

LETTERS
TO THE EDITOR

Reaction of Selenium Dibromide with Divinyl Sulfide

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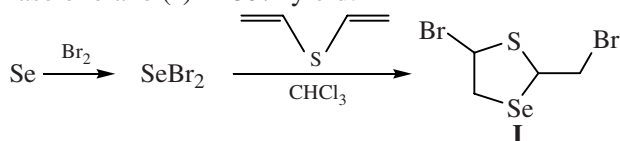
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There are few data in the literature concerning reactions of selenium dibromide. It is known that in solution selenium dibromide exists in equilibrium with Se_2Br_2 and bromine [1]. We used the example of the addition of selenium dibromide to diethynyldimethylsilane to show for the first time that this reagent can be used in the synthesis of organoselenium compounds [2, 3].

We earlier found that selenium dichloride reacts with divinyl sulfide to form an unsaturated heterocycle, 2-chloromethyl-1,3-thiaselenol (yield 30%) which was isolated by distillation [4]. The reaction of selenium dibromide with divinyl sulfide have never been reported in the literature.

We found that the reaction of selenium dibromide with divinyl sulfide leads to an earlier unknown heterocyclic compound 5-bromo-2-bromomethyl-1,3-thiaselenolane (**I**) in 80% yield.



The reaction proceeds in chloroform at room temperature. Product **I** represents a mixture of diastereomers in a 3 : 2 ratio.

The structure of heterocycle **I** was established by ^1H , ^{13}C , and ^{77}Se NMR spectroscopy and confirmed by elemental analysis. It is a dark liquid which decomposes upon vacuum distillation.

It can be assumed that the reaction of selenium dichloride with divinyl sulfide [4], too, involves initial formation of a saturated heterocycle, 5-chloro-2-chloromethyl-1,3-thiaselenolane, which undergoes subsequent dehydrochlorination to form 2-chloromethyl-1,3-thiaselenol.

Selenium dibromide was prepared in situ by the reaction of selenium with bromine in chloroform.

5-Bromo-2-bromomethyl-1,3-thiaselenolane (I). Major diastereomer. ^1H NMR spectrum, δ , ppm: 3.79–3.84 m (2H, CH_2Se), 3.86 m (1H, CH_2Br), 3.99 d. d (1H, CH_2Br , 2J 9.4, 3J 8.0 Hz), 5.03 t (1H, SCHSe , 3J 8.0 Hz), 6.10 d.d (1H, SCHBr , 3J 3.3, 3J 3.4 Hz). ^{13}C NMR spectrum, δ , ppm: 38.47 (CH_2Br), 45.97 (CH_2Se), 48.18 (SCHSe), 59.69 (SCHBr). ^{77}Se NMR spectrum, δ , ppm: 410. Minor diastereomer. ^1H NMR spectrum, δ , ppm: 3.69–3.73 m (2H, CH_2Br), 3.70 m, 3.89 m (2H, CH_2Se), 5.05 t (1H, SCHSe , 3J 7.9 Hz), 5.91 d. d (1H, SeCHBr , 3J 4.1, 3J 4.3 Hz). ^{13}C NMR spectrum, δ , ppm: 37.50 (CH_2Br), 44.39 (CH_2Se), 47.27 (SCHSe), 58.36 (SCHBr). ^{77}Se NMR, δ , ppm: 415. Found, %: C 15.00; H 1.69; Br 49.38. $\text{C}_4\text{H}_6\text{Br}_2\text{SSe}$. Calculated, %: C 14.79; H 1.86; Br 49.18.

The NMR spectra were taken on a Bruker DPX-400 instrument in CCl_4 at working frequencies of 400.13 (^1H , HMDS), 100.61 (^{13}C , HMDS), and 76.30 MHz (^{77}Se , Me_2Se).

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