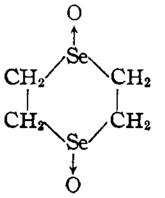
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

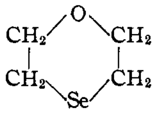
The Synthesis of 1,4-Diselenane[1]

BY EDWIN S. GOULD AND JAMES D. McCULLOUGH

Although there is good reason to believe that the configuration of the selenium atom in selenoxides is similar to that of the sulfur atom in sulfoxides, no chemical proof for such a similarity has appeared. As one of the early demonstrations of the non-planarity of the bonds to the sulfur atom in sulfoxides, Bell and Bennett[2] prepared dithiane-1,4-dioxide and separated it into *cis-* and *trans-*isomers. Similar work has been carried out in this Laboratory in an attempt to prepare *cis-* and *trans-*isomers of diselenane-1,4-dioxide (I), during the course of which it became necessary to prepare 1,4-diselenane. Although our ultimate objective was not attained, the synthesis of this compound involved a number of points of interest.



I



II

The methods which were first attempted, and which later proved to be unsuitable, were based on the synthesis of dithiane from ethylene bromide and sodium sulfide by Masson[3] and the synthesis of 1,4-selenoxane (II) from β,β′-dichlorodiethyl ether and sodium selenide by Gibson and Johnson.[4] In our earlier attempts to synthesize diselenane, both ethylene bromide and β,β′-dichlorodiethyl selenide (selenium mustard gas) were treated with solutions of sodium or lithium selenide in alcohol–water mixtures of various compositions. In all such cases, only water-soluble products resulted, indicating that 1,4-diselenane, which is practically insoluble in water, was not formed in appreciable quantity.

The failure of our first attempts is explicable if one assumes parallelism between the behavior of β,β′-dichlorodiethyl sulfide, as described by Bartlett and Swain,[5] and it selenium analog. In order to minimize the undesired solvolytic reactions indicated by the work of those authors, the synthesis of 1,4-diselenane was then attempted in anhydrous acetone using carefully dried β,β′-dichlorodiethyl selenide and powdered lithium selenide. Although the yield was disappointingly small, a crystalline product was isolated which was unambiguously identified as 1,4-diselenane through chemical analysis and a complete determination of the structure through an X-ray diffraction study.[6]

Experimental

Lithium Selenide.—Hydrogen selenide gas was generated by treatment of aluminum selenide (from 55 g. of aluminum powder and 33 g. of dried selenium) with water and with dilute hydrochloric acid.[7] The gas was diluted with dry nitrogen, dried by passing it over anhydrous calcium chloride, then passed into a solution of lithium ethoxide in ethanol (prepared from 8.4 g. of lithium metal and 900 ml. of absolute ethanol), while gentle stirring was maintained. The solution became red, and considerable solid lithium selenide precipitated. When all of the aluminum selenide was hydrolyzed, dry nitrogen gas was passed through the alcoholic solution, and the solution was evaporated to about 200 ml., after which it was transferred to a smaller flask, and the remainder of the alcohol removed. The last traces of alcohol were taken off by heating the selenide to 400° *in vacuo* for a period of 1 hour. The selenide was removed from the flask in a dry-box and thoroughly pulverized, then transferred to a 3-neck round-bottom flask which was kept tightly stoppered until ready for use.

β,β′-Dichlorodiethyl Selenide.—β,β′-Dichlorodiethylselenium dichloride was prepared in benzene solution from selenium monochloride and ethylene as described by Boord and Cope.[8] The solid was not purified, but the benzene solution, after evaporation to a convenient volume, was treated with twice its volume in 1 *N* sulfuric acid, to which 2 g. of potassium iodide and 2 ml. of starch solution had been added. The mixture was shaken vigorously in a separatory funnel, adding a saturated solution of sodium thiosulfate in portions until the starch–iodine color disappeared and the benzene layer was a pale yellow. The benzene layer was dried with anhydrous sodium sulfate, filtered, the benzene removed, and the dichloro selenide distilled *in vacuo* (b.p. 80–81° at 2 mm.). The yield from 290 g. of selenium monochloride was 113 g. of dichloro selenide (45%). CAUTION: As might be expected, selenium mustard gas is a powerful eye irritant. The eyes of the operator should be fully protected in all operations.

1,4-Diselenane.—To the entire quantity of powdered lithium selenide prepared above was added 800 ml. of dry acetone and 10 g. of finely powdered potassium iodide. The mixture was stirred vigorously and protected from the air by passing a slow stream of nitrogen gas through the flask. A solution of 32 g. of selenium mustard gas in 100 ml. of dry acetone was added dropwise to the suspension of the selenide, the entire addition requiring about 90 minutes. The mixture was then refluxed for 48 hours, continuing the stirring, at the end of which time most of the lithium selenide appeared to be undissolved. The mixture was then evaporated to a volume of 200 ml., continuing the stirring in order to minimize bumping. The mixture was then filtered hot and the residue discarded. To the filtrate was added 100 ml. of a 20% solution of potassium hydroxide in methanol, and the solution was refluxed an additional hour in order to destroy any unreacted selenium mustard gas. The solution was allowed to cool, and 300 ml. of a half-saturated solution of sodium chloride in water was added. The resulting mixture was extracted with three 200-ml. portions of benzene, and the benzene extractions were dried with anhydrous sodium sulfate. Most of the benzene was then removed on a steam-bath, and the last traces were taken off at 40° using a water-pump. The remaining liquid was then distilled at 22 mm. Almost all of the distillate fell into two portions, a liquid boiling in the range 75–80°, and a solid boiling (or subliming) at 115–120°. The liquid was mesityl oxide, identified by its 2,4-dinitrophenylhydrazone. The solid was recrystallized from methanol, and a final purification was carried out by vacuum sublimation at 100° and 2 mm. The sublimed product melted at 112.5–113.5°. The yield was 100 mg. (0.3%). Attempts to prepare diselenane, using similar procedures, but with either ethanol or dioxane as a solvent, produced none of the de-

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[1] Based on research carried out under Task Order I of Contract N6onr-275, between the Office of Naval Research and the University of California, Los Angeles.

[2] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798 (1927).

[3] O. Masson, *ibid.*, **49**, 234 (1886).

[4] C. S. Gibson and J. B. Johnson, *ibid.*, 266 (1931).

[5] P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1406 (1949).

[6] R. E. Marsh and J. D McCullough, *ibid.*, **73**, 1106 (1951).

[7] G. R. Waltkins and R. Shutt, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 183.

[8] C. E. Boord and F. F. Cope, THIS JOURNAL, **44**, 395 (1922).

sired compound. Combustion analysis by the method of McCullough, Campbell and Krilanovich[9] showed a selenium content of 72.6% (calculated, 73.8). This low value would be expected to result from the method used, due to the high volatility of the compound. Appreciable amounts of diselenane vapor were carried out of the burner by the oxygen stream between the time that the flame was lit and the absorber and chimney were brought into place. A semi-quantitative bromination of a 10.8-mg. sample of the compound showed that 1.91 moles of bromine was absorbed for each mole of diselenane (theor. 2.00). The resulting product, presumably 1,1,4,4-diselenane tetrabromide, melted at 149°.

The density of solid 1,4-diselenane was found by flotation in mixtures of bromoform and ethylene bromide to be 2.2. The volume of the unit cell, as determined by Marsh and McCullough,[6] was 313 Å.^{3} with two molecules of diselenane per unit cell. The molecular weight of the compound as determined from these data is 206 (calcd. for $C_4H_8Se_2$, 214).

Acknowledgments.—It is a pleasure to acknowledge the assistance of Professors Theodore A. Geissman and Saul Winstein, whose suggestions proved extremely valuable in carrying out this synthesis.

Summary

1,4-Diselenane has been synthesized in 0.3% yield from β,β'-dichlorodiethyl selenide and lithium selenide in anhydrous acetone. The compound has been identified by selenium analysis, semi-quantitative bromination, and by X-ray crystallographic determination of its molecular weight and structure.

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[9] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Crystal Structure of 1,4-Diselenane[1]

BY RICHARD E. MARSH AND JAMES D. McCULLOUGH

One of the projects under investigation in this Laboratory has as its objective the synthesis of stereoisomeric cyclic selenoxides. As an intermediate in the attempted synthesis of diselenane-1,4-dioxide, Gould and McCullough[2] isolated a product which, from the method of preparation, was expected to be 1,4-diselenane. As part of the structure proof of this compound, it was thought advisable to take X-ray diffraction photographs in order to determine the size of the unit cell; this, in conjunction with the measured density of the crystals, would give the molecular weight (or a sub-multiple thereof) of the compound. Upon examination of the X-ray diffraction photographs, it was found that the space-group was advantageous for a complete structure determination. This accordingly, was undertaken.

Preparation of the Crystals.—1,4-Diselenane is a white crystalline compound with a relatively high vapor pressure at room temperature, and with a melting point of 113°. The crystals used for the diffraction photographs were prepared by slow sublimation in a small, sealed glass tube at about 40°. The crystals, which formed on the cooler end of the tube, were rather small, colorless, and lath-shaped, with elongation in the *b* direction. The principal faces were of the form (101). Due to the appreciable vapor pressure of the compound at room temperature, the crystals were wedged into small, thin-walled glass capillaries, which were then sealed off and mounted on a goniometer head. Two crystals of appropriate size and shape (approximately 0.05 × 0.1 × 0.2 mm.) were used, one with the *b* axis parallel to the axis of the capillary and the other with the *b* axis perpendicular to the axis of the capillary. By suitable mounting of the capillary on the goniometer head, it was possible to obtain photographs about all three monoclinic axes, as well as about the $(10\bar{1})$ zone.

X-Ray Diffraction Data.—Rotation and Weissenberg photographs about the three crystallographic axes, as well as about one oblique axis, were prepared using unfiltered copper radiation and exposure times of about 35 hours. A double film technique was used, the intensity factor for the two films being about 3. The intensities of the diffraction spots were estimated visually with the aid of a calibrated comparison strip and were corrected for Lorentz and polarization factors in the usual way. Due to the small size and fairly regular shape of the crystals, no correction for absorption was made.

Measurements made on the photographs showed a monoclinic space-group, with the following unit cell dimensions (using $CuK_\alpha = 1.5418$ Å.): $a = 6.97$ Å., $b = 5.62$ Å., $c = 8.01$ Å. (all ± 0.02 Å.), $\beta = 93.6 \pm 0.1°$. Assuming two molecules of diselenane in the unit cell, the calculated density 2.27 g./cc. is obtained; the observed density from flotation measurements is 2.2 g./cc.

Determination of the Structure.—The systematic absences are $h0l$ with $(h + l)$ odd and $0k0$ with k odd; these absences establish uniquely the space-group $C_{2h}^5 - P2_1/n$. Since this space-group has four-fold general positions in the unit cell, the presence of only two molecules in the unit requires that the molecules be centro-symmetric. Assuming the compound to be 1,4-diselenane, $C_4H_8Se_2$, the asymmetric unit will contain one selenium atom and two carbon atoms. The positions of the four hydrogen atoms cannot be determined in this case because of their relatively low scattering power compared to that of the heavy

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[1] Based on work performed under Contract N6onr-275 between the Office of Naval Research and the University of California, Los Angeles. For detailed material supplementary to this article order Document 3032 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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