the subsequent ring closure involves the α-carbon atom therein.

Selenium dichloride was prepared *in situ* by reaction of selenium with sulfuryl chloride in chloroform, and the structure of compound **I** was determined on the basis of the ^{1}H and ^{13}C NMR and mass spectra and elemental analysis.

4-Chloro-2-chloromethyl-1,3-diselenolane (I). Major diastereoisomer: ^{1}H NMR spectrum, δ, ppm: 3.83 d.d (1H, CH_2Cl, ^2J = 11.0, ^3J = 8.5 Hz), 3.85 d (2H, CH_2Se, ^3J = 4.0 Hz), 3.94 d.d (1H, CH_2Cl, ^2J = 11.0, ^3J = 7.0 Hz), 5.14 d.d (1H, SeCHSe, ^3J = 7.0, 8.5 Hz), 6.35 t (1H, SeCHCl, ^3J = 4.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 38.66, 44.41, 50.50, 65.73. Minor diastereoisomer: ^{1}H NMR spectrum, δ, ppm: 3.90 d (2H, CH_2Se, ^3J = 4.5 Hz), 4.05 d.d (1H, CH_2Cl, ^2J = 11.8, ^3J = 7.9 Hz), 4.08 d.d (1H, CH_2Cl, ^2J = 11.8, ^3J = 7.7), 5.05 d.d (1H, SeCHSe, ^3J = 7.9, 7.7 Hz), 6.18 t (1H, SeCHCl, ^3J = 4.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 38.83, 44.82, 50.80, 63.68. Mass spectrum, *m*/*z* (I_{rel}, %): 284 (100) $[M]^+$, 235 (34), 222 (57), 199 (20), 187 (18), 169 (23), 160 (90), 142 (28), 133 (19), 107 (58), 93 (20), 80 (23), 27 (65). Found, %: C 17.23; H 2.29; Cl 24.54; Se 56.38. $C_4H_6Cl_2Se_2$. Calculated, %: C 16.98; H 2.14; Cl 25.04; Se 55.84.

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

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