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LETTERS TO THE EDITOR

Stereospecific Synthesis of *E,E*-Bis(2-chlorovinyl)selenide

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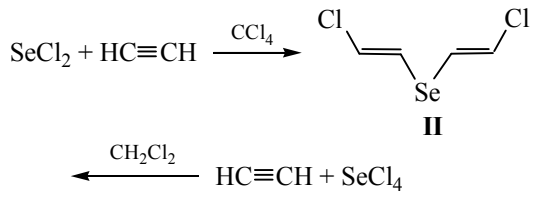
Bis(2-chlorovinyl)selenide was obtained as a mixture of the *E,E-, E,Z-* and *Z,Z*-isomers by the reaction of acetylene with selenium tetrachloride generated in the system SeO_2/conc. HCl/ether. A side product of this reaction is *E*-2-chlorovinyl 1,2,2-trichloroethyl selenide (**I**) [1]. Addition of selenium tetrachloride to acetylene at atmospheric pressure in ether at -45ºC was shown to result in bis(2-chlorovinyl)selenium dichloride in 9% yield; the stereochemistry of the product was not established [2]. According to [3], selenium monochloride, Se_2Cl_2, with acetylene gives *E*-2-chlorovinylselenenyl chloride, CHCl=CHSeCl. There are no data in the literature on the reaction of acetylene with selenium dichloride.

We have first shown that selenium dichloride can be used for synthesis of organoselenium compounds [4, 5]. For example, its addition to diorganyldiethynylsilanes or -germanes, and to divinyl chalcogenides affords new five- and six-membered heterocyclic compounds [6–9].

Here, we report on stereospecific methods of synthesis of *E,E*-bis(2-chlorovinyl) selenide (**II**) based on the reaction of selenium dichloride and tetrachloride with acetylene.



The reactions were performed in an autoclave under the acetylene pressure of 10–12 atm. Addition of selenium dichloride to acetylene in carbon tetrachloride at 30–40°C affords selenide **II** in 92% yield calculated with respect to selenium dichloride taken in the reaction. The reaction of selenium tetrachloride with acetylene in methylene chloride at 30–40°C affords selenide **II** in 70% yield. No selenide **I**, a side product of the reaction of acetylene with selenium tetrachloride generated in the system SeO_2/conc. HCl/ether [1], is formed under these conditions.

It should be mentioned that the nature of the solvent strongly affects the selectivity of the reactions. Thus, when chloroform is used instead of methylene chloride under similar conditions, compounds **II** and **I** are formed in 66% and 32% yield, respectively. The spectral characteristics of compound **I** correspond to those reported in the literature [1].

Therefore, based on acetylene and selenium dichloride or tetrachloride, we have developed stereospecific preparative methods of synthesis of selenide **II**, which is a new promising intermediate for organic synthesis. The isomeric *E,Z-* and *Z,Z*-bis(2-chlorovinyl) selenides, which are difficultly separated from the target product **II** are not formed under these conditions.

***E,E*-Bis(2-chlorovinyl) selenide (II),** light-yellow liquid, purified by flash chromatography on silica gel (eluent hexane). ^{1}H NMR, δ, ppm: 6.31 d (2H, ^3J 13.3 Hz), 6.63 d (1H, ^3J 13.3 Hz). ^{13}C NMR, δ, ppm: 121.56 ($^1J_{CH}$ 197.0 Hz), 117.31 ($^1J_{CH}$ 178.9 Hz). ^{77}Se NMR, δ, ppm: 336 ($^2J_{SeH}$ 20.5, $^3J_{SeH}$ 5.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 202 $[M]^+$ (89), 167 (100), 141 (67), 131 (64), 115 (35), 106 (60), 87 (69), 80 (39), 61 (67), 51 (65). Found, %: C 23.51; H 2.27. $C_4H_4Cl_2Se$. Calcd, %: C 23.79; H 2.00.

NMR spectra were taken on a Bruker DPX-400 spectrometer in $CDCl_3$ at working frequencies of 400 (^{1}H), 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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