FORMATION OF 1,2-DISELENOL-3-ONE IN THE COPYROLYSIS OF PROPARGYL ALCOHOL AND DIMETHYL SELENIDE

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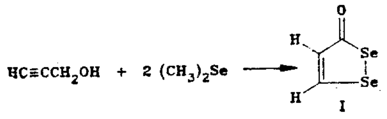
We have established that the gas-phase reaction of propargyl alcohol and dimethyl selenide at 450-480° unexpectedly yields the previously unknown 1,2-diselenol-3-one (I).

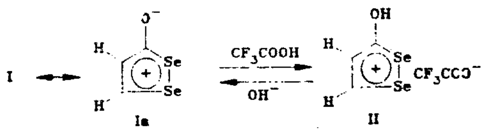
Excess of dimethyl selenide favors an increased yield of the diselenol I.



The reaction was carried out by introducing the mixture of reagents at 21 ml/h into a quartz tube reactor with heating zone 650 × 30 mm in a stream of nitrogen (4 liter/h). After unreacted materials were distilled from the condensate the crystalline residue was recrystallized from methanol. Compound I was isolated in up to 25% yield. Other reaction products were gaseous compounds, selenium, a small amount of selenophene, and a number of so far unidentified liquid materials.

1,2-Diselenol-3-one is a light brown crystalline material that is stable in air, soluble in benzene, acetone, and chloroform, moderately soluble in alcohols, and insoluble in water. Mp 50-51°. Elemental composition corresponds to the calculated values. The IR spectrum (tablets with KBr) has a series of bands in the 3070-3000 cm^{-1} region, two intense bands at 1635 and 1615 cm^{-1}, and narrow medium-intensity bands at 1515, 1285, 1130, 1020, 745, and 520 cm^{-1}. The ^{1}H NMR spectrum (in CDCl$_3$) shows two doublet signals at 7.23 and 8.72 ppm, J = 6.1 Hz. The ^{13}C NMR spectrum shows three signals: 200.66, 152.93, and 128.54 ppm. The mass spectrum (at 70 eV) has intense peaks that correspond to the molecule ion with isotope distribution typical for a molecule with two selenium atoms (M^+ for isotope ^{80}Se, 214), and Se_2^+, $(C_2H_2Se)^+$, and $(C_3H_2O)^+$ fragment ions.

These data are evidence for the aromatic nature of compound I. The aromaticity of 1,2-dithiol-3-ones and 1,2-dithiol-3-thiones is determined by the substantial contribution to their state of the isomeric dipolar forms [1] which have a system of six π-electrons. Evidently the substantial contribution of compound I to the electron structure has, by analogy, the form of Ia:



Compound I is easily protonated by the trifluoroacetic acid. The ^{1}H NMR spectrum of the resulting cation II shows the expected shift of the C-H proton signals toward the weaker field (7.52 and 9.10 ppm, respectively).

LITERATURE CITED

1. D. Barton and W. D. Ollis (eds.), General Organic Chemistry [Russian translation], Vol. 9, Khimiya, Moscow (1985), p. 300.

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