ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 7, pp. 1387–1388. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © S.V. Amosova, M.V. Penzik, A.I. Albanov, V.A. Potapov, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 7, pp. 1221–1222.

LETTERS TO THE EDITOR

Reaction of Divinyl Sulfide with Selenium Tetrachloride

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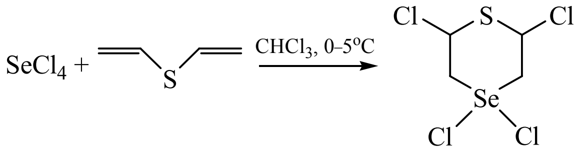
Received April 1, 2010

DOI: 10.1134/S1070363210070339

Divinyl sulfide is a multipurpose product in modern organic synthesis [1]; various heterocyclic compounds were obtained on its basis [2]. Earlier, we have studied the reactions of divinyl sulfide with selenium dichloride and dibromide, which, when carried out at room temperature in chloroform, result in 5-halo-2-halomethyl-1,3-thiaselenolanes, whereas in CCl_4, in 2,6-dihalo-1,4-thiaselenanes [3–6].

Addition of selenium tetrachloride to vinyl sulfides was not described. It is known that its reactions with alkenes may result in either the Markownikoff or anti-Markownikoff adducts [7, 8]. In the reaction of selenium tetrachloride with diallyl sulfide the anti-Markownikoff adduct, 3,5-bis(chloromethyl)-1,4-thiaselenane-4,4-dichloride is formed [8].

Thus we first performed the reaction of selenium tetrachloride with divinyl sulfide, which proceeds regioselectively and results in the Markownikoff adduct, the earlier unknown 2,4,4,6-tetrachloro-1,4-thiaselenane (**I**) in 70% yield.



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The reaction was performed in chloroform at 0–5°C with equimolar ratio of the reagents. Thiaselenane **I** is a powder of beige color, decomposed at heating. Its structure was proved by ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy, and the composition was confirmed by elemental analysis. From the NMR data, thiaselenane **I** exists as a mixture of the *cis* and *trans* diastereomers in the ratio of 6:5. The data of the NMR spectra, in particular, the coupling constants $J_{Se–C}$, point to the fact that the selenium atom is directly linked to the CH_2 groups having nonequivalent protons.

2,4,4,6-Tetrachloro-1,4-thiaselenane (I). *cis*-Diastereomer. ^{1}H NMR spectrum, δ, ppm: 4.05 d.d (1H, CH_2Se, ^2J 11.2 Hz, ^3J 11.2 Hz), 4.47 d.d (1H, CH_2Se ^2J 11.2 Hz, ^3J 3.5 Hz), 5.80 d.d (1H, CHCl, ^3J 11.2 Hz, ^3J 3.5 Hz). ^{13}C NMR spectrum, δ, ppm: 54.16 (CHCl), 55.33 (CH_2Se, $^1J_{SeC}$ 67.1 Hz). ^{77}Se NMR spectrum, δ, ppm: 510. *trans*-Diastereomer. ^{1}H NMR spectrum, δ, ppm: 4.02 d.d (1H, CH_2Se, ^2J 11.3 Hz, ^3J 11.3 Hz), 4.56 d.d (1H, CH_2Se, ^2J 11.3 Hz, ^3J 4.1 Hz), 6.04 d.d (1H, CHCl, ^3J 11.3 Hz, ^3J 4.1 Hz). ^{13}C NMR spectrum, δ, ppm: 53.66 (CHCl), 55.59 (CH_2Se, $^1J_{SeC}$ 66.0 Hz). ^{77}Se NMR spectrum, δ, ppm: 494. Found, %: C 15.86; H 2.04; Cl 46.10; S 10.50. $C_4H_6Cl_4SSe$. Calcd, %: C 15.65; H 1.97; Cl 46.20; S 10.45.

NMR spectra were registered on a Bruker DPX-400 spectrometer in $CDCl_3$ at working frequencies 400.13 (^{1}H, HMDS), 100.61 (^{13}C, HMDS) and 76.30 MHz (^{77}Se, Me_2Se).

ACKNOWLEDGMENTS

This work was performed with the financial support from the Russian Foundation for Basic Research (grant no. 10-03-00543).

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