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LETTERS TO THE EDITOR

Reaction of Selenium Tetrabromide with Acetylene

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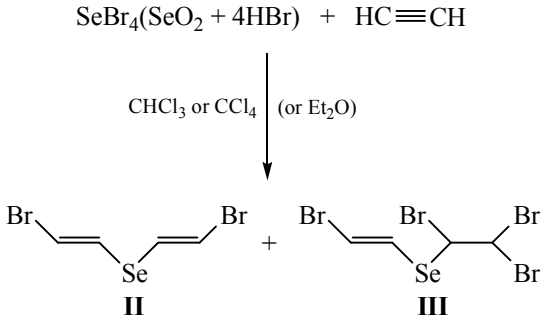
The reaction of selenium dioxide with concn. HBr is known to give selenium tetrabromide, which adds to acetylene in the absence of solvent leading to bis(2-bromovinyl)selenium dibromide (**I**) (the yield and isomeric composition were not given) [1]. According to the data of [2], the reaction of acetylene with selenium tetrabromide generated in the system SeO_2/conc. HBr/ether, results in compound **I** as a mixture of the *E,E*- and *Z,Z*-isomers in the 1 : 1.15 ratio in the yield of 54% and 1,1-dibromoselenophene in 40% yield [2]. The mixture of the *E,E*- and *Z,Z*-isomers failed to be separated by column chromatography (only one value of R_f for the presumed mixture of the *E,E*- and *Z,Z*-isomers of compound **I** was given [2]). The structure of compound **I** was proved by ^{1}H NMR spectra and elemental analysis, no ^{13}C NMR spectra were given in [2] for compound **I**.

Reactions of selenium halogenides with acetylene [3–5] and its derivatives, divinylsulfide [6, 7], divinylsulfone [8, 9], divinylselenide [10], is the subject of our systematic studies. The reactions of selenium dibromide and monobromide with acetylene proceed stereospecifically as the *anti*-addition with the formation of *E,E*-bis(2-bromovinyl)selenide (**II**) in high yield (90–98%) [3–5].

In continuation of these studies, we examined the reaction of selenium tetrabromide with acetylene in $CHCl_3$ and CCl_4 (autoclave, acetylene pressure 10–12 atm, 30–40°C), and also under the conditions given in [2] (generation of selenium tetrabromide in the system SeO_2/conc. HBr/ether). In the later case, the solution of SeO_2 in conc. HBr was added dropwise to the solution of acetylene in ether at –78°C and atmospheric pressure. In all cases the main products of the reaction are selenide **II** (45–70%) and the earlier unknown *E*-(2-bromovinyl)-1,2,2-tribromoethylselenide (**III**) (30–55%).



Selenide **III** was isolated by column chromatography on silica (eluent hexane). The parameters of the ^{1}H NMR spectrum of selenide **III** are practically identical to those for compound **I** given in [2]. Since compounds **I** and **III** have the same molecular formula, the data of elemental analysis also coincide. In the ^{13}C NMR spectrum of selenide **III** two signals of olefin carbons at 116.43 and 125.23 ppm, and two signals of carbon atoms of the saturated moiety at 41.78 and 51.42 ppm are observed.

Therefore, the compound obtained in [2] was selenide **III** rather than the mixture of the *E,E*- and *Z,Z*-isomers of compound **I**. This accounts for the failure in [2] of the attempt to separate the obtained product to the *E,E*- and *Z,Z*-isomers, only one value of R_f for this product, as well as the coupling constant of 3.8 Hz, which is too small to be assigned to $^3J_{HH}$ of the olefin protons. Indeed, the conventional values of $^3J_{HH}$ for olefin protons in 2-halovinylselenides are equal to

~6–7 Hz for the *Z*-isomers and 13–14 Hz for the *E*-isomers [3–5].

***E*-(2-Bromovinyl)-1,2,2-tribromoethylselenide (III),** dark-yellow liquid, purified by chromatography on silica (eluent hexane). ^{1}H NMR spectrum, δ, ppm: 5.50 d (1H, ^3J 3 Hz), 6.06 d (1H, ^3J 3 Hz), 6.82 d (1H, ^3J 14 Hz), 7.11 d (1H, ^3J 14 Hz). ^{13}C NMR spectrum, δ_C, ppm: 125.23 (SeCH=), 116.43 (BrCH=), 51.42 (CBr_2), 41.78 (CHBr). ^{77}Se NMR spectrum, δ_{Se}, ppm: 328. Found, %: C 10.24; H 0.94; Br 71.31; Se 17.28. $C_4H_4Br_4Se$. Calcd, %: C 10.66; H 0.89; Br 70.92; Se 17.52.

NMR spectra were recorded 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). The EI mass spectrum was obtained on a GCMS-QP5050A Shimadzu chromatomass spectrometer with the energy of ionizing electrons 70 eV.

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