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LETTERS TO THE EDITOR

# Stereoselective Synthesis of 5-Bromo-2-bromomethyl-1,3-thiaselenolane 1,1-Dioxide by Addition of Selenium Dibromide to Divinyl Sulfone

**V. A. Potapov, E. O. Kurkutov, and S. V. Amosova**

*Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*
*e-mail: v_a_potapov@irioch.irk.ru*

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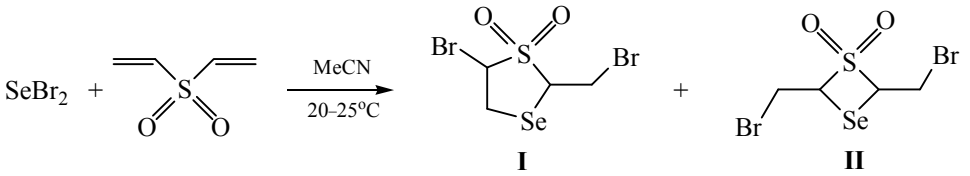
It is known that selenium dibromide cannot be isolated as an individual compound and exists in solution in equilibrium with $Se_2Br_2$ and bromine [1]. We have first shown [2, 3] that freshly prepared selenium dibromide can be used as a selective electrophile in the synthesis of organoselenium compounds.

Earlier we have studied the reactions of selenium dichloride and dibromide with divinyl sulfide and have shown that the course of the reactions is strongly solvent-dependent [4–8]. Reactions of selenium dihalides with divinyl sulfide in $CCl_4$ at room temperature result in the six-membered heterocycles, 2,6-dihalo-1,4-thiaselenanes [4–6]. The same reagents in chloroform at room temperature react with the formation of the five-membered heterocycles, 5-halo-2-halomethyl-1,3-thiaselenolanes [5–8]. The reaction of selenium dibromide with divinyl sulfone in chloroform proceeds with high selectivity at room temperature and gives rise exclusively to the four-membered heterocycle, 2,4-bis(bromomethyl)-1,3-thiaselenetane 1,1-dioxide **II** in quantitative yield with respect to the reacted divinyl sulfone whose conversion was 24% [9]. Product **II** is a mixture of two diastereomers in the ratio of 7 : 1.

We have found that if the reaction of selenium dibromide with divinyl sulfone is carried out in acetonitrile, along with thiaselenetane 1,1-dioxide **II** (yield 72%, the ratio of diastereomers 20:1), the hitherto unknown five-membered heterocycle, 5-bromo-2-bromomethyl-1,3-thiaselenolane 1,1-dioxide **I**, is formed in 24% yield with respect to the reacted divinyl sulfone whose conversion was 80%.




**I** **II**

The reaction proceeds at room temperature by addition of divinyl sulfone to the solution of selenium dibromide in acetonitrile. Heterocycle **I** is formed with high stereoselectivity: the content of the main diastereomer reaches 95% with 5% of the minor diastereomer.

Heterocycle **I** was isolated by flash chromatography (eluent: benzene–hexane, 3:1). Its structure was proved by $^1H$, $^{13}C$, $^{77}Se$ NMR spectroscopy and confirmed by the data of mass spectrometry and elemental analysis. The data of NMR spectroscopy, in particular, the values of the coupling constants $J$(Se–C), suggest that the selenium atom is linked both to the CH and the $CH_2$ groups.

**5-Bromo-2-bromomethyl-1,3-thiaselenolane 1,1-dioxide (I)**, mp 133°C. $^1H$ NMR, δ, ppm: 5.20 d.d

(1H, $SO_2CHBr$, $^3J$ 10.1, $^3J$ 5.6 Hz), 4.61 d.d (1H, $SO_2CHSe$, $^3J$ 6.4, $^3J$ 9.1 Hz), 4.15 d.d (1H, $CH_2Br$, $^2J$ 10.6, $^3J$ 6.4 Hz), 3.73 d.d (1H, $CH_2Br$, $^2J$ 10.6, $^3J$ 9.1 Hz), 3.38 m (2H, $SeCH_2$, $^3J$ 10.1, $^3J$ 5.6 Hz). $^{13}C$ NMR, δ, ppm: 21.19 ($SeCH_2$, $^1J_{Se-C}$ 55.6 Hz), 28.57 ($CH_2Br$), 49.36 (SCHSe, $^1J_{Se-C}$ 80.7 Hz), 59.51 (SCHBr). $^{77}Se$ NMR, δ, ppm: 287. MS, *m/z* ($I_{rel}$, %): 276 $[M - HBr]^{+\cdot}$, 108 (42), 106 (100), 104 (94), 102 (38), 80 (14), 48 (14). Found, %: C 13.12; H 1.75; Br 44.34. $C_4H_6O_2Br_2SSe$. Calculated, %: C 13.46; H 1.69; Br 44.77.

NMR spectra were taken on a Bruker DPX-400 spectrometer in $CDCl_3$ at working frequencies of 400 ($^1H$), 100 ($^{13}C$) and 76 MHz ($^{77}Se$) relative to HMDS and $Me_2Se$. Mass spectrum was obtained on GCMS-QP5050A chromatomass spectrometer (Shimadzu) at 70 eV.

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