

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Some Reactions of 1,4-Diselenane¹

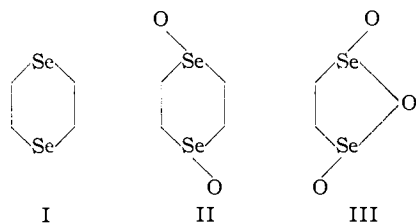
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The synthesis of 1,4-diselenane (I) from aluminum selenide and ethylene dibromide has been modified and the yield substantially improved. Oxidation of I with 32% peroxyacetic acid yields both 1,4-diselenane dioxide (II) and *trans*-ethanediseleninic anhydride (III). Oxidation with concentrated nitric acid gives IV, the dihydronitrate of 1,4-diselenane dioxide. 1,4-Diselenane forms addition compounds with cadmium chloride and palladium(II) chloride, having the formulas DS·2CdCl₂ and DS·PdCl₂. Treatment of I with excess methyl iodide gives a monomethylated cyclic selenonium salt V.

If the configuration of the bonds about the selenium atom in selenoxides is assumed to be pyramidal rather than planar, the 1,4-dioxide of 1,4-diselenane (II) should exist in both *cis* and *trans* forms. The parent compound I was first reported² as an intermediate in the projected synthesis of its dioxide; but with the very small amount of diselenane available, the attempted oxidation to II was unsuccessful.

Recently, McCullough and Tideswell³ have described an improved synthesis for 1,4-diselenane; by controlling reaction conditions, it has been found possible to increase the yield from about 2% reported by these workers to 10%. The availability of 1,4-diselenane having been greatly increased, we reattempted the synthesis of the dioxide(s). Careful oxidation of I with 32% peroxyacetic acid

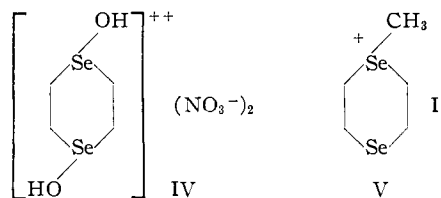


at 0° yields a compound C₄H₈Se₂O₂, which is rapidly converted back to I by reduction with sulfurous acid or hydroxylamine. The possibility that this oxidation product is the 1,1-dioxide (a selenone) is ruled out by its reaction with aqueous hydrogen halides to form the known diselenane 1,1,4,4-tetrahalides.³ Our compound is thus the 1,4-dioxide, although we cannot say whether it is a *cis* or *trans* form or (less likely) a dioxide in which the configuration about the selenoxide groups is planar rather than pyramidal. We are at present attempting a complete structure determination of this dioxide using X-ray diffraction.

During the conversion of diselenane to its dioxide, some oxidative degradation of the ring occurs, for if the oxidation product is recrystallized from aqueous methanol (in which the dioxide is very soluble) *trans*-ethanediseleninic anhydride (III) is obtained in small yield. The determination of the structure of this remarkable anhydride, using X-ray diffraction, is described in another paper.⁴ Both the dioxide and the anhydride decompose rapidly if heated above 80°, both darken slowly if allowed to

stand in moist air for more than 2 days, and both are extremely sensitive to base. The course of the decompositions is not yet clear, but elemental selenium is a final product in each case. At least one other product is formed in the oxidation, for powder photographs of the crude product show lines characteristic neither of the dioxide, the anhydride nor the starting material.

Oxidation of 1,4-diselenane with concentrated nitric acid at 0° gives IV, the dihydronitrate of II. The hydronitrate may be reduced to I and converted to the diselenane tetrahalides with hydrogen chloride or hydrogen bromide; however, the high solubility of the dioxide in water and its sensitivity to base has prevented our conversion of IV to pure samples of II.



Preliminary experiments revealed marked but selective donor characteristics of 1,4-diselenane. Complexes of the type DS·HgX₂ are known,⁵ and we have found that diselenane also forms the complexes DS·2CdCl₂ and DS·PdCl₂ when treated with alcoholic solutions of the respective chlorides. No evidence of complex formation was found with the chlorides of nickel, iron(III), copper(II), chromium(III) or cobalt(II). Diselenane reacts also with methyl iodide; even with a large excess of the latter, only the monomethylated selenonium salt V is formed.

Experimental

1,4-Diselenane.—Aluminum selenide was prepared from 100 g. of selenium powder and 40 g. of aluminum powder.⁶ The pellet of excess aluminum was removed and the selenide pulverized quickly using an iron mortar. The powdered selenide was added to 200 g. of ethylene dibromide, and the flask was slowly heated until reaction began. From that point, agitation was maintained, and the temperature of the mixture was controlled carefully with external heating and cooling. During the first hour the temperature was kept between 80 and 85°, during the second hour between 85 and 95°, during the third hour between 95 and 105°, then the temperature was brought slowly up to 140° over a period of 8 hours, and kept at that temperature for an additional five hours. The mixture was allowed to cool, and 2500 ml. of water was cautiously added (considerable quantities of the very poisonous H₂Se were released). Twenty grams of solid potassium hydroxide was added and

(1) This work was supported in part by a grant from the Research Corporation.

(2) E. S. Gould and J. D. McCullough, *THIS JOURNAL*, **73**, 1105 (1951).

(3) J. D. McCullough and N. W. Tideswell, *ibid.*, **76**, 3091 (1954).

(4) E. S. Gould and B. Post, *ibid.*, **73**, 5161 (1950).

(5) J. D. McCullough, private communication.

(6) G. R. Waitkins and R. Shutt, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 183.

the mixture was refluxed for one hour. The mixture was then steam distilled, 1500 ml. of distillate being collected. Much of the solid diselenane was caught in the condenser, and some orange oil was collected in the receiver. The solid material in the condenser was recrystallized from 200 cc. of methanol, whereas the orange oil was separated, refluxed with 50 cc. of ethanol and 2 g. of potassium hydroxide for 15 minutes, then cooled to 45°. The additional solid diselenane separating at this temperature was removed, and the filtrate was diluted with 100 cc. of water and cooled to 0°, whereupon an additional 1.2 g. of diselenane crystallized. The three crops of diselenane crystals were combined and recrystallized once more from methanol. The yield was 11.0 g. (10%), m.p. 112° (reported 112.5–113.5°).

1,4-Diselenane Complex with Cadmium Chloride.—Hot alcoholic solutions of 110 mg. of diselenane and 150 mg. of cadmium chloride were mixed. A white microcrystalline complex precipitated almost immediately. The mixture was allowed to cool and the complex filtered off. It could not be crystallized from the common organic solvents; yield 170 mg. (55%).

Anal. Calcd. for $C_4H_8Se_2Cd_2Cl_4$: Se, 28.2. Found: Se, 28.0.

1,4-Diselenane Complex with Palladium(II) Chloride.—To 5 cc. of alcohol was added 10 drops of 12 *N* HCl. Thirty milligrams of palladium(II) chloride was dissolved in this solution with heating. The resulting solution was added dropwise to a solution of 21.3 mg. of 1,4-diselenane in 2 cc. of hot ethanol until the red palladium chloride color persisted. The bright yellow precipitate was allowed to settle, was washed with ethanol (in which the complex is almost completely insoluble), and allowed to dry in air to constant weight. The complex could not be analyzed for selenium iodometrically in the usual way⁷ since the color of the PdI_4 complex interferes with the starch-iodine end-point. However, 38.8 mg. of the complex was formed; if it is assumed that the complex is essentially insoluble in ethanol, the mole ratio $PdCl_2$ /diselenane may be calculated to be 1.01.

1,4-Diselenane Methiodide (V).—To 2.0 cc. of methyl iodide was added 100 mg. of diselenane. The solution was allowed to stand 3 days. The pale-yellow precipitate (94 mg., 91%) was filtered off and dried in air, m.p. 133° dec.

Anal. Calcd. for $C_5H_{11}Se_2I$: C, 16.85; H, 3.09. Found: C, 16.93; H, 3.22.

1,4-Diselenane Dioxide Dihydrate (IV).—To 1.2 cc. of concentrated nitric acid at 0° was added 300 mg. of 1,4-diselenane in small portions. The mixture was kept cold during the reaction, and the white crystalline dihydrone hydrate precipitated almost immediately. The mixture was allowed to stand for five minutes and the dihydrone hydrate removed by filtration. The product was allowed to dry in air for 3 days; yield 407 mg. (78%), m.p. 111.5° (vigorous decomposition).

Anal. Calcd. for $C_4H_{10}Se_2N_2O_8$: Se, 42.5. Found: Se, 42.0.

Solutions of the hydrate are distinctly acid but cannot be titrated with base since the color change in the vicinity of the equivalence point is not at all sharp. Attempts were made to convert this compound to 1,4-diselenane dioxide by neutralization, first with calcium carbonate, then with excess ammonia, then with a stoichiometric quantity of

ammonia. When calcium carbonate was used for neutralization, beautiful crystals (apparently a solid solution of calcium nitrate with the desired dioxide) separated, but no pure dioxide was isolated. With an excess of ammonia, the solution slowly became yellow and malodorous and a sticky yellow mass precipitated. With a stoichiometric quantity of ammonia, decomposition was avoided, but separation of the dioxide from ammonium nitrate could not be carried out. Separation of the dioxide from dilute aqueous solutions is complicated by its rather high solubility in water (6.3 g. in 100 cc. of water at 0°). We have succeeded in converting the hydrate IV to diselenane dioxide in 31% yield by treatment with the anion exchange resin Dowex 1 (4% cross-linked) in the bicarbonate form. Under these conditions, very little of the dioxide is converted to *trans*-ethanediseleninic anhydride.

1,4-Diselenane Dioxide (II).—To 1 cc. of glacial acetic acid was added 200 mg. of 1,4-diselenane. The mixture was cooled to 0°, and 1.0 cc. of a 32% solution of peroxyacetic acid in glacial acetic acid was added dropwise. The mixture was allowed to stand 10 minutes, and 2 cc. of ice-water was added. The solution was extracted 3 times with 10-cc. portions of ether, the ether extracts being discarded. The aqueous layer was evaporated to dryness *in vacuo* at 25°. The residue was dissolved in a minimum volume of water at 45°, and the solution was diluted with 20 times its volume of boiling ethanol. Slow cooling yielded 70 mg. (30%) of white crystals, m.p. 109° dec. The density of the dioxide (as determined by flotation using mixtures of CCl_4 and CH_2I_2) is 2.58 g./cc.

Anal. Calcd. for $C_4H_8Se_2O_2$: C, 19.52; H, 3.27; Se, 64.2. Found: C, 19.64; H, 3.45; Se, 64.5.

Acidified aqueous solutions of the dioxide or its hydrate are reduced to diselenane with hydroxylammonium sulfate or sodium hydrogen sulfite. Treatment of a solution of the dioxide or its hydrate with concentrated HCl gives 1,4-diselenane tetrachloride, m.p. 223° (reported² 183–185°).

Anal. Calcd. for $C_4H_8Se_2Cl_4$: Se, 44.6. Found: Se, 44.9.

Similarly, treatment of a solution of the dioxide or its hydrate with concentrated HBr gives 1,4-diselenane tetrabromide, m.p. 151° (reported² 149°).

***trans*-Ethanediseleninic Anhydride (III).**—The preparation of this compound is similar to that of 1,4-diselenane dioxide. Here, however, the residue from the evaporation to dryness is dissolved in a minimum volume of water, and the solution is quickly diluted to eight times its volume of boiling methanol. Upon cooling, the dioxide remains in solution, and a small yield of dense white crystals separates. The quantity of the anhydride is increased slightly by carrying out the oxidation with 40% instead of 32% peroxyacetic acid, but in no case did the yield of this compound exceed 30 mg. (14%), m.p. 100–102° dec., d. 2.92 g./cc.

Anal. Calcd. for $C_2H_4Se_2O_3$: Se, 67.5. Found: Se, 67.5.

Treatment of aqueous solutions of this compound with hydrochloric or hydrobromic acids yields no precipitate of tetrahalide. Treatment with sulfurous acid yields an orange, non-crystalline material (probably a polymer), insoluble in the common organic solvents and therefore not purifiable by crystallization. The composition of the latter material is variable, its selenium content lying between 70 and 80%.

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(7) E. S. Gould, *Anal. Chem.*, **23**, 1502 (1951).