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SHORT COMMUNICATIONS

New Data on the Reaction of Selenium Tetrachloride with Acetylene

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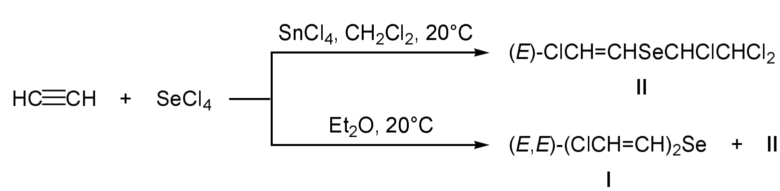
The reactions of SCl_2 and Se_2Cl_2 with terminal and symmetric alkynes are known to give bis(chlorovinyl) sulfides and bis(chlorovinyl) diselenides according to the *trans*-addition pattern [1–4]. The reaction of Se_2Cl_2 with acetylene is accompanied by liberation of selenium, and the product is *trans*-2-chlorovinylselenenyl chloride (*E*)-CHCl=CHSeCl [5]. Selenium tetrahalides were reported [6–10] to react with alkynes at –45 to –78°C, yielding bis(2-halovinyl)chalcogen dihalides. According to Brintzinger et al. [7], $(CHCl{=}CH)_2SeCl_2$ formed from acetylene and selenium tetrachloride undergoes disproportionation to $(CHCl_2CHCl)_2Se$, while Lendel et al. [9] identified the product obtained from acetylene and selenium tetrabromide as a mixture of (*Z*,*Z*)- and (*E*,*E*)-bis(2-bromovinyl)selenium dibromides. However, the spectral data given in [9] for (*Z*,*Z*)-bis(2-bromovinyl)selenium dibromide, in particular too small coupling constant (3.85 Hz), cast doubt on the assignment made by the authors.

We have found that acetylene reacts at 20°C with selenium tetrachloride (both prepared preliminarily and generated *in situ* from selenium dioxide) to give (*E*,*E*)-bis(2-chlorovinyl) selenide (**I**) containing small amounts of the (*Z*,*E*) and (*Z*,*Z*) isomers and (*E*)-2-chlorovinyl 1,2,2-trichloroethyl selenide (**II**). When the reaction was carried out in the presence of $SnCl_4$, selenide **II** is formed as the only product.

Selenides **I** and **II** were identified on the basis of their ^1H NMR spectra and GC–MS data. Isomeric selenides **I** characteristically showed in the ^1H NMR spectra doublet signals from the vinyl protons with coupling constants $^3J_{HH}$ of 13.3 Hz for the (*E*,*E*) isomer and 6.5 Hz for the (*Z*,*Z*) isomer. By comparing the signal intensity we succeeded in identifying a group of signals with coupling constants $^3J_{HH}$ of 6.5 and 13.5 Hz, which correspond to the (*Z*,*E*) isomer. Apart from downfield signals from the *trans*-vinyl protons ($^3J_{HH}$ = 13.4 Hz), selenide **II** gives upfield signals from protons in the trichloroethyl group with a coupling constant $^3J_{HH}$ of 3.4 Hz. The mass spectra of isomeric selenides **I** contain peaks from the molecular ions with *m*/*z* 202 (^{80}Se, ^{35}Cl). It is known that diorganylselenium dihalides do not give molecular ion peak in the mass spectra, while peak from the $[M - Cl]^+$ fragment ion is present [11, 12]. The absence of $[M - Cl]^+$ ion peaks in the spectra of isomeric selenides **I** unambiguously indicates formation of just selenides rather than selenium dichlorides. Compound **II** showed in the mass spectrum a strong peak of the molecular ion, *m*/*z* 272 (^{80}Se, ^{35}Cl), and peaks from $[M - CHCl_2]^+$ and $[M - CHClCHCl_2]^+$ fragment ions; these data are consistent with the structure of **II** as (*E*)-2-chlorovinyl 1,2,2-trichloroethyl selenide.

The formation of selenide **I** is rationalized in terms of halogenating ability of diorganylchalcogen dihalides like R_2SeCl_2 [13, 14] which are likely to be formed initially from $SeCl_4$ and acetylene. The chlorination of acetylene with selenium dichloride gives selenide **I**,



while rearrangement of selenium dichloride leads to selenide **II**. In the presence of $SnCl_4$, only the rearrangement occurs. Our results also suggest that the product identified in [9] as a mixture of (*E*,*E*)- and (*Z*,*Z*)-bis(bromovinyl)selenium dibromides is in fact (*E*)-2-bromovinyl 1,2,2-tribromoethyl selenide $CHBr{=}CHSeCHBrCHBr_2$, for the chemical shifts and coupling constants given in [9] almost coincide with those found by us for compound **II**.

Reaction of selenium tetrachloride with acetylene. Selenium dioxide, 2.2 g (20 mmol) SeO_2, was dissolved in 200 ml of diethyl ether, the solution was cooled to 0°C, 200 ml of 36% hydrochloric acid was added, the mixture was stirred for 30 min, and acetylene was passed through the resulting solution over a period of 30 h at 20°C. The organic phase was separated, and the solvent was removed at room temperature to obtain 3.44 g of a mixture of (*E*,*E*)-bis(2-chlorovinyl) selenide, (*Z*,*Z*)-bis(2-chlorovinyl) selenide, (*Z*,*E*)-bis(2-chlorovinyl) selenide (**I**), and selenide **II** at a ratio of 72 : 3.5 : 14.5 : 10 (according to the ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm: isomeric selenides **I**: (*E*,*E*): 6.65 d and 6.32 d (2H, *trans*-CH=CHCl, $^3J_{HH}$ = 13.3 Hz); (*Z*,*Z*): 6.77 d and 6.52 d (2H, *cis*-CH=CHCl, $^3J_{HH}$ = 6.2 Hz); (*Z*,*E*): 6.77 d and 6.42 d (2H, *trans*-CH=CHCl, $^3J_{HH}$ = 13.3 Hz), 6.47 d (2H, *cic*-CH=CHCl, $^3J_{HH}$ = 6.2 Hz); the signal from the second vinyl proton is overlapped by those of the other isomers; selenide **II**: 6.88 d and 6.67 d (2H, *trans*-CH=CHCl, $^3J_{HH}$ = 13.3 Hz), 6.03 d and 5.32 d (2H, $CHClCHCl_2$, $^3J_{HH}$ = 3.4 Hz). Mass spectrum, *m*/*z* (^{80}Se, ^{35}Cl) (I_{rel}, %): **I**: 202 (57.2) $[M]^+$, 167 (100) $[M - Cl]^+$, 141 (43.5) $[M - CH{=}CHCl]^+$, 106 (44.3) $[C_2H_2Se]^+$; **II**: 272 (41.0) $[M]^+$, 189 (100) $[M - CHCl_2]^+$, 176 (31.6) $[CHCl{=}CHSeCl]^+$, 141 (76.6) $[M - C_2H_2Cl_3]^+$.

(*E*)-2-Chlorovinyl 1,2,2-trichloroethyl selenide (II). Acetylene was passed over a period of 3 h through a solution of 0.76 g (3.5 mmol) of $SeCl_4$ and 0.80 g (3 mmol) of $SnCl_4$ in 20 ml of methylene chloride, maintained at 20°C. The mixture was washed with water to remove $SnCl_4$ and dried over $CaCl_2$. Removal of the solvent under reduced pressure left 0.58 g (62%) of selenide **II** which contained (according to the GC–MS data) about 5% of isomeric selenides **I**.

The ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 MHz from solutions in $CDCl_3$. The mass spectra (70 eV) were obtained on an HP-5971A mass-selective detector.

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