every detail to the formation of $[(CH_3)_2PBH_2]_3$ from $(CH_3)_2PH \cdot BH_3$.[4]

Proof of the Trimer Formula.—A 43.7 mg. sample of the substance conjectured to be $(C_4H_8PBH_2)_3$ gave a 0.145° lowering of the m.p. of 5.1836 g. of benzene, indicating the mol. wt. to be 298 (calcd., 299.8). An analysis by the Simmons–Robertson method[8] gave 31.1% P (calcd., 31.0). These results, taken with knowledge of the source and properties of the compound, leave no doubt of the formula $(C_4H_8PBH_2)_3$.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Preparation and Properties of Disilanyl Iodide and Bis-disilanyl Ether[1]

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RECEIVED AUGUST 10, 1959

The interaction at room temperature of Si_2H_6 and HI in the presence of aluminum iodide catalyst has yielded disilanyl iodide, SiH_3SiH_2I, which is hydrolyzed instantaneously to give good yields of bis-disilanyl ether, $(SiH_3SiH_2)_2O$. The physical properties and the thermal stability of these compounds have been determined.

During recent years much interest has been shown in simple compounds containing the SiH_3 or "silyl" group.[2–7] These may be regarded as the silicon analogs of methyl compounds. Similarly, compounds containing the SiH_3SiH_2 or "disilanyl" group[8] may be regarded as the silicon analogs of ethyl compounds. The only disilanyl compounds previously reported are SiH_3SiH_2Cl, SiH_3SiH_2Br[9,10] and $(SiH_3SiH_3)_2O$,[9] none of which have ever been isolated in the pure state. In the case of the chloride and the bromide, isolation and characterization has not been possible due to the ease with which they so readily disproportionate according to the equation

$$2SiH_3SiH_2X \longrightarrow Si_2H_4X_2 + Si_2H_6 \qquad (1)$$

Stock and Somieski were able to obtain the ether only as a dilute solution in benzene from which final traces of water were not removed.

The present paper describes the preparation and properties of pure disilanyl iodide, SiH_3SiH_2I, and pure bis-disilanyl ether, $(SiH_3SiH_2)_2O$.

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. Stopcocks were lubricated with Apiezon N grease in preference to silicone grease in order to eliminate the possibility of foreign silicon compounds appearing through attack on the grease by the substances handled.

Unless otherwise indicated, all pressure readings (as in mol. wt. determinations) were made with a glass bourdon gauge in order to eliminate contamination and possible reaction of compounds with mercury.

Melting points were determined by a magnetic plunger technique.[11]

All temperatures below 0° were measured by an iron–constantan thermocouple, standardized by the National Bureau of Standards. Temperatures between 0 and 100° were measured with either a thermometer calibrated by the National Bureau of Standards or with a thermometer standardized in this Laboratory.[12] In the use of these thermometers, stem corrections were applied where they were significant.[12]

Disilane.—This was obtained by the reduction of hexachlorodisilane in di-*n*-butyl ether with lithium aluminum hydride[13] in yields ranging from 30–45% based on the amount of hexachlorodisilane used. The purity of the disilane was checked by determining its mol. wt. (found, 62.5; calcd., 62.2) and its vapor pressure at − 64.0° (found, 66.6 mm.; lit. value,[14] 69.0 mm.). Its infrared spectrum was identical to published infrared spectra of the pure compound.[13,15]

Hydrogen Iodide.—This reagent was prepared from red phosphorus, pulverized iodine and water and purified by distillation from a trap at − 96°.

Aluminum Iodide.—This material was prepared from the elements in boiling benzene[16] and after distillation at atmospheric pressure, was purified for use as a catalyst by sublimation *in vacuo*.

Disilanyl Iodide, SiH_3SiH_2I, Synthesis.—This was prepared by the reaction for 2.5 hr. at room temperature of disilane (0.123 mole) and hydrogen iodide (0.04 mole) in a 5 liter round-bottom flask containing aluminum iodide (0.4 g.) sublimed on to its inner wall. The hydrogen evolved was pumped away through five traps in series, each at − 196°. The crude SiH_3SiH_2I (3.5 g.; 76% yield based on disilane used according to equation 2) was separated from less volatile more highly iodinated materials and from unreacted disilane by condensation in a trap at − 96°. Purification was effected by repeatedly evaporating the product from a trap at − 46° and condensing it in a trap at − 78°. The pure material obtained (mol. wt. found, 192.0; calcd., 188.1), exerted a vapor pressure of 9.5 mm. at 0°, m.p., − 86.1 ± 0.3°; density, 1.764 g./ml. at 0°.

Disilanyl iodide was stored at either −78 or −196° in order to prevent its decomposition. In the gas phase at room temperature the rate of disproportionation was sufficiently slow to permit its manipulation in the vacuum line. Care was taken to exclude traces of mercury or mercury va-

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(1) This report is based on portions of a thesis to be submitted by Laird G. L. Ward to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(12) National Bureau of Standards Circular 600, January 8, 1959, "Calibration of Liquid-in-Glass Thermometers," by James F. Swindells, available from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

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por with which it reacts readily. Unlike its lower homolog silyl iodide (SiH_3I), SiH_3SiH_2I is spontaneously inflammable in air.

Analysis.—Disilanyl iodide (0.2252 g.; 1.198 mmole; vapor pressure at 0°, 9.5 mm.), upon hydrolysis in 35% aqueous sodium hydroxide, yielded after three days, 160.1 ml. of hydrogen (calcd., 160.8 ml.). The iodine was determined volumetrically by oxidation to ICl with KIO_3[17]: I found, 67.70%; calcd., 67.60%. Silicon was determined upon the combined residues, as SiO_2[18]: Si found, 29.92%; calcd., 29.80%. Another sample (0.2491 g., vapor pressure at 0°, found 9.3 mm.) contained I, 68.25%; Si, 29.60%.

Thermal Stability. (a) **Decomposition at 0°.**—The vapor pressure of a sample of SiH_3SiH_2I, maintained at 0°, increased steadily from an initial value of 10.0 mm., to a value of 12.7 mm. after 255 minutes.

(b) **Decomposition at Room Temperature.**—SiH_3SiH_2I (0.4148 g.; vapor pressure at 0°, 10.1 mm.) was stored in the dark in a Pyrex tube (15 ml.) for 57 days. Hydrogen (6.45 ml.) was formed, together with Si_2H_6 (0.0532 g., mol. wt. found, 65.6; calcd., 62.2), SiH_4 (0.01–0.02 g.; identified by infrared spectrum)[19] and impure SiH_3SiH_2I (0.0733 g.). A non-volatile viscous liquid remained in the reaction tube.

(c) **Decomposition at 90°.**—SiH_3SiH_2I (0.330 g.; vapor pressure at 0°, 9.5 mm.), was heated at 90 ± 1° for 5 hr. in a sealed Pyrex tube (15 ml.). The products isolated were hydrogen (6.66 ml.), Si_2H_6 contaminated with a trace of SiH_4 (0.0342 g.; mol. wt. found, 61.9, calcd., 62.2; confirmed by infrared spectrum[13,15]), SiH_3SiH_2I (0.0806 g.; vapor pressure at 0°, 9.0 mm.) and a considerably less volatile product (0.1214 g.) retained as long clear crystalline needles at −46°. A white involatile product remained in the reaction tube.

Vapor Pressure.—An all-glass immersible tensimeter sensitive to ±0.2 mm. difference in pressure, involving no ground glass joints or stopcocks, was employed. The constant temperature bath was controlled to ±0.05°.[20] Vapor pressures in the range 1.3 to 90.1° are represented by the equation $\log P_{cm} = -1767.9/T + 6.5843$ (Table I).

TABLE I

THE VAPOR PRESSURE OF DISILANYL IODIDE[a]

Temp., °C.	Vap. press., cm.		Temp., °C.	Vap. press., cm.	
	Obsd.	Calcd.		Obsd.	Calcd.
1.3	1.43	1.39	76.9	36.86[b]	34.25
5.3	1.72	1.72	57.9	22.04[b]	17.64
11.2	2.29	2.33	45.9	16.06[b]	11.08
20.5	3.72	3.67	20.8	8.28[b]	3.72
30.1	5.69	5.69	2.8	5.34[b]	1.51
39.8	8.70	8.62	−196.0	0.67[b]	...
50.0	13.01	12.93	0.0	1.70[c]	1.30
60.4	19.15	19.27			
80.2	38.21	38.17			
90.1	51.83	52.25			

[a] Duration of the determination, approximately 9 hr. [b] Pressure observed on decreasing the temperature. [c] Vapor pressure of the residue at 0° after removal of the non-condensable gas.

The extrapolated boiling point is 102.8°. The molar heat of vaporization is calculated as 8087 cal. mole^{-1} and Trouton's constant as 21.5 cal. deg.$^{-1}$ mole^{-1}. A second experiment, carried out on an independent sample, gave results which were very closely represented by the same equation, giving an extrapolated boiling point of 102.5°. The irreversibility of the vapor pressure curve upon decreasing the temperature indicates that some decomposition of the material had occurred. The fact that the curve is reproducible and that it falls both on points determined at low temperatures where decomposition is not extensive and also, on points at high temperatures, indicates that the decomposition products do not seriously interfere with the vapor pressure values of the compound.

Bis-disilanyl Ether, $(SiH_3SiH_2)_2O$, Synthesis.—The hydrolysis vessel consisted of a tube 3 cm. × 26 cm. with a vacuum stopcock and standard taper joint. At an angle of 15–20° to the main body of this tube, 4 cm. from the shoulder, was fused a side arm 1 cm. × 26 cm. terminated with a second vacuum stopcock. The freeze-drying vessel consisted of a tube 1.2 cm. × 21 cm. long, surrounded 6 cm. from one end by a cup 10 cm. deep and 4.5 cm. in diameter, so as to form a stem 15 cm. long, to the ends of which were fused a standard taper cone and socket.

Crude disilanyl iodide (6.5 g.; vapor pressure at 0°, 15.0 mm.) was distilled on to 10 ml. of degassed distilled water in the main body of the hydrolysis vessel. Upon thawing, an immediate reaction commenced, there being formed a mobile, highly refractive liquid floating on the water and in the water, a white precipitate. Some hydrogen evolution was observed. With nitrogen in the vessel, the contents were transferred to the side arm and the lower layer of water was removed. The ether was freed of much water by *repeatedly* distilling from room temperature into a trap at −196° (much of the water remaining as ice) and by distilling into the stem of the freeze-drying vessel, melting the ether rapidly and permitting it to flow into a cooled take-off tube. The water which remained as a ring of ice in the stem was pumped away. Final drying of the liquid ether was effected with P_2O_5. Prolonged contact with this drying agent resulted in some decomposition of the ether and in the formation of phosphine. Repeated distillation (with pumping) from a trap at −46° *via* traps at −96° and −196°, yielded the pure ether which condensed in the trap at −96°. The pure material obtained (mol. wt. found, 135.0; calcd., 138.4) exerted a vapor pressure of 11.4 mm. at 0°; m.p., −111.7 ± 0.2°; density, 0.876 g./ml. at 0°. The yield of $(SiH_3SiH_2)_2O$ according to equation 3 was 96% based on pure SiH_3SiH_2I taken. Storing in the dark for 16 days at room temperature in a sealed Pyrex tube produced no change in appearance or vapor pressure. It did not appear to attack mercury. However, unlike its lower homolog, disiloxane, $(SiH_3)_2O$, $(SiH_3SiH_2)_2O$ is spontaneously inflammable in air.

Analysis.—$(SiH_3SiH_2)_2O$ (0.0892 g., 0.046 mmole; vapor pressure at 0°, found, 11.6 mm.), upon hydrolysis in 35% aqueous sodium hydroxide, yielded, after 2.5 days, 173.7 ml. of hydrogen (calcd., 174.0 ml.). Silicon was determined as SiO_2[18]: Si found, 81.7%; calcd., 81.2%.

Thermal Stability.—(a) $(SiH_3SiH_2)_2O$ (0.0896 g.; vapor pressure at 0°, 11.6 mm.) was heated for 9 hr. at 70° in a sealed Pyrex tube (15 ml.). The residue, after removal of the hydrogen (0.36 ml.), exerted a vapor pressure of 12.7 mm. at 0°.

(b) $(SiH_3SiH_2)_2O$ (1.0 g.; vapor pressure at 0°, 11.5 mm.) was heated slowly over mercury during 4 hr. to 90° then cooled during 2 hr. to 0° in a newly constructed glass apparatus. Slightly impure ether (mol. wt. found, 132.5; calcd., 138.4), remained after the removal of the hydrogen (approximately 0.8 ml.). It exerted a vapor pressure of 16.7 mm. at 0°, but its infrared spectra at 29.2 mm. and 4.2 mm. were identical with those of the spectra of the pure compound at comparable pressures. Considerably less hydrogen (<0.03 ml.) was evolved in a subsequent experiment carried out in an identical manner using the *same* apparatus. It therefore appears probable that the rate and/or degree of decomposition is dependent, at least to some extent, on the previous history of the glass surfaces of the container.

Vapor Pressure.—The vapor pressure of $(SiH_3SiH_2)_2O$ was determined over mercury in an immersible tensimeter,[21] in conjunction with compensating manometers at room temperature in order to avoid the necessity of making corrections due to the change in density of mercury with the increase in temperature. Vapor pressures in the range 1.3 to 89.5° are represented by the equation $\log P_{cm.} = -1901.1/T + 7.0472$ (Table II).

The extrapolated boiling point is 94.8°. The molar heat of vaporization is 8700 cal. mole^{-1} and Trouton's con-

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(17) "Scott's Standard Methods of Chemical Analysis," N. H. Furman, Ed., Vol. I, 5th ed., D. Van Nostrand Co., Inc., 1939, p. 454.

(18) Arthur I. Vogel, "A Textbook of Quantitative Inorganic Analysis, Theory and Practice," 2nd Ed., Longmans, Green and Co., London, 1951, p. 503.

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(20) Sargent Thermonitor, Model S, E. H. Sargent and Co., Chicago.

(21) Designed after the one described by A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937), the inner surfaces of which had been thoroughly pre-treated with liquid $(SiH_3SiH_2)_2O$ and its vapor at room temperature during 24 hr.

TABLE II

THE VAPOR PRESSURE OF BIS-DISILANYL ETHER[a]

Temp., °C.	Vap. press., cm. Obsd.	Vap. press., cm. Calcd.	Temp., °C.	Vap. press., cm. Obsd.	Vap. press., cm. Calcd.
0.7	1.25	1.28	70.0	32.30	32.20
2.2	1.38	1.40	80.0	45.31	46.19
5.0	1.62	1.63	89.5	62.81	63.91
10.0	2.12	2.16	78.5	43.79[b]	43.82
20.5	3.83	3.75	55.5	19.46[b]	18.34
30.2	6.23	6.04	37.0	9.27[b]	8.29
40.0	9.78	9.49	18.5	4.08[b]	3.27
50.0	15.21	14.62	0.0	1.66[b]	1.23
60.0	22.20	21.96	−196.0	<0.01[b]	

[a] Duration of the determination, approximately 7 hr. [b] Pressure observed on decreasing the temperature.

stant, 23.6 cal. deg.$^{-1}$ mole^{-1}. Two further determinations on two independent samples gave similar results yielding extrapolated boiling points of 94.7 and 94.8°. The irreversibility of the vapor pressure curve upon decreasing the temperature indicates that slight decomposition had taken place. The results of the thermal stability experiment b (the fact that the curve is reproducible, and that it falls both on points determined at low temperatures where decomposition is not extensive and also, on points at high temperatures) indicate that the observed values are very close to those to be expected if no decomposition had occurred.

Infrared Spectra.[22]—Infrared measurements were made with a Perkin–Elmer Model 21 double beam recording spectrophotometer, employing a sodium chloride optical system. All measurements were made on the gaseous phase at 25° with the sample confined in a 10 cm. cell with 30 mm. potassium bromide windows cemented with glyptal resin.

SiH_3SiH_2I, observed at pressures of 3.5 mm. and 22.5 mm.: 2400 cm.$^{-1}$, shoulder, and 2360 cm.$^{-1}$, very strong; 1875 and 1820 cm.$^{-1}$, very weak; 1025 cm.$^{-1}$, weak; 944 cm.$^{-1}$, shoulder, medium, and 934 cm.$^{-1}$, medium; 876 and 868 cm.$^{-1}$, doublet, strong; 761 and 735 cm.$^{-1}$, doublet, very strong. $(SiH_3SiH_2)_2O$, observed at pressures of 0.5 mm. and 6.5 mm.: 2155 cm.$^{-1}$, very strong; 1680 cm.$^{-1}$, weak; 1143 cm.$^{-1}$, strong; 1071 cm.$^{-1}$, very strong; 937 cm.$^{-1}$, very strong; 853 cm.$^{-1}$, weak; 808 cm.$^{-1}$, strong; 755 cm.$^{-1}$, weak.

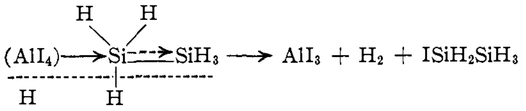
Results and Discussion

Disilanyl iodide may be prepared in good yields from Si_2H_6 and HI in the presence of anhydrous aluminum iodide at room temperature as shown by the equation

$$Si_2H_6 + HI \xrightarrow{Al_2I_6} SiH_3SiH_2I + H_2 \qquad (2)$$

The yield of more highly iodinated disilanes which are also formed in the above reaction may be held at a minimum by using an excess of Si_2H_6. Whereas SiH_4 and HI react slowly and incompletely, even on heating,[23] the analogous reaction with Si_2H_6 proceeds at room temperature very much more rapidly and all the HI is consumed. It is interesting to note that no cleavage of the Si–Si bond occurs under the above experimental conditions to produce substances such as SiH_3I and SiH_4.

The increased rate of reaction of the Si_2H_6 is probably related to the fact that the proposed intermediate complex $H(AlI_4) \rightarrow SiH_3SiH_3$ can be formed more readily than the analogous complex in the SiH_4 reaction since the negative charge of the coordinate linkage can be distributed over two silicon atoms, *viz.*



The vacant 3d orbitals of the silicon could readily permit the formation of the coördinate linkages indicated above. It therefore seems reasonable to predict that the higher silanes will react even more rapidly with HI in the presence of aluminum iodide.

It is important to note that whereas SiH_3SiH_2Cl and SiH_3SiH_2Br disproportionate so rapidly that they cannot be isolated in the pure state, SiH_3SiH_2I is sufficiently stable to isolate and characterize although disproportionation *does* occur on heating or on standing as indicated by equation 1. The greater stability of the iodide follows the same trend as that found with the silyl halides and it was, in fact, predicted in an earlier communication.[2] A mechanism for the disproportionation of disilanyl halides and an explanation of the fact that their rate of disproportionation is greater than that of silyl halides was also presented in an earlier paper.[2]

Bis-disilanyl ether may be prepared in good yields by the instantaneous hydrolysis of disilanyl iodide

$$2SiH_3SiH_2I + H_2O \longrightarrow (SiH_3SiH_2)_2O + 2HI \qquad (3)$$

It is extremely difficult to separate the ether from traces of water since both substances have a similar volatility and many dehydrating agents react readily with the ether. In order to eliminate the use of water, the conversion of SiH_3SiH_2I to $(SiH_3SiH_2)_2O$ was attempted by treating the iodide with PbO and also with Ag_2CO_3 under a variety of conditions. Complex reactions occurred in all cases with the formation of small quantities of disilane, hydrogen and in the reaction with Ag_2CO_3, carbon dioxide. No $(SiH_3SiH_2)_2O$ could be isolated in any of these experiments.

$(SiH_3SiH_2)_2O$ is considerably more stable thermally than SiH_3SiH_2I but it is less stable than $(SiH_3)_2O$.

It is of interest to note that whereas CH_3CH_2I boils at a temperature 36.9° above that of $(CH_3CH_2)_2O$, the boiling points of the silicon analogs differ only by 8.0°. This undoubtedly is related, at least partly, to the fact that changing the atom attached to a SiH_3SiH_2 group (which is heavier than a CH_3CH_2 group) represents a smaller percentage change in molecular weight and, hence, a smaller change in boiling point is observed. This strongly suggests that it should be possible to prepare other pure disilanyl derivatives since their boiling points should not be very much greater than SiH_3SiH_2I and hence it should be possible to effect their purification with vacuum system techniques.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for a Frederick Gardner Cottrell Grant which was used to support this investigation.

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[22] The infrared spectra of the compounds discussed, together with the assignments of the absorption maxima, have been deposited as Document number 6063 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

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