ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 7, pp. 1560–1561. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © E.P. Levanova, V.A. Grabel'nykh, N.V. Russavskaya, A.I. Albanov, A.V. Elaev, O.A. Tarasova, N.A. Korchevin, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 7, pp. 1213–1214.

LETTERS TO THE EDITOR

Features of the Reaction of 2,3-Dichloroprop-1-ene with Selenium in a Hydrazine Hydrate–Base Systems

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Received February 3, 2011

DOI: 10.1134/S1070363211070267

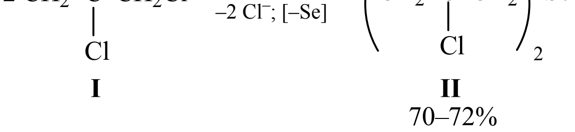
The direction of the reaction of sulfur with 2,3-dichloro-1-propene **I** in the hydrazine hydrate–base system was shown to depend on the nature of the used bases. In the hydrazine hydrate–KOH system (molar ratio KOH:S = 1:1) the reaction with dichloride **I** affords bis(2-chloro-1-propen-3-yl)sulfide (78%) [1]. The disulfide anion generated in the system hydrazine hydrate–monoethanolamine reacts with dichloride **I** to give bis(2-chloro-1-propen-3-yl)disulfide (70%) [2]. Tellurium, which is reduced to the anions Te_n^{2-} only in the hydrazine hydrate–alkali system, reacts with 2,3-dichloro-1-propene **I** with elimination of both chlorine atoms, and the reaction product is allene [1].

We carried out the reaction of selenium dichloride **I** and found that in both cases (KOH or monoethanolamine) the reaction product in the used basic-reducing systems is bis(2-chloro-1-propen-3-yl)selenide **II**.

Thus, in the course of the reaction there is a decrease in the number of selenium atoms (degree of selenidity) from 2 in the starting diselenides to 1 in the resulting bis(2-chloro-1-propen-3-yl)selenide **II**.

$$4\,Se + 4\,KOH + N_2H_4{\cdot}H_2O \rightarrow 2\,K_2Se_2 + N_2 + 5\,H_2O,$$

$$4\,Se + 2\,H_2NCH_2CH_2OH + 3\,N_2H_4{\cdot}H_2O \rightarrow (H_3NCH_2CH_2OH)_2Se_2 + (N_2H_5)_2Se_2 + N_2 + 3\,H_2O,$$



$$2\,CH_2{=}\underset{\displaystyle Cl}{C}{-}CH_2Cl \xrightarrow[-2\,Cl^-;\,[-Se]]{Se_2^{2-}} \left(CH_2{=}\underset{\displaystyle Cl}{C}{-}CH_2\right)_2Se$$

I **II**

70–72%

Despite the milder reaction conditions than those described in [1, 2] (25–50°C), the corresponding bis(2-chloro-1-propen-3-yl)diselenide **III** is detected only by the NMR spectroscopy.

An increase in the temperature of the system hydrazine hydrate–KOH up to ~50°C changes significantly the reaction direction. Selenide **II** is formed in a yield of only 13%, the formation of allene (3.5%) and probable products of the selenide **II** transformation is observed (total yield 28% relative to the used selenium).

Bis(2-chloro-1-propen-3-yl)selenide (II). *a*. To a solution of potassium selenide prepared from 2.8 g of KOH and 4.0 g of selenium in 20 ml of hydrazine hydrate at 0–5°C was added 9.2 g of 2,3-dichloro-1-propene **I**. The mixture was stirred for 2 h at the same temperature. The obtained selenide **II** was separated as an organic layer. Yield 72%, bp 84–87°C (3 mm Hg). ^{1}H NMR spectrum, δ, ppm: 3.46 s (CH_2Se, $^2J_{HSe}$ 14.8 Hz), 5.26 d (*cis*-H–C=C–C, ^2J 1.4 Hz), 5.31 d (*trans*-H–C=C–C, ^2J 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 31.08 (CH_2Se, J_{CSe} 68.9 Hz), 114.30 (CH_2=), 139.03 (=CCl). ^{77}Se NMR spectrum: δ_{Se} 252.86 ppm (quintet, $^2J_{HSe}$ 14.8 Hz). Mass spectrum, *m*/*z* (^{35}Cl, ^{80}Se) (*I*, %): 230 (1) $[M^{+\cdot}]$, 195 (6) $[M - Cl]^+$, 155 (27) $[M - C_3H_4Cl]^+$, 127 (3) $[SeCCl]^+$, 93 (16) $[CHSe]^+$, 80 (6) $[Se^{+\cdot}]$, 75 (11) $[C_3H_4Cl]^+$, 61 (2) $[C_2H_2Cl]^+$, 49 (6) $[CH_2Cl]^+$, 41 (1) $[C_3H_5]^{+\cdot}$, 40 (5) $[C_3H_4]^{+\cdot}$. Found, %: C 30.92; H 3.63; Cl 30.52; Se 35.20. $C_6H_8Cl_2Se$. Calculated, %: C 31.33; H 3.51; Cl 30.83; Se 34.33.

b. To a mixture of 4.0 g of selenium, 3.6 ml of monoethanolamine, and 30 ml of hydrazine hydrate at

15–20°C was added 11.2 g of 2,3-dichloro-1-propene **I**. The mixture was stirred for 6 h at the same temperature. By the NMR data, the separated organic layer contains diselenide **III** [~7%, δ_{Se} 376.43 ppm (t, $^2J_{SeH}$ 17.4 Hz)] along with selenide **II** (70%) isolated as described above. Diselenide was not found by the chromatography.

The ^{1}H, ^{13}C, and ^{77}Se NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 100.62, and 76.31 MHz, respectively) in $CDCl_3$, internal references TMS (^{1}H, ^{13}C) and Me_2Se (^{77}Se). The mass spectra were recorded on a Shimadzu GCMS–QP5050A chromato-mass-spectrometer (column SPB-5, 60000×0.25 mm), quadrupole mass-analyzer, electron ionization (70 eV, ion source temperature 190°C, range of detected mass 34–650 Da).

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