ments were made on the gaseous phase at 25° with the sample confined in a 10-cm. cell fitted with 4-mm. potassium bromide windows cemented with glyptal resin. SiH_4 was prepared by the reduction of $SiCl_4$ with $LiAlH_4$.[8]

In preliminary experiments it was observed that SiH_4 could be converted to higher silanes in reasonably good yields merely by touching a glass tube of the vacuum system through which SiH_4 was passing with the tip of a standard tesla coil, "leak detector."[11] The SiH_4 was allowed to vaporize from one trap and was condensed in an adjacent trap surrounded by liquid nitrogen, the tesla coil point being applied to the glass tubing an inch or two above the level of the liquid nitrogen. After several such passes the higher silanes were separated from SiH_4 by passage through a trap held at −134°. Although this method was satisfactory for the preparation of small quantities of Si_2H_6 and Si_3H_8 (~130 mg.; 33% yield), the following apparatus was used for the preparation of larger quantities of these and other higher silanes.

An automatic Toepler pump[12] of 250-ml. capacity was used to pump SiH_4 through an ozonizer and then through two traps immersed in baths held at approximately −134°. The higher silanes formed in the ozonizer were removed by the cold baths and the hydrogen formed in the reaction together with unchanged SiH_4 then was automatically recycled through the ozonizer. A 2-l. surge bulb was incorporated into the apparatus in order to minimize pressure fluctuations caused by the operation of the Toepler pump, which was adjusted to cycle 500 ml. of gas per min. The ozonizer was constructed from an all-glass Pyrex condenser (water jacket 250 mm. long; outer diameter of water jacket 19.0 mm.; outer diameter of inner tube 12.0 mm.; thickness of glass 1.0 mm.). The outer surface of the water jacket was wrapped with aluminum foil, and a cork was placed in the smaller end of the inner tube which then was filled with copper sulfate solution. A wire which dipped into this solution then was attached to one secondary terminal of a 7500-v. neon sign transformer,[13] and a wire from the other terminal of the secondary coil of the transformer was wrapped around the aluminum foil.

In a typical experiment 1.895 g. of SiH_4 (mol. wt.: found, 32.2; calcd., 32.12; purity confirmed by infrared spectrum[14]) was circulated through the apparatus for 5 hr. The pressure in the system at the start of the experiment was 143 mm. (minimum) on the downstroke of the Toepler pump and 156 mm. (maximum) on the upstroke. After removing hydrogen, recycling was continued for an additional 1 hr. Some yellowish-brown powder, assumed to be silicon subhydrides, had formed in and near the exit of the ozonizer.

The volatile products of the reaction were passed through a trap at −96° and then into a trap surrounded by liquid nitrogen. On holding the condensate in the latter trap at −134°, SiH_4 (0.669 g., mol. wt.: found, 32.6; calcd., 32.12; confirmed by infrared spectrum[14]) distilled off. The material remaining was almost pure Si_2H_6 (0.510 g., mol. wt.: found, 63.2; calcd., 62.23). Further distillation through a −96° trap gave a sample of pure Si_2H_6 (mol. wt.: found, 62.5, confirmed by infrared spectrum[15]; vapor pressure at −69.01°: found, 50.2 mm.; calcd.,[16] 50.71 mm.; calcd.,[17] 49.40 mm.).

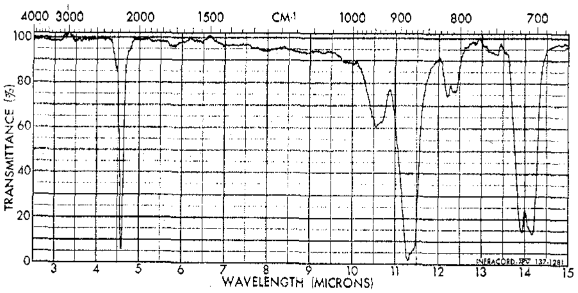

Figure 1.

After passing the condensate in the −96° trap through a −46° and then into a −196° trap the most volatile fraction was found to consist of almost pure Si_3H_8 (0.144 g., mol. wt.: found, 93.4; calcd., 92.33). A slightly less volatile material also was obtained which appeared to be an approximately equimolar mixture of Si_3H_8 and Si_4H_{10} (0.065 g., mol. wt.: found, 107.4; calcd. for Si_3H_8, 92.33; calcd. for Si_4H_{10}, 122.44). Further purification of the Si_3H_8 fraction gave a sample of mol. wt. 93.0 (vapor pressure at −23.72°: found 26.2 mm.; calcd.[18] 26.2 mm.). The infrared spectrum of pure Si_3H_8 (4.0 mm. pressure) is given in Fig. 1 and its absorption maxima are: 2180 $cm.^{-1}$, s (Si–H-stretch); 948 $cm.^{-1}$, m; 884 $cm.^{-1}$, vs; 819 $cm.^{-1}$, m; 808 $cm.^{-1}$, m; 747 $cm.^{-1}$, w; 717 $cm.^{-1}$, d.s.; 705 $cm.^{-1}$, d.s.

From the condensate in the −46° trap a little impure Si_4H_{10} (0.01 g., mol. wt.: found, 130; calcd., 126.4) was obtained in addition to 0.039 g. of higher silanes which exerted a vapor pressure of 3.2 mm. at room temperature. The vapor in equilibrium over this liquid had a molecular weight of 161 (calcd. for Si_5H_{12}, 152.55).

In an attempt to increase the yield of Si_3H_8 and higher silanes, the −134° traps in the recycling apparatus were replaced by −96° traps. As expected, the percentage of Si_3H_8 and Si_4H_{10} in the higher silane mixture increased but the over-all yield of higher silanes was reduced. The greatest weight of Si_3H_8 and higher silanes per experiment was obtained when the −134° traps were used.

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[11] Central Scientific Co., Chicago 13, Illinois.

[12] Delmar Scientific Co., Maywood, Illinois.

[13] General Electric No. 51G75 luminous tube transformer.

[14] J. W. Straley, C. H. Tindal, and H. H. Nielsen, *Phys. Rev.*, **62**, 151 (1942).

[15] H. S. Gutowsky and E. O. Stejskal, *J. Chem. Phys.*, **22**, 939 (1954).

[16] A. Stock, C. Somieski, and R. Wintgen, *Ber.*, **50**, 1754 (1917).

[17] R. Wintgen, *ibid.*, **52**, 724 (1919).

[18] A. Stock, P. Stiebeler, and F. Zeidler, *ibid.*, **56**, 1695 (1923).

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Nitrile Derivatives of Chromium Group Metal Carbonyls

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It has been reported that nitrile complexes of the group VIB metal carbonyls are prepared by photolytic displacement of carbonyl groups to give mono- and disubstituted derivatives[1] or by displacement of diglyme in (diglyme)$Mo(CO)_3$ to give trisubstituted derivatives.[2]

We find that tris-nitrile derivatives are prepared very conveniently by direct reaction. For instance on refluxing $Mo(CO)_6$ in excess acetonitrile under nitrogen, a near quantitive yield of $(CH_3CN)_3Mo(CO)_3$ is obtained with evolution of 3 moles of gas in less than 4 hr. It is identical with the compound prepared by Werner and Coffield *via* a different route.

Similarly $W(CO)_6$ after 40-hr. reflux gives $(CH_3CN)_3W(CO)_3$. It can be crystallized from acetone–hexane to give a yellow solid of somewhat greater air stability. *Anal.* Calcd. for $C_9H_9N_3O_3W$: C, 27.64; H, 2.32; N, 10.75. Found: C, 27.6; H, 2.22; N, 10.55. Three moles of gas are evolved on treatment with iodine in methanol.

The corresponding chromium compound $(CH_3CN)_3Cr(CO)_3$ is a yellow pyrophoric solid. *Anal.* Calcd. for $C_9H_9N_3O_3Cr$: C, 41.71; H, 3.50; N, 16.21. Found: C, 43.00; H, 3.95; N, 13.90. Exact analysis was made difficult because of its extreme sensitivity.

These compounds serve as excellent intermediates in the formation of new compounds not available by other routes.

[1] (a) W. Strohmeier and G. Schönauer, *Chem. Ber.*, **94**, 1346 (1961); (b) W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 622 (1960).

[2] R. P. M. Werner and T. H. Coffield, VIth Intern. Conf. on Coördination Chemistry, Detroit, 1961, Preprint p. 534, Macmillan Co., New York, N. Y.

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Preparation and Properties of Boron Sesquiselenide[1]

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The reaction of boron with the chalcogenides was investigated by a number of persons prior to 1900,[2–7] but the majority of work was carried out with boron and sulfur and their reaction product, boron sesquisulfide. Although Sabatier[5] and Moissan[6,7] have reported the preparation of a compound believed to be boron sesquiselenide, no characterization was performed to substantiate or refute their beliefs.

As a result of renewed interest in boron chemistry, the reaction of boron and sulfur has been re-examined,[8,9] but not that of boron and selenium. The purpose of this study was to develop a technique for preparing boron sesquiselenide and to determine some of its physical properties.

Experimental

Starting materials consisted of 99% pure electrolytic boron and 99.9% pure selenium powder obtained from the Fairmount Chemical Company, Inc., Newark, New Jersey.

The preparation apparatus was a 25-mm. Vycor heating tube in which a tantalum boat filled with boron was located. The inlet to the tube was connected by a standard taper joint to a round bottom 250-ml. flask adapted with a ring-sealed side arm which extended into the bottom of the flask. To the outlet end of the heating tube a fritted disk and a bubbler filled with carbon disulfide were attached in series with standard taper joints. Dry hydrogen, bubbled through the selenium which was heated to about 250° in the round bottom flask, was swept over the boron which had been heated to between 850 and 950°. The hydrogen flow was maintained between 20 and 30 cc. per min. and the reaction product, minute yellow particles which appeared as smoke, was swept from the reaction zone to the fritted disk collector. The collector was isolated from the system and transferred into an argon-filled drybox equipped with a vacuum entry lock and a recirculating system. Because of the moisture sensitivity of the product, subsequent handling of it was performed in this dry atmosphere.

Analysis and Measurement of Physical Properties.—The product was placed in an erlenmeyer flask equipped with a cork stopper and a tared drying tube containing glass wool saturated with nitric acid. Approximately 20 ml. of a dilute sodium hydroxide solution was added to 0.1 g. of product by injecting the hydroxide solution through the stopper with a hypodermic needle. Two portions of hydrochloric acid then were added to this solution, the second portion of which was saturated with sulfur dioxide to precipitate the red form of selenium.[10] This procedure minimized the escape of hydrogen selenide. The selenium was filtered, washed with alcohol and ether,

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[1] Abstracted in part from the M.S. thesis of W. E. Hutchinson presented to the Graduate College of Michigan State University. Presented at the September, 1960, American Chemical Society National Meeting, New York, N. Y.

[2] (a) J. J. Berzelius, *Pogg. Ann.*, **2**, 113 (1824); (b) F. Wohler and H. St. C. Deville, *Ann. chim. phys.*, **52**, 63 (1858).

[3] P. Sabatier, *Compt. rend.*, **112**, 862 (1891).

[4] H. Moissan, *ibid.*, **115**, 203 (1892).

[5] P. Sabatier, *ibid.*, **112**, 1000 (1891).

[6] H. Moissan, *ibid.*, **114**, 617 (1892).

[7] H. Moissan, *Ann. chim. phys.*, (7) **6**, 296 (1895).

[8] P. B. Zeeman, *Phys. Rev.*, **80**, 902 (1950).

[9] F. T. Greene and J. L. Margrave, *J. Am. Chem. Soc.*, **81**, 5555 (1959).

[10] N. H. Furman, Ed., "Scott's Standard Methods of Chemica Analysis," 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, Vol. 1, p. 784.