The general structural principle of such polymers probably relates closely to that of the thermoplastic materials derived from trimethylamine and pentaborane-9.[7] It is not difficult to imagine a boron-hydride polymer network of a type suggested by the structure of decaborane[15] or the more condensed metal polyborides.[16] Now if basic units were inserted into such a network, the greater availability of bonding electrons would lead to a decrease in the amount of low-order boron–boron bonding. Hence there would be less cross-linking and thermoplasticity would become possible. This idea offers ample opportunity for trapping of phosphinoborine units, rings or chains (as well as tertiary amines or phosphines or aminopolyborane structures) in highly polymeric aggregates. The recently-determined structural pattern of $(CH_3CN)_2B_{10}H_{12}$[17] shows a relatively simple example of the kind of base-to-B-network bonding here considered.

An expected effect of the entrapped base units would be to bring the average bonding of the boron atoms closer to the four-coördinate situation. Thus the lability of bonding would be decreased and there would be less opportunity for H atoms to congregate near certain boron atoms as a first step toward easily activated processes forming H_2. Hence it is not wholly surprising that these base-inclusive polymers show much higher thermal stability than the $(BH)_x$ type of polymer.

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(16) Reviewed by R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

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LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Chemistry of the C_4H_8P Ring: the Aminophosphine $(CH_3)_2NPC_4H_8$, the Cyclophosphine C_4H_8PH and the Tetracyclic Trimer $(C_4H_8PBH_2)_3$[1]

BY ANTON B. BURG AND PETER J. SLOTA, JR.

RECEIVED AUGUST 26, 1959

The new amino-cyclophosphine $(CH_3)_2NPC_4H_8$ (liquid, b.p. est. 170°) was made from $(CH_3)_2NPCl_2$ and $BrMgC_4H_8MgBr$. It forms a 1:1 adduct with CH_3I and reacts with 2HCl to make C_4H_8PCl (liquid, b.p. est. 165°), reconvertible to $(CH_3)_2NPC_4H_8$ by reaction with $2(CH_3)_2NH$. The slightly volatile liquid adduct $(CH_3)_2NPC_4H_8\cdot BH_3$ on heating forms the new cyclic C_4H_8PH (30% yield; m.p. −88°; b.p. est. 105°), aminoborines and a trace of the tetracylic trimer $(C_4H_8PBH_2)_3$ (m.p. 169.3 ± 0.4°). This trimer was made almost quantitatively from the liquid complex $C_4H_8PH\cdot BH_3$. The ring structure of C_4H_8PH was confirmed by its infrared spectrum. For the isolation of C_4H_8PH, the accompanying compound $[(CH_3)_2N]_2BH$ was converted by 2HCl to $(CH_3)_2NH_2Cl$ and $[(CH_3)_2NBHCl]_x$.

Cyclic phosphines of the type $C_nH_{2n}PH$ seem not to have been reported, although numerous efforts have been made toward their synthesis. We now have made such a phosphine, through a double-Grignard synthesis of the aminophosphine $(CH_3)_2NPC_4H_8$. Just as the prototype aminophosphine $(CH_3)_2NP(CH_3)_2$[2] forms the slightly volatile liquid adduct $(CH_3)_2NP(CH_3)_2\cdot BH_3$,[3] so also the new $(CH_3)_2NPC_4H_8$ reacts with a deficient proportion of diborane to form the still less volatile liquid $(CH_3)_2NPC_4H_8\cdot BH_3$. On heating, this adduct produces hydrogen, dimethylamine, the aminoborines, the expected phosphinoborine polymers (including resinous material) and the corresponding phosphine, C_4H_8PH.

The phosphinoborine trimer $(C_4H_8PBH_2)_3$, which is a minor product of this decomposition, can be made almost quantitatively from the adduct $C_4H_8PH\cdot BH_3$, just as $[(CH_3)_2PBH_2]_3$ can be made from $(CH_3)_2PH\cdot BH_3$.[4] Assuming the same kind of $(PB)_3$ ring as in $[(CH_3)_2PBH_2]_3$,[5] this new phosphinoborine trimer would have an unusual paddle-wheel structure, with the three C_4H_8P rings in planes perpendicular to the B–P–B planes of a somewhat puckered $(PB)_3$ ring.

Part of the evidence proving the formula of $(CH_3)_2NPC_4H_8$ was its conversion by HCl to the corresponding chlorophosphine C_4H_8PCl, and the reversion of this to the aminophosphine by the action of dimethylamine. Final evidence of the C_4H_8P ring came from the infrared spectrum of C_4H_8PH, which has significant features in common with the spectra of C_4H_8NH and C_4H_8O.

The Amino-cyclophosphine

Synthesis.—Two solutions, one containing the double Grignard reagent $BrMgC_4H_8MgBr$ made from 200 g. (920 mmoles) of 1,4-dibromobutane in 600 ml. of diethyl ether and the other containing 136 g. (930 mmoles) of $(CH_3)_2NPCl_2$ in 500 ml. of ether, were added simultaneously to 500 ml. of ether at −78°. This process was carried out during 2 hr., in a 2-l. three-neck flask with a Hershberg stirrer and a slow stream of dry nitrogen. The $(CH_3)_2NPCl_2$ was kept slightly in excess throughout the process. Crystallization of the double Grignard reagent in the dropping funnel was minimized by the use of an infrared lamp. The first observable reaction was the precipitation of hard white crystals. After the mixing was complete, the flask was held at −78° for an hour and then warmed to room temperature during another hour. Near room temperature the crystals changed to a light-brown gum which made stirring difficult. After 1 hr. of refluxing, the solution was decanted off and the amino-cyclophosphine was isolated by column-distillation. The final purification was done by micro-column distillation (0° reflux) under high vacuum. The main yield was 9 g.

The recovered ether was returned to the flask containing the gummy residue and the stirred mixture was treated with

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[1] This research was supported by the United States Air Force under Contracts AF 33(616)-2743 and 5435 (Subcontract No. 1), monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio. It is a pleasure also to acknowledge the assistance of Dr. David A. Dows in the interpretation of the infrared spectra.

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(3) A. B. Burg and P. J. Slota, Jr., *ibid.*, **82**, 2145 (1960).

(4) A. B. Burg and R. I. Wagner, *ibid.*, **75**, 3872 (1953).

(5) W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

200 g. of ammonia, bubbled in slowly. The energetic reaction converted the gummy material to fine loose crystals, which were filtered out by means of a Soxhlet thimble. Distillation now yielded a further 1 g. of the desired aminocyclo-phosphine, bringing the total to 10 g., or 8.1%.

It is probable that much of the desired aminophosphine formed a magnesium complex, from which it was liberated by the ammonia. However, the subsequent observation of the reactivity of $(CH_3)_2NP(CH_3)_2$ toward ammonia[2] leads us to suppose that a better recovery might be had by using dimethylamine, which would have the extra advantage of converting a possible trace of C_4H_8PCl or C_4H_8PBr to the desired aminophosphine. As it was, the ammonia treatment led to a considerable yield of an oil having no appreciable volatility at room temperature. This probably was a complex mixture, for we could not isolate any definite compound from it. It might have contained some of the bis-phosphinoamine $(C_4H_8P)_2NH$, but one might consider also $P{-}C_4H_9$ compounds resulting from the ammonolysis of $=P{-}C_4H_8MgBr$ materials, as well as ring polymers of the $(CH_3)_2NPC_4H_8{-}$ unit. And then there is also the possibility of some P–N bond cleavage by the double Grignard reagent, acting either singly or doubly. The feasible combinations of these principles suggest so many by-products that an 8% yield of the desired $(CH_3)_2NPC_4H_8$ must be regarded as relatively successful.

Physical Properties.—A middle fraction from the micro-column distillation was taken for the vapor tension measurements shown in Table I, which were made by means of an immersible tensimeter.[6] The results are correlated by the equation $\log P_{\text{mm.}} = 5.4766 - 0.003700\,T + 1.75 \log T - 2479/T$. This gives the b.p. as 170.4° and the Trouton constant as 21.5 cal./deg. mole, in good conformity to expections for a pure substance. The substance appeared to be a glassy liquid at −78°; the m.p. could not be observed.

TABLE I

VAPOR TENSIONS OF LIQUID $(CH_3)_2NPC_4H_8$

t (°C.)	$P_{\text{mm.}}$ (obsd.)	$P_{\text{mm.}}$ (calcd.)	t	P (obsd.)	P (calcd.)
22.4	2.07	2.08	75.9	34.09	34.14
28.6	3.06	3.05	82.9	45.93	45.92
37.1	5.00	5.00	90.9	63.38	63.43
50.8	10.46	10.45	113.5	145.4	145.4
63.6	19.66	19.59			

The mol. wt. was determined for the vapor at 139° and 239 mm. (condensation point 129° for this pressure), giving the value as 132.9 (calcd., 131.16).

Quantitative Formation of the Methiodide.—A 34.9 mg. sample of the supposed $(CH_3)_2NPC_4H_8$ was treated with a larger measured sample of CH_3I, of which 0.266 mmole reacted to form a non-volatile white solid. This result corresponds exactly to the formation of $(CH_3)_2NPC_4H_8{\cdot}CH_3I$. Taken with the mol. wt. result, it leaves no doubt of the formula $(CH_3)_2NCP_4H_8$.

Conversion to the Chlorophosphine.—The R_2PX character of the aminophosphine (where R_2P can represent a ring) was shown by its nearly quantitative conversion to a chlorophosphine: $(CH_3)_2NPC_4H_8 + 2HCl \rightarrow (CH_3)_2NH_2Cl + C_4H_8PCl$. For best results it was necessary to use a slightly deficient proportion of HCl, because any excess would be difficult to remove from the product. A separate experiment showed that HCl is soluble in the chlorophosphine at low temperatures, and difficult to remove by high-vacuum distillation methods—although it was not possible to demonstrate the definite existence of a hydrochloride.

Just as in the parallel synthesis of $(CH_3)_2PCl$,[2] the reaction was carried out in a temperature range of −100 to 25°, in a plain 50 ml. reaction tube jointed to a stopcock leading to the high vacuum system. For such reactions it has been found advantageous to distil the immediate product to a second reaction tube, heating the solid residue to 100° to drive out the aminophosphine which failed to react on account of capture by the solid or because of the formation of a complex with the chlorophosphine. Thus the reaction could be completed only by repeating the back-and-forth distillation three or four times, until there was no further formation of the non-volatile solid.

In one such experiment, 197.0 mg. (1.502 mmoles) of $(CH_3)_2NPC_4H_8$ and 2.931 mmoles of HCl produced a highly uniform volatile liquid weighing 165.8 mg. Taken as pure C_4H_8PCl (1.353 mmoles), this represents a 92.3% yield based upon the HCl directly; or, considering that the excess aminophosphine would form a 1:1 complex with the chlorophosphine,[2] the yield of this would be 94.8% of the calcd. value.

This chlorophosphine formed a glass at −78° so that its m.p. could not be observed. Exactly like $(CH_3)_2PCl$,[2] it slowly formed a buff-colored torch-sublimable solid on contact with mercury. The reaction seemed not to form any mercury compound but probably was a catalytic disproportionation. This effect of mercury made it difficult to determine the mol. wt. or to obtain dependable vapor tension values at elevated temperatures; however, mol. wt. values of 123.9 and 124.1 (calcd. 122.5) were obtained on samples at 100° and 50–80 mm. Two fairly dependable vapor-tension values were 3.4 mm. at 23.4° and 42.5 mm. at 71.8°. The corresponding equation ($\log P_{\text{mm.}} = 8.357 - 2321/T$) would give the Trouton constant as 25.0 cal./deg. mole, suggesting that the log P *vs.* $1/T$ line curves toward a higher b.p. than the 151° value implied by the equation. From a Clapeyron–Clausius equation based on the higher vapor tension value and the assumption that the real Trouton constant is the normal 21.0, the b.p. is estimated as 165 ± 3°.

The reconversion reaction $C_4H_8PCl + 2(CH_3)_2NH \rightarrow (CH_3)_2NH_2Cl + (CH_3)_2NPC_4H_8$ could not be done quantitatively in a vacuum system involving mercury and stopcock grease, on account of side reactions probably related to disproportionation. However, even reactions such as $2C_4H_8PCl \rightarrow Cl_2PC_4H_8PC_4H_8$ or $4C_4H_8PCl \rightarrow Cl_2PC_4H_8PCl + C_4H_8PC_4H_8PC_4H_8$ would not alter the number of P–Cl bonds, so that the amine treatment led to a correct analysis for chloride. A 106.7 mg. sample of C_4H_8PCl was treated in a weighing bulb with excess dimethylamine, producing 72.3 mg. (0.551 mmole, or 60% yield) of $(CH_3)_2NPC_4H_8$ and a non-volatile solid. The low yield of the aminophosphine could be explained by the presence of a liquid which distilled under high vacuum only when heated at least to 100°. The non-volatile solid (weighing 5% more than expected because of the by-product) was dissolved in water, neutralized to methyl red by slight addition of sodium hydroxide and titrated by the adsorption indicator method to show 0.89 mmole of Cl^- (calcd., 0.87).

The Cyclophosphine C_4H_8PH

Synthesis.—The slightly volatile liquid adduct $(CH_3)_2NPC_4H_8{\cdot}BH_3$ was formed by slowly warming 0.768 mmole of $(CH_3)_2NPC_4H_8$ with 0.370 mmole of B_2H_6 from −196° to room temperature, in a sealable tube attached to the high-vacuum system. Briefly heated by an oil-bath at 220°, the liquid refluxed vigorously, as expected of an adduct analogous to the noticeably volatile $(CH_3)_2NP(CH_3)_2{\cdot}BH_3$.[3] The tube was sealed off and heated for 21 hr. at 210°, yielding 0.146 mmole of H_2, 0.065 mmole of $(CH_3)_2NH$ and 0.020 mmole of $(CH_3)_2NBH_2$ as the most immediately recognizable products. Identified later was 10.0 mg. of the tetracyclic trimer $(C_4H_8PBH_2)_3$ (m.p. 169.5°). Also there was a non-volatile mixture consisting of 1.6 mg. of an acetone-soluble white solid, a little more of an acetone-insoluble white solid, and a transparent brown resin.

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(6) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 785 (1937).

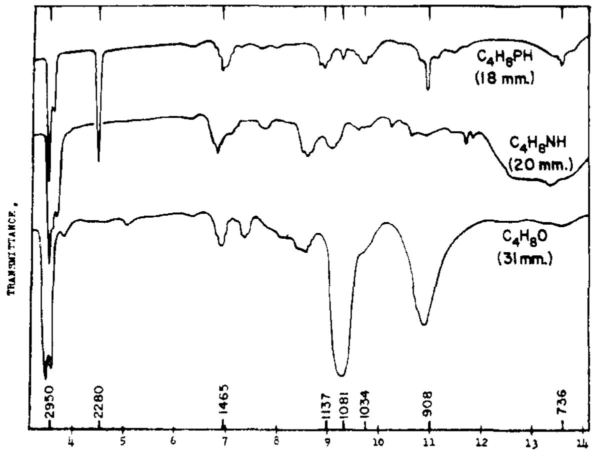

Fig. 1.—Comparison of infrared spectra of C_4H_8PH, C_4H_8NH and C_4H_8O. The wave numbers (cm.$^{-1}$) of significant peaks are shown by the vertical numbers. The deepest peak (2950 for C_4H_8O) showed 4% transmission, uncorrected for the empty cell, which showed 60–70% transmission.

The desired C_4H_8PH was in a 56.1 mg. fraction (10 mm. at 0°) containing $[(CH_3)_2N]_2BH$, which could not be removed by distillation methods. Accordingly it was necessary to find a chemical method of eliminating the bis-aminoborine. The possibility of using HCl for this purpose was demonstrated by the experiment next described.

TABLE II

VAPOR TENSIONS OF C_4H_8PH

t (°C.)	$P_{mm.}$ (obsd.)	$P_{mm.}$ (calcd.)	t	P (obsd.)	P (calc.)
−16.40	3.04	3.04	30.1	44.8	44.4
− 9.00	4.98	4.98	35.6	57.5	57.5
0.00	8.74	8.74	40.2	70.6	70.9
12.90	18.21	18.24	44.25	84.0	84.3
15.47	20.98	20.94	63.0	181.4	182.9
27.80	27.68	27.68	73.8	274.1	272.7

The Reaction of *Bis-(dimethylamino)-borine* with HCl.—A mixture of 0.935 mmole of nearly pure $[(CH_3)_2N]_2BH$ and 0.897 mmole of HCl reacted during a slow warming from −78° (finally standing overnight at room temperature), producing non-volatile solids and leaving 0.456 mmole of $[(CH_3)_2N]_2BH$ unused. The indicated equation, $[(CH_3)_2N]_2BH + 2HCl \rightarrow (CH_3)_2NH_2Cl + (CH_3)_2NBHCl$, was confirmed by dissolving the solid products in chloroform and water-extracting the ionic chloride. This was titrated as 0.451 mmole (calcd., 0.448). The formation of $(CH_3)_2NBHCl$ (presumably in dimeric or higher-polymer form) evidently was fairly clean and not disturbed by disproportionation, for only 0.023 mmole of $(CH_3)_2NBH_2$ could be found afterwards—probably having been an impurity in the bis-aminoborine.

Isolation of the Cyclophosphine.—The 56.1 mg. fraction (10 mm. at 0°) was treated with 0.9 mmole of HCl in small portions, with warming from −78°, to form the non-volatile amino compounds and the hydrochloride $C_4H_8PH_2Cl$. The latter could be sublimed away; like the previously observed $(CH_3)_2PH_2Cl$, it showed a dissociation pressure near 2 mm. at room temperature. It was purified carefully by high-vacuum fractional condensation and then treated with $(CH_3)_2NH$ to liberate the cyclophosphine; yield, 20.7 mg. (0.228 mmole, or 30%). By difference, the yield of $[(CH_3)_2N]_2BH$ was estimated as 0.357 mmole, representing 46% of the boron.

Physical Properties.—The phosphine C_4H_8PH melted sharply at −88°. Its mol. wt. was determined at 60° and 50 mm., as 88.04 ± 0.3 (calcd. 88.08). The vapor tensions, shown in Table II, determined the equation $\log P_{mm.} = 4.7472 - 0.003059T + 1.75 \log T - 1976/T$, which gives the b.p. as 105.4° and the Trouton constant as 22.1 cal./deg. mole.

The Infrared Spectrum.—The presumed ring structure of C_4H_8PH was confirmed by its infrared spectrum, which was compared with those of pyrrolidine and tetrahydrofuran, as shown in Fig. 1. All three spectra were run under comparable conditions by means of the same instrument (Perkin–Elmer Infracord, with a 71 cm. cell having KBr windows). The spectrum of polystyrene was used as a reference for determining the wave numbers of the most significant peaks. The tracings shown in Fig. 1 are corrected for noise effects (as demonstrated by comparisons of different runs), and the negative peak at 2340 cm.$^{-1}$ (due to CO_2 in the comparison path) also is omitted.

The P–H stretching frequency at 2280 cm.$^{-1}$ is strong and clearly recognizable. Its simplicity argues against a PH_2 type of vibration analogous to the double-peak effect for the CH_2 stretching near 2900; hence a secondary phosphine is indicated. The CH_2 region around 1465 cm.$^{-1}$ is roughly the same in all three spectra: a sharp peak with shoulders attributed to rotational effects. Also similar are the C–C bands around 1137 for C_4H_8PH, 1160 for C_4H_8NH and 1175 for C_4H_8O. Especially significant is the strict absence of any absorption at 1370, which would have indicated a methyl group. In sum, the features characteristic of C_4H_8X rings are similar in all three spectra; all effects agree with the ring-C_4H_8-PH interpretation.

Further evidence of the identity of C_4H_8PH is found in its conversion to $(C_4H_8PBH_2)_3$, as next described.

The Tetracyclic Phosphinoborine Trimer

The trimer $(C_4H_8PBH_2)_3$ was obtained from three sources: (1) the previously described decomposition of $(CH_3)_2NPC_4H_8 \cdot BH_3$; (2) as a by-product from the reaction of $(CH_3)_2NPC_4H_8$ with B_5H_9[7]; (3) by loss of hydrogen from the complex $C_4H_8PH \cdot BH_3$. All three products melted at 169.1 ± 0.4°; the long-needle crystals had the same fairly slow and limited solubility in acetone. The third method was so nearly quantitative as to constitute further evidence supporting the formula C_4H_8PH; for only a secondary phosphine would give the trimer form and do so in such a clean manner.[4]

Synthesis from the Phosphine.—A 0.354 mmole sample of C_4H_8PH was treated with half as much diborane to form the complex $C_4H_8PH \cdot BH_3$, which was found to be solid at −78° but liquid at 0°. Heated in a sealed tube for 46 hr. at 198°, it yielded 0.353 mmole of H_2 and 0.007 mmole of C_4H_8PH. The main product sublimed slowly under high vacuum at 100°, leaving a tiny trace of white residue. The sublimate melted over a range around 162°, but recrystallization from acetone brought its m.p. to 169.0–169.3°, corresponding to pure $(C_4H_8PBH_2)_3$. The yield of the crude sublimate was 34.6 mg., or 99.7%, based upon the unrecovered C_4H_8PH. This crude sample may have contained a trace of the tetramer $(C_4H_8PBH_2)_4$, which has not yet been isolated. If so, the conversion of $C_4H_8PH \cdot BH_3$ to $(C_4H_8PBH_2)_3$ is parallel in

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(7) Technical Report WADC TR 56-82 (Part II) p. 9 (January, 1957), available through the Library of Congress Photoduplication Service, through O.T.S. Identification Number PB 131180.

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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LOS ANGELES 7, CALIFORNIA

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

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

BY LAIRD G. L. WARD AND ALAN G. MACDIARMID

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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