collected at 155–156° (3 mm.). Another fraction of 8 g. collected at 157–167° (3 mm.) probably contained a high percentage of diphenyldi-(methylamino)-silane.

Anal. Calcd. for $C_{14}H_{18}N_2Si$: Si, 11.6. Found: Si, 11.5.

Diphenyldi-(*n*-propylamino)-silane.—To a stirred solution of 9.8 g. (0.166 mole) of *n*-propylamine in 50 ml. of toluene a solution of 9.0 g. (0.036 mole) of diphenyldichlorosilane in 15 ml. of toluene was added dropwise. After all had been added the stirring was continued for another 15 minutes and then the mixture was refluxed (with continued stirring) for 15 minutes. After cooling the mixture was filtered and the precipitate washed with toluene to give 6.1 g. of solid on the filter, which corresponds with the calculated amount of *n*-propylamine hydrochloride. After removal of the toluene from the filtrate by distillation under reduced pressure the liquid residue was distilled from a claisen flask giving a center fraction of 7.6 g. (70%) of diphenyldi-(*n*-propylamino)-silane boiling at 178–182° (2 mm.).

Anal. Calcd. for $C_{18}H_{26}N_2Si$: Si, 9.4. Found: Si, 9.6.

The substance could be distilled under atmospheric pressure without decomposition.

Diphenyldi-(*n*-hexylamino)-silane.—This substance was prepared exactly as described for diphenyldi-(*n*-propylamino)-silane from 21 g. (0.21 mole) of *n*-hexylamine and 12 g. (0.047 mole) of diphenyldichlorosilane giving a center fraction of 5.5 g. boiling at 215–230° (3 mm.). On redistillation 1.5 g. of diphenyldi-(*n*-hexylamino)-silane were collected at about 215° (2 mm.).

Anal. Calcd. for $C_{24}H_{38}N_2Si$: Si, 7.3. Found: Si, 7.5.

Diphenyldi-(benzylamino)-silane.—A solution of 13 g. (0.051 mole) of diphenyldichlorosilane in 15 ml. of toluene was run slowly during a period of 15 minutes into a stirred, refluxing solution of freshly distilled benzylamine in 50 ml. of toluene. The mixture was stirred and refluxed for 15 minutes longer. Filtration of the hot mixture and washing with toluene gave 14 g. of solid on the filter, corresponding with the calculated amount of benzylamine hydrochloride. From the filtrate toluene was removed by distillation under reduced pressure at about 30°. The liquid residue was cooled in the ice-box. On scratching with a glass rod crystallization started and proceeded till the whole mass had solidified to yield 20 g. of substance, which was the calculated amount of diphenyldi-(benzylamino)-silane. Recrystallization from 10 ml. of ether yielded 8.4 g. of white crystals, which slowly decomposed on standing in a closed vessel at room temperature. On account of this no defined melting point can be recorded.

Anal. Calcd. for $C_{26}H_{26}N_2Si$: Si, 7.1. Found: Si, 7.4.

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Selenium Dithiocyanate

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Three investigators[2–4] have reported the reduction of selenious acid to elemental selenium by the reaction between selenious acid and thiocyanic acid. Selenic acid, also, is reduced by the latter reagent to elemental selenium. In a series of experiments designed to study this latter reaction, a yellow crystalline substance was obtained as an intermediate product. The same crystalline product is obtained by the reaction between selenious and thiocyanic acid under certain conditions of temperature, concentration and acidity of the solution.

A survey of the literature revealed that only two investigators have reported compounds containing selenium and a thiocyanogen radical, Baroni[5] has prepared thiocyanogen selenide, $Se_2(SCN)_2$, and thiocyanogen thioselenide, $SeS(SCN)_2$. Ivanov[4] describes thiocyanoselenious acid, $(HSCN)_2 \cdot H_2SeO_3$. An analysis of our crystalline product did not agree with any of the compounds described heretofore, but agreed very closely with the formula for selenium dithiocyanate, $Se(SCN)_2$. The preparation of this new compound, and its properties are described below.

Experimental

1. Preparation of Selenium Dithiocyanate.—The best product was obtained by the reaction between selenious acid and thiocyanic acid. A 1.1-g. portion of selenium dioxide[6] was treated with 8.6 ml. of concentrated hydrochloric acid, the mixture was diluted to 50 ml. with water, and cooled to room temperature. Thiocyanic acid was prepared by the method of Gluud, Keller and Klempt[7] and diluted to produce a tenth molar solution. The thiocyanic acid solution was poured, with stirring, into the selenious acid solution, and the mixture was allowed to stand at room temperature for 30 minutes.

The crystals were then collected in a Gooch crucible, excess mother liquor was pressed out by tamping with a glass rod, and the product was washed, first with a little glacial acetic acid, then with anhydrous ether, and tamped again to remove the ether as completely as possible. Finally the product was transferred to a vacuum desiccator containing sodium hydroxide pellets and paraffin shavings. The desiccator was evacuated to 2 mm. and kept in a refrigerator at 5°. The yield was about 70%, based on the SeO_2 used in the preparation.

The compound can also be prepared by bringing together, at room temperature, 50 ml. of a solution containing 1.1 g. of selenium dioxide, 12.9 ml. of concentrated hydrochloric acid, with 50 ml. of another solution containing 3.8 g. of ammonium thiocyanate in water, and allowing the mixture to stand for 30 minutes.

Analysis of the Compound.—Selenium was determined by weighing out a 0.3 to 0.5 g. sample, transferring to a 250-ml. beaker by means of a porcelain spatula (metal is attacked), and dissolving in 10 ml. of concd. nitric acid. The beaker was washed down with distilled water, placed on a steam-bath, and the solution evaporated nearly to dryness. It was then diluted, with 5 *N* hydrochloric acid, hydroxylamine hydrochloride was added, and selenium determined by the procedure described by Hillebrand and Lundell.[8]

Sulfur was determined in the filtrate from the selenium determination. The solution was diluted to 250 ml. and a 50-ml. aliquot was evaporated nearly to dryness on a steam-bath. The subsequent operations were carried out by the method described by Rieman, Neuss and Naiman.[9]

Carbon was determined by a micro method.[10]

For the determination of nitrogen, a 0.5-g. sample was weighed into a Kjeldahl flask, digested with a sulfuric acid–salicylic acid mixture and treated as described by Hillebrand and Lundell.[11]

The results of these determinations are: Calcd. for $Se(SCN)_2$: Se, 40.47; S, 32.86, C, 12.31; N, 14.35. Found: Se, 40.44; S, 32.72; C, 12.5; N, 14.3.

Properties of Selenium Dithiocyanate.—The crystal structure of selenium dithiocyanate has been determined by X-ray diffraction methods. The results will be presented in a separate communication.

Selenium dithiocyanate is fairly stable if kept in a cool, dark place, out of contact with water vapor. The dry compound can be kept for weeks in a tightly stoppered container, in a refrigerator (at 5°). If heated, it decomposes

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[1] From a thesis submitted by Stanley M. Ohlberg to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

[2] H. A. Ljung, *Ind. Eng. Chem., Anal. Ed.*, **9**, 328 (1937).

[3] W. T. Hall, *ibid.*, **10**, 395 (1938).

[4] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, **40**, 661 (1908).

[5] A. Baroni, *Reale Accademia del Lincia*, **23**, 139 (1936).

[6] Best grade, furnished by American Smelting and Refining Co.

[7] W. Gluud, K. Keller and W. Klempt, *Ber.*, **58B**, 1384 (1926).

[8] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 265.

[9] W. Rieman, J. D. Neuss and B. Naiman, "Quantitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 280.

[10] The carbon determinations were performed by Dr. Carl Tiedcke, Teaneck, N. J.

[11] W. F. Hillebrand and G. E. F. Lundell, ref. 8., p. 639.

suddenly at 83–85° yielding an orange smoke and a maroon-colored residue. Chemical analysis indicated that neither of these were pure substances.

The compound is practically insoluble in bromoform, symmetrical tetrachloroethane, hexane, heptane and carbon tetrachloride. It is slightly soluble in diethyl ether, benzene, carbon disulfide and liquid sulfur dioxide, and appreciably soluble in the following solvents: anhydrous dioxane, anhydrous acetone, acetophenone, vinyl trichloride and glacial acetic acid. If small amounts of water are added, decomposition takes place. However, the solutions are reasonably stable if kept in tightly stoppered containers and stored in a dark place. Attempts to obtain accurate solubility data have not been successful, but are being continued.

Selenium dithiocyanate is best recrystallized by carefully adding anhydrous ether to a saturated solution of selenium dithiocyanate in anhydrous dioxane until a faint turbidity persists and then keeping the mixture at 0° for eight hours.

The density of crystalline selenium dithiocyanate was determined by preparing a mixture of bromoform and symmetrical tetrachloroethane having the same density as the crystals. The density found in this manner was 2.265 ± 0.005.

The molecular weight of the compound was determined by cryoscopic method using acetophenone in one case, and dioxane in another, as the solvents. The molecular weight found in acetophenone was 206, and in dioxane 204. Although the experimentally determined values are all higher than the calculated value (195) based on the simple formula, the existence of selenium dithiocyanate in the monomeric form is definitely established.

Selenium dithiocyanate decomposes more or less rapidly at room temperature in the following liquids: water, dilute hydrochloric acid solution, dilute sodium hydroxide solution, methyl-, ethyl-, propyl-, *t*-butyl alcohol and pyridine. It also decomposes violently in liquid ammonia.

While it was not found possible accurately to represent the reaction between selenious acid and thiocyanic acid by a single equation, the following appears to be the main reaction

$$3H_2SeO_3 + 7HSCN = 3Se(SCN)_2 + 5H_2O + HCN + H_2SO_4$$

To ascertain whether this equation correctly represents the main reaction, the preparation of selenium dithiocyanate from selenious acid and thiocyanic acid, as described above, was carried out in a closed vessel attached to a suction flask through a tube provided with a sintered glass disc. The suction flask contained sodium hydroxide in excess of that required to neutralize all of the acid.

When the reaction was completed the liquid part of the contents of the reaction vessel were passed through the sintered disc into the sodium hydroxide solution, while the selenium dithiocyanate was retained on the disc. Air was aspirated through the apparatus to complete the transfer of hydrogen cyanide to the caustic soda solution, which contained, in addition to the hydrogen cyanide also the sulfuric acid formed in the reaction. The tube with the sintered disc was then disconnected from the reaction vessel and washed with small portions of nitric acid. Selenium and sulfur were determined in the nitric acid solution as described above.

The potassium hydroxide solution to which the liquid part of the reaction mixture had been added was analyzed for cyanide and sulfate. Cyanide was determined by the Liebig[12] method. An aliquot was acidified slightly with nitric acid, the thiocyanate precipitated with silver nitrate, and the filtrate was used for the sulfate determination. The results are given in Table I.

TABLE I

FORMATION OF SELENIUM DITHIOCYANATE, HYDROGEN CYANIDE AND SULFURIC ACID FROM SELENIOUS AND THIOCYANIC ACID

Millimoles formed	Millimoles HCN Theory	Found	Millimoles H_2SO_4 Theory	Found
6.83	2.28	1.61	2.28	2.12
15.37	5.12	3.84	5.12	4.93
16.41	5.47	3.93	5.47	5.15

It is apparent, that while the equation as written does not describe quantitatively the over-all reaction involved in the formation of selenium dithiocyanate, the results indicate that this equation is in agreement with the main reaction.

The fact that less than the theoretical amounts of hydrogen cyanide and sulfuric acid were found is in agreement with the work of other investigators[13] who studied the hydrolysis of thiocyanogen.

Reaction of Selenium Dithiocyanate with Water.—The decomposition of selenium dithiocyanate by water yields, as the major products, elemental selenium, selenious acid and thiocyanate ion. As a result of the interaction of selenious acid with thiocyanic acid there is also formed a considerable amount of sulfate ion. This result is in agreement with an observation of Hall.[3]

Synthetic Applications.—Selenium dithiocyanate can be used as a reagent for introducing the thiocyanate group into organic compounds. For example, the treatment of dimethylaniline with selenium dithiocyanate in glacial acetic acid yields *p*-thiocyanodimethylaniline, with a yield of 55%.

In the same manner, the reaction between 1-naphthol and selenium dithiocyanate in glacial acetic acid results in the formation of 4-thiocyano-1-naphthol, with a yield of 60%.

The compound will also react with an olefinic type of double bond. Attempts to thiocyanate cyclohexene yielded a crystalline addition product whose empirical formula corresponded to one molecule of selenium dithiocyanate and two molecules of cyclohexene.

Finally, the intermediate oxidation state of the selenium suggests that selenium dithiocyanate might find further application as either an oxidizing agent or a reducing agent for synthetic purposes.

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[12] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 661.

[13] H. Lecher, M. Wittmer and W. Speer, *Ber.*, **56**, 1104 (1923).

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The Microbiological Activity of Pyridoxylamines

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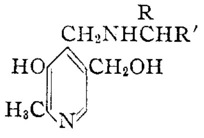
Several pyridoxylamines (I), recently described by Heyl, *et al.*,[3] were reported to possess vitamin B_6 activity for rats 50 to 100% that of pyridoxine, although the corresponding pyridoxylamino acids[4] (II) possessed relatively low activity. Because of



I, R = H, R' = H or organic radical
II, R = -COOH, R' as in I

this high activity, and because comparable structural modifications of other vitamins with similar maintenance of activity has not proved possible, they suggested that "compounds of this type may occur in living systems as members of the vitamin B_6 group or as intermediates in their function."

In view of these suggestions, it appears worthwhile to present results of assays of these compounds with other organisms that require vitamin B_6 (Table I). For *Saccharomyces carlsbergensis*, *Streptococcus faecalis* and *Lactobacillus casei*, most of the compounds have negligible activity, pyri-

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[3] D. Heyl, E. Luz, S. A. Harris and K. Folkers, THIS JOURNAL, **74**, 414 (1952).

[4] D. Heyl, S. A. Harris and K. Folkers, *ibid.*, **70**, 3429 (1948).