residue. Recrystallization of the picrate from ethanol gave 1.2 g of yellow needles, mp 155–158°.

Anal. Calcd for $C_{11}H_{10}N_2O \cdot C_6H_3N_3O_7$: C, 49.16; H, 3.16; N, 16.86. Found: C, 49.07; H, 3.35; N, 17.10.

The free base was obtained from the picrate by the same treatment as described in the 4-methoxy analog.

4,5-Dimethoxy-2-methylpyrimidine.—To a solution of 2.4 g of sodium methoxide in 20 ml of absolute methanol was added 2.1 g of 4-chloro-5-methoxy-2-methylpyrimidine.[17] After refluxing on a steam bath for 6 hr, the reaction mixture was evaporated under reduced pressure, diluted with water, and extracted with ether. The ethereal layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from petroleum ether gave 1.5 g of colorless needles, mp 54°.

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.53; H, 6.63; N, 18.31.

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Acknowledgment.—The authors wish to express their deep appreciation to Dr. K. Takeda, Director of this laboratory, for his helpful advice and encouragement.

Hypophosphorous Acid, a Novel Reagent for the Reduction of Diselenides and the Selenol-Catalyzed Reduction of Disulfides[1,2]

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Received November 3, 1965

Aliphatic and aromatic diselenides are reduced to the corresponding selenols by treatment with hypophosphorous acid. Disulfides, sulfoxides, and aromatic azo compounds do not react with hypophosphorous acid alone, but a catalytic reduction results when small amounts of diselenides are present. The preparation of γ-selenolbutyrolactone, the first aliphatic selenolactone, is described.

The recent finding[2,3] that bis(2-trimethylammoniumethyl)diselenide diiodide[4] is smoothly reduced to the corresponding selenol by treatment with hypophosphorous acid in ethanol appeared to merit an investigation into the general applicability of this novel reduction method.

The reduction of diselenides to selenols or selenol anions has been carried out by a variety of procedures. Diphenyl diselenide can be reduced by treatment with metallic sodium in ethanol.[5] Zinc and hydrochloric acid at 40–50° have also been employed with aromatic diselenides.[6] Sodium in liquid ammonia was used to reduce dialkyl diselenides,[7] for example, to prepare methylselenol from dimethyl diselenide,[8] as well as to remove the protecting groups from benzyl alkyl monoselenides.[9] The treatment of diaryl or dibenzyl diselenides with sodium ethoxide has resulted in the formation of selenomercaptide anion, which was then utilized for further reactions without isolation.[10,11] The above alkali treatment does, however, result in poor yields owing to the concomitant formation of selenenate ion which, in turn, can be avoided, if a reducing agent such as glucose is present.[12] The latter mode of reduction was applied especially to dinitrodiaryl diselenides, which were reported to be resistant to reduction by other methods. The most convenient method, so far, appears to be the cleavage of diselenide groups by sodium borohydride[4,13] in aqueous or methanolic solution or by lithium aluminum hydride in ether[14] to form the selenols quantitatively, if oxidative losses during the work-up are avoided.

The choice of any of the above methods is determined to a large extent by the further reactions the selenol is to be subjected to and by the many desirable or undesirable side reactions which may occur. Thus, alkaline conditions are contraindicated if the selenol itself is unstable or if it contains other groups which are affected at high pH, such as the quaternary ammonium group in the preparation of cholineselenol.[3] The oxidation of selenols by atmospheric oxygen does, also, proceed most readily in alkaline solution. Use of heavy metals may be disadvantageous owing to the ease with which selenols form stable salts or complexes with the metal ion.[15] Sodium in liquid ammonia is very useful to remove protecting benzyl groups from sulfides and selenides as well as from oxygen functions. The ability to cleave a carbon–chalcogen bond, which is utilized here to great advantage, does, however, extend to the cleavage of aliphatic carbon–selenium bonds and may result in the complete removal of selenium from the desired organic residue.[16] Sodium borohydride again has the disadvantage of being used in alkaline solution. It does, also, generate hydrogen gas during the reaction and the preparation of large amounts of selenol has to be undertaken very cautiously to avoid overheating. This reagent's main advantage is the possibility of working in aqueous solution and its inertness toward many other functional groups[17] in contrast to lithium aluminum hydride, which requires nonpolar solvents and where many functional groups are reduced as well.[17]

(1) This work was supported, in part, by a grant from the U. S. Public Health Service (CA 3937).

(2) A preliminary account of this work was presented before the Medicinal Chemistry Section at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p 27-N.

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(4) W. H. H. Günther and H. G. Mautner, *ibid.*, **7**, 229 (1964).

(5) F. Krafft and R. E. Lyons, *Ber.*, **27**, 1763 (1894).

(6) H. Rheinboldt in Houben–Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1955, p 961.

(7) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).

(8) G. E. Coates, *ibid.*, 2839 (1953).

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(11) O. Behagel and K. Hofmann, *Ber.*, **72**, 699 (1939).

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(15) A. Fredga, *Arkiv Kemi Mineral. Geol.*, **B11**, No. 44 (1934); Dissertation, University of Uppsala, 1935.

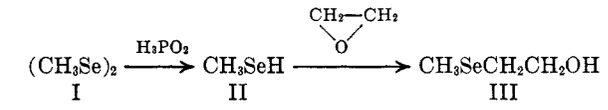
(16) W. H. H. Günther and H. G. Mautner, *J. Am. Chem. Soc.*, **87**, 2708 (1965).

(17) N. C. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p 13 ff.

Hypophosphorous acid has been used extensively to replace diazotized aromatic amino groups by hydrogen.[18] Its use as a reducing agent in other areas has largely been restricted to inorganic applications, such as the regeneration of hydrogen bromide and hydrogen iodide from the elements,[19] and to a few isolated instances in organic chemistry, such as the elimination of bromide and iodide blocking groups,[20] the reduction of an aromatic arsonic acid to the corresponding arseno compound,[21] and the conversion of seleninic acids into selenenic acids and diselenides.[22] Hypophosphorous acid appears to be reasonably inert toward most organic groups, which explains the limited use this compound has had in preparative organic chemistry. Its reducing ability seems to be greatest in strongly acidic solution, since at neutral pH it is not even oxidized by elemental iodine[23] in contrast to phosphorous acid which, under the same conditions, gives a quantitative yield of phosphoric acid. Hypophosphorous acid is commercially available as an aqueous solution[24] from which the pure compound can be obtained as colorless crystals, mp 26.5°.[25] The repeated crystallization of the compound at low temperature does, however, involve losses totaling about 90% of the starting material.[25] Since the impurity in the commercial samples consists nearly entirely of a small amount of phosphorous acid, and since the latter compound is inert toward diselenides or selenols under the conditions used for the reaction, the experiments described below were usually carried out with the commercial material. Yields and purity of products were not noticeably affected by this procedure, when compared to reactions carried out with the recrystallized compound.

Diselenides show an ultraviolet absorption peak of low intensity at approximately 300 mμ.[26] Extension of this band into the visible spectrum is the cause of the yellow or orange color observed for this group of compounds. Disappearance of the color or, more specifically, of the ultraviolet peak indicates cleavage of the chromophore and, thus, the progress of the reduction may be followed visually. The synthesis of cholineselenol iodide by reduction of the diselenide in ethanol solution at the boiling point of the solvent has been described earlier.[3] A related compound, bis(2-dimethylaminoethyl) diselenide dihydrochloride, was reduced in a similar manner and the resultant selenol was isolated as the hydrochloride by crystallization from ethanol and ether. As the new reduction method appeared to be a convenient way of obtaining volatile selenols, the reduction of dimethyl diselenide was undertaken. Dimethyl diselenide (I) was prepared by reaction of dimethyl sulfate with an excess of potassium selenosulfate[27] in alkaline solution with continuous removal of the product in a current of steam (Scheme I). The compound had been prepared previously by a similar procedure from potassium diselenide.[28] When the dimethyl diselenide was heated with 50% aqueous hypophosphorous acid, a rapid evolution of gas set in and methylselenol (II, bp 25°)[8] condensed in a cold trap. For identification the selenol was allowed to react with ethylene oxide to give 2-methylselenoethanol (III) in excellent yield.

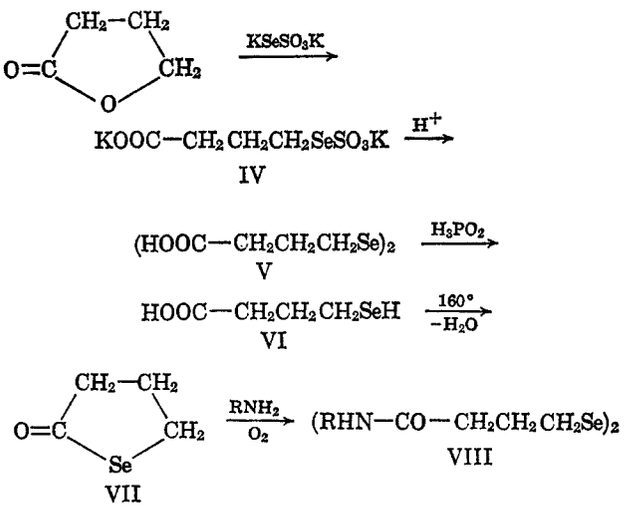
SCHEME I



I II III

To test the scope of the reaction further, the reduction of a diselenide carrying an acidic side chain was attempted next (Scheme II). 4,4-Diselenodibutyric acid (V), a compound first prepared by Fredga and Bendz,[29] was synthesized by two different routes. One involved the direct nucleophilic attack of selenosulfate ion on γ-butyrolactone in aqueous solution, followed by acid hydrolysis of the intermediate selenium Bunte salt IV. A higher yield of the desired diselenide was obtained by reacting methyl 4-bromobutyrate with potassium selenosulfate, followed by a similar hydrolytic step.

SCHEME II



When 4,4-diselenodibutyric acid was heated with hypophosphorous acid, the initially yellow solution was rapidly decolorized, indicating cleavage of the diselenide bond. Distillation of the reaction mixture at about 160° in a partial vacuum resulted in ring closure of the 4-selenolbutyric acid (VI) and formation of γ-selenolbutyrolactone (VII), a very heat-stable (bp 200–210°) compound with ultraviolet absorption at ϵ_{197}^{max} 5500 and $\epsilon_{258.5}^{max}$ 3100 (ethanol). The uniformity of the compound was established by its constant ultraviolet extinction, by the fact that it migrated as a single peak in vapor phase chromatograms, and by elemental analysis. The identity of the material with the proposed structural formula was shown by conversion to 4,4′-diselenodibutyric acid (V) upon hy-

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(19) P. N. Craig, *et al.*, *J. Am. Chem. Soc.*, **74**, 1316 (1952).
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(22) H. Rheinboldt and E. Giesbrecht, *Chem. Ber.*, **88**, 1974 (1955).
(23) R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953).
(24) Hypophosphorous acid, 50%, purified; Catalog No A 154, Fisher Scientific Co.
(25) W. A. Jenkins and R. T. Jones, *J. Am. Chem. Soc.*, **74**, 1353 (1952).
(26) G. Bergson, *Arkiv Kemi*, **9**, 121 (1955); Dissertation, University of Uppsala, 1962.
(27) F. Foerster, F. Lange, O. Drossbach, and W. Seidel, *Z. Anorg. Allgem. Chem.*, **128**, 312 (1923).
(28) H. J. Backer and W. van Dam, *Rec. Trav. Chim.*, **54**, 531 (1935).
(29) A. Fredga and G. Bendz, *Svensk Kem. Tidskr.*, **54**, 119 (1942); *Chem. Abstr.*, **38**, 2317[9] (1944).

drolysis in water in the presence of atmospheric oxygen and by conversion to amides of 4,4′-diselenodibutyric acid (VIII) by aminolysis with ammonia or *n*-butylamine, again followed by oxidation with atmospheric oxygen. The selenolbutyrolactone was also obtained when 4,4′-diselenodibutyric acid was reduced by sodium borohydride, followed by extraction of the resulting 4-selenolbutyric acid from the acidified reaction mixture and distillation under reduced pressure.

From the preparations of methylselenol and of cholineselenol iodide the approximate stoichiometry of the reaction was determined to 1 mole of hypophosphorous acid reacting with 1 mole of diselenide to yield 2 moles of selenol. Tlc of the phosphorus-containing reaction products[30] showed only the presence of phosphorous acid and traces of hypophosphorous acid. This indicated that the reaction may follow this equation.

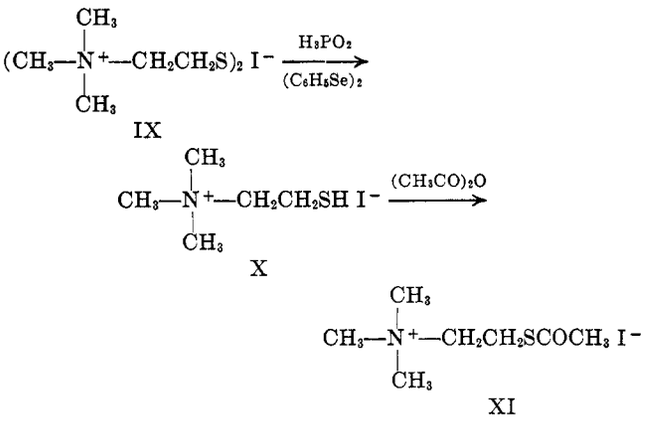
$$H_3PO_2 + (RSe_2) + H_2O \longrightarrow 2RSeH + H_3PO_3$$

The usefulness of hypophosphorous acid for the reduction of diselenides did, thus, appear to be established, and attention was given to a more general application of the reagent in the reduction of other functional groups. When some disulfide analogs of the above diselenides were treated with hypophosphorous acid, no reaction was observed under conditions which had led to a smooth production of selenols. It is well known that disulfides can be reduced by reaction with suitable thiols; diselenides, on the other hand, do not appear to react with such commonly used reducing agents as 2-mercaptoethanol.[16] It could, therefore, be expected that disulfides should be reduced to thiols by addition of selenols, the latter being converted to diselenides in the process. Thus, a reduction of a disulfide might be effected by addition of a small amount of a diselenide to the hypophosphorous acid reducing agent. The same catalysis should be applicable to other functional groups resistant toward attack by hypophosphorous acid, but capable of converting selenols to diselenides. When bis(2-trimethylammoniumethyl) disulfide diiodide (thiocholine disulfide diiodide, IX) (Scheme III) in ethanolic suspension was heated with hypophosphorous acid in the presence of diphenyl diselenide, reduction of the disulfide was observed and a high yield of cholinethiol iodide (X) in crystalline form was obtained. The product was freed from both reagents by recrystallization from ethanol and washing with ether. Its identity was confirmed by conversion to acetylthiocholine iodide (XI), which then had infrared and ultraviolet spectra identical with a commercially available sample.[31] In a similar manner, cystine and homocystine were reduced in high yield to cysteine and homocysteine, respectively.

Since thiols react with sulfoxides, reducing the latter to the corresponding sulfides,[32,33] a similar behavior might be expected for selenols in an analogous reaction. Dimethyl sulfoxide does not appear to react with hypophosphorous acid, but a nearly quantitative yield of dimethyl sulfide was obtained when the reaction was carried out in the presence of diselenides.

(30) H. Seiler, *Helv. Chim. Acta*, **44**, 1754 (1961).
(31) Nutritional Biochemicals Corp., Cleveland, Ohio.
(32) C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).
(33) T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).

SCHEME III



The reaction of 1 mole each of the reactants, catalyzed by 2.5×10^{-4} mole of bis(2-dimethylaminoethyl) diselenide dihydrochloride at 60°, was completed within about 1 hr. Less catalyst decreased the rate of the reaction; more catalyst, such as 10^{-3} mole at 80°, resulted in an extremely vigorous reaction which was very difficult to control. In a similar manner an ethanolic solution of azobenzene was reduced to give hydrazobenzene in quantitative yield.

Hypophosphorous acid is, thus, an excellent general reducing agent for diselenides and the combination of hypophosphorous acid and a suitable diselenide can be used to reduce, under mild conditions, disulfides, sulfoxides, and aromatic azo compounds. While organic derivatives of divalent sulfur and selenium frequently show quantitative differences in their reaction rates, the present reduction of diselenides with hypophosphorous acid is one of the few examples of a qualitative difference between the two elements.

Experimental Section

2-Dimethylaminoethylselenol Hydrochloride.—A suspension of bis(2-dimethylaminoethyl) diselenide dihydrochloride (9.4 g, 0.05 mole) in absolute ethanol (30 ml) was mixed with hypophosphorous acid (5 ml of 50% aqueous solution) and the reaction was allowed to proceed at the boiling point of the solvent. When complete decolorization indicated that the reaction was complete, the clear solution was diluted with ether until turbid and allowed to cool in an atmosphere of pure nitrogen. 2-Dimethylaminoethylselenol hydrochloride precipitated as a white powder, mp[34] 140°, resolidified, and decomposed at 150°.

Anal.[35] Calcd for $C_4H_{12}ClNSe$: C, 25.47; H, 6.41; N, 7.42; Se, 41.88. Found: C, 25.19; H, 6.22; N, 7.19; Se, 42.12.

Dimethyl Diselenide. (I).—A strongly alkaline solution of potassium selenosulfate[4,27] was prepared from finely powdered selenium (160 g, 2 g-atoms), potassium sulfite (320 g, 2 moles), potassium hydroxide (225 g, 4 moles), and water (1000 ml). The dark brown solution, contained in a three-necked flask fitted with a steam inlet, a dropping funnel reaching below the surface of the liquid, and a descending condenser, was heated by passage of steam. Then dimethyl sulfate (250 g, 2 moles) was added slowly through the dropping funnel and the orange oily product was removed continuously by steam distillation. The steam distilled oil was separated from the aqueous phase, dried over sodium sulfate, and redistilled to yield dimethyl diselenide (139.7 g, 73%) as an orange oil: bp 157–160°, lit.[28] bp 155–157°.

Methylselenol (II).—A mixture of dimethyl diselenide (47 g, 0.25 mole) and 50% hypophosphorous acid (45 g, 0.3 mole) was placed into a 250-ml flask fitted with a nitrogen inlet and a

(34) All melting points are uncorrected.
(35) Microanalyses were carried out at the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

vertical air condenser (45 cm), the top of which was connected to a cold trap immersed in a Dry Ice–acetone bath. The exit tube from the system was linked to a gas-washing bottle containing 10% aqueous hydrogen peroxide, which was periodically replaced if needed. Nitrogen was passed through the apparatus at a slow rate, while the contents of the flask were stirred magnetically and heated to about 80°. The evolution of gas set in almost immediately and slightly wet methylselenol (bp 24–26°, lit.[8] bp 25.5°) condensed in the cold trap. The reaction rate can be controlled well by varying the rate of stirring, and the initial dimethyl diselenide phase in the reaction flask has usually disappeared within about 20–45 min. The product (42 g, 88%) was used for the next reaction without further purification.

2-Methylselenoethanol (III).—Ethylene oxide (22 g, 0.5 mole) and methylselenol (42 g, 0.44 mole) were combined in a flask cooled in an ice bath and connected to the atmosphere by a gas-washing bottle filled with 10% hydrogen peroxide. Care must be taken to connect the gas-washing bottle in such a way that the oxidizing agent cannot enter the reaction flask, as large variations of the inside pressure may occur. The reaction mixture was kept in the ice bath for 2 days until the smell of methylselenol had largely disappeared. The product was then distilled under vacuum to yield 2-methylselenoethanol (52 g, 85%) as a colorless oil, bp 70–71° (8 mm).

Anal. Calcd for C_3H_8OSe: C, 25.91; H, 5.80; Se, 56.78. Found: C, 25.98; H, 5.94; Se, 56.71.

4,4′-Diselenodibutyric Acid (V). A.—To a boiling solution of potassium selenosulfate (1.0 mole, from 79 g of elemental selenium and 160 g of potassium sulfite in 500 ml of water) was added dropwise over a period of 5 hr γ-butyrolactone (86 g, 1.0 mole). The mixture was heated under reflux overnight and filtered from precipitated elemental selenium (35 g), and concentrated hydrochloric acid (220 ml) was added slowly. A small amount of red selenium precipitated at this stage and was removed by filtration. The yellow solution was then heated to reflux with stirring until the precipitation of a heavy orange oil appeared complete and until no more sulfur dioxide was evolved from the solution. The mixture was cooled in ice and the yellow solid (86 g, 52%) was isolated by filtration. The compound at this stage was contaminated by large amounts of polyselenides which caused it to turn red on exposure to air. It was thus dissolved in an excess of hot sodium bicarbonate solution, aerated until precipitation of selenium appeared complete, and filtered, and the acid was precipitated by addition of hydrochloric acid. If necessary, this procedure may be repeated once more to yield pure 4,4′-diselenodibutyric acid (63 g, 39%): mp 88°, lit.[29] mp 87.5–88°.

B.—Methyl 4-bromobutyrate (110 g, 0.6 mole) was added dropwise to a hot stirred solution of potassium selenosulfate (from 50 g of elemental selenium and 130 g of potassium sulfite in 350 ml of water). The reaction mixture was then heated under reflux for another 15 min and concentrated hydrochloric acid was added cautiously until the solution had a pH of 1. A heavy orange oil precipitated which was, after cooling, extracted several times with chloroform. The combined organic layers were washed with water, dried, and evaporated to a heavy oil. This was dissolved in acetone (300 ml) and 6 *N* hydrochloric acid (150 ml) and the mixture was heated under reflux overnight. Evaporation of all solvents yielded 4,4′-diselenodibutyric acid, which was purified as described above to yield 86 g (87%) of compound identical with the one obtained previously.

γ-Selenolbutyrolactone (VII). A.—4,4′-Diselenodibutyric acid (30 g, 0.18 mole) was suspended in water (100 ml) and reduced by addition of solid sodium borohydride (7 g) in small portions, while the mixture was cooled in ice and stirred magnetically. The addition of further reducing agent was stopped when a colorless solution had resulted. The reaction mixture was then acidified by addition of 6 *N* hydrochloric acid (pH 1) and extracted with ether (three 100-ml portions), the solvent was evaporated without previous drying, and the residue was distilled quickly using an open flame. The distillation product (21 g, bp 200–210°) was dissolved in ether and extracted with small portions of distilled water to remove traces of butyrolactone. The ethereal solution was then filtered through a short column of activated alumina, the solvent was evaporated under reduced pressure, and the residual oil was distilled *in vacuo* to give γ-selenolbutyrolactone (16.3 g, 59%), bp 86–88° (13 mm). The compound showed a single peak in a vapor phase chromatogram; two ultraviolet absorption peaks had $\epsilon^{max}_{258.5}$ 3100 and ϵ^{max}_{197} 5500 (ethanol).

Anal. Calcd for C_4H_6OSe: C, 32.23; H, 4.06; Se, 52.98. Found: C, 32.20; H, 4.22; Se, 53.14.

B.—A mixture of 4,4′-diselenodibutyric acid (134 g, 0.4 mole) and 50% hypophosphorous acid (65 g, 0.5 mole) was heated to about 80° until a colorless oily mixture of liquids resulted. The reaction product was then distilled under an aspirator vacuum from an oil bath maintained at 160° to yield a crude product (112 g) which was treated as described above to give pure γ-selenolbutyrolactone (98 g, 82%) which was identical with the product obtained from the sodium borohydride reaction.

Reaction of γ-Selenolbutyrolactone with Water.—A suspension of selenolbutyrolactone in distilled water was stirred vigorously overnight by means of a magnetic stirrer. Access of atmospheric oxygen was assured through the use of an open beaker in this reaction. A quantitative yield of 4,4′-diselenodibutyric acid, mp 88°, was obtained.

Reaction with Ammonia and with *n*-Butylamine.—γ-Selenolbutyrolactone was suspended in aqueous solutions of ammonia or *n*-butylamine and the resulting mixtures were stirred overnight while access of air was maintained. High yields of the corresponding amides were obtained.

4,4′-Diselenodibutyramide (VIII, R = H) was obtained as a yellow crystalline powder, mp 175° (from ethanol).

Anal. Calcd for $C_8H_{16}N_2O_2Se_2$: C, 29.10; H, 4.89; N, 8.48. Found: C, 29.29; H, 4.85; N, 8.68.

N,N′-Di-*n*-butyl-4,4′-diselenodibutyramide (VIII, R = *n*-Bu) was obtained as yellow needles from ethanol and ether, mp 97–98°.

Anal. Calcd for $C_{16}H_{32}N_2O_2Se_2$: C, 43.44; H, 7.29; N, 6.33. Found: C, 43.55; H, 7.29; N, 6.56

2-Trimethylammoniumethylthiol Iodide (Cholinethiol Iodide).—A mixture of bis(2-trimethylammoniumethyl) disulfide diiodide[36] (choline disulfide diiodide) (5.0 g, 0.01 mole), hypophosphorous acid (5 ml of 50% aqueous solution), and diphenyl diselenide (250 mg) in absolute ethanol (50 ml) was stirred and heated to a gentle boil until all solid had dissolved and the initially yellow solution appeared colorless. The clear solution was allowed to cool in an atmosphere of pure nitrogen, yielding colorless plates of cholinethiol iodide (4.5 g, 0.018 mole, 90%), mp 155–156°.

2-Trimethylammoniumethylthiolacetate Iodide (Acetylthiocholine Iodide).—Cholinethiol iodide (2.0 g) was heated with acetic anhydride (5 ml) until all solid had dissolved. The solution was cooled, dry peroxide-free ether was added, and the crystalline product was collected by filtration. The compound was free from sulfhydryl groups and had an infrared spectrum identical with that of a commercially available sample.[31]

Catalytic Reduction of Dimethyl Sulfoxide.—A mixture of dimethyl sulfoxide (78 g, 1 mole), 50% hypophosphorous acid (130 g, 1 mole), and bis(2-dimethylaminoethyl) diselenide dihydrochloride (100 mg, 2.5×10^{-4} mole) was heated, with stirring, to about 60°, when a rapid evolution of vapor set in. Dimethyl sulfide (61 g, 98.5%), bp 34–6° (lit.[37] bp 37.5°) distilled from the reaction mixture. Addition of more dimethyl sulfoxide to the reaction flask after the distillation had ceased failed to give any more product, indicating an over-all stoichiometry of 1 mole of hypophosphorous acid reacting with 1 mole of dimethyl sulfoxide to give 1 mole of dimethyl sulfide.

Catalytic Reduction of Cystine.—Cystine (4.0 g, 0.017 mole) was heated with hypophosphorous acid (10 ml of 10% aqueous solution) and bis(2-dimethylaminoethyl) diselenide dihydrochloride (200 mg) until a colorless solution was obtained. Addition of ethanol (100 ml) and pyridine (5 ml) yielded shiny plates of cysteine (3.85 g, 97%), with an infrared spectrum identical with that of an authentic sample.

Catalytic Reduction of Homocystine.—The reaction was carried out in the same fashion as described above for cystine. A yield of 47% homocysteine was isolated by addition of ethanol and pyridine to the reaction mixture. The compound had an infrared spectrum identical with that of an authentic sample.

Catalytic Reduction of Azobenzene.—An ethanolic solution of azobenzene was treated with hypophosphorous acid and diphenyl diselenide as described above to give a quantitative yield of hydrazobenzene, mp 124°. The infrared spectrum of the product was identical with that of an authentic sample.

Acknowledgment. —The author wishes to express his thanks to Dr. Henry G. Mautner for many helpful discussions during the course of this investigation.

(36) R. R. Renshaw, *et al.*, *J. Am. Chem. Soc.*, **60**, 1765 (1938); see also J. Fakstorp, *Acta Chem. Scand.*, **10**, 15 (1956).

(37) "Handbook of Chemistry and Physics," 44th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p 1103.