

crystalline distillate, which again liquefied on standing. Carbon and hydrogen analyses (see Table II) of the oil are in good agreement with a dimethylethylenedioxyasilane formula and it is evident that the crystal-oil transformation represents some kind of labile polymerization. The cryoscopic molecular weight, in cyclohexane, of the washed crystals was found to be 243 (theory for dimer 236). Both the molecular weight and the boiling point are therefore in good agreement with a dimeric structure. The oil, on the other hand, has an average molecular weight of 1164, which is 9.9 times that of the monomeric structure. All attempts to distil the unpolymerized dimer out of the oil at low pressures and temperatures resulted in depolymerization, substantially all of the oil distilling over as crystalline dimer. The average degree of polymerization of the polymer itself is therefore not known.

The infrared absorption of a solution of 114 mg. of freshly prepared crystalline dimeric dimethylethylenedioxyasilane in 1.14 cc. of dioxane was measured in the region of 3μ . A very small absorption (almost too small to be noticeable) was found at 2.9μ . A second portion of these same crystals was allowed to stand in a well-stoppered bottle for a period of one week during which time it polymerized to an oil. A solution of 113 mg. of this oil in 1.13 cc. of dioxane was prepared and a moderately strong band was observed at 2.9μ . A sample of liquid polymeric dimethylethylenedioxyasilane of molecular weight 1164, that had stood at room temperature for a period of about three and one-half months, likewise showed absorption at 2.9μ with an intensity about equal to that of the sample that had stood for only one week. The region in which this absorption has been observed is characteristic of the hydroxyl groups.

In the preparation of VI, X was substituted for dimethyldiethoxyasilane. About half the crude product could be distilled up to a pot temperature of 250° . The distillate was almost entirely cyclic monomer. The residue was a thick oil.

Hexamethylene glycol and dimethyldiethoxyasilane were allowed to react by method B. The product was a viscous oil which did not depolymerize to volatile products at 250° and 4 mm.

Hydrolysis and Alkoxy Interchange with Dimethyldi-*d*-2-butoxyasilane.—A mixture of 27 g. of VIII, $[\alpha]^{20}_D +24.9^\circ$, 20 g. of dimethyldiethoxyasilane and 0.50 g. of *p*-toluenesulfonic acid was allowed to stand at room temperature for one week, after which it was separated into dimethyl-*d*-2-butoxyethoxyasilane, $[\alpha]^{20}_D +13.7^\circ$, di-

methyl-*d*-2-butoxyasilane, $[\alpha]^{20}_D +19.8^\circ$ (in CHCl_3), and dimethyldiethoxyasilane. Dimethyl-1-butoxyethoxyasilane and dimethyl-*dl*-2-butoxyethoxyasilane were likewise prepared by equilibration of the corresponding dimethyldi-alkoxyasilanes with *p*-toluenesulfonic acid as the catalyst.

A sample of VIII was shaken with water acidified with a trace of *p*-toluenesulfonic acid. The aqueous layer was separated and found to contain 3.33 g. of 2-butanol per 100 g. of solution by comparing its refractive index with those of synthetic mixtures. From the observed α^{20}_D of $+0.4^\circ$ an $[\alpha]^{20}_D$ of $+12^\circ$ is calculated for the pure 2-butanol. $[\alpha]^{20}_D$ for the original *d*-2-butanol from which VIII was made was $+11.5^\circ$.

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Summary

1. Cyclic polymethylenedioxydimethylsilanes, of six to eleven annular atoms, have been prepared and characterized. Several of these compounds are found to polymerize and their polymers to depolymerize with great ease.

2. Dimethyldi-*d*-2-butoxyasilane was prepared and equilibrated with dimethyldiethoxyasilane to give dimethylethoxy-*d*-2-butoxyasilane. Dimethylethoxy-1-butoxyasilane was prepared in a similar manner using the corresponding dibutoxyasilane.

3. The hydrolysis and alkoxy interchange reactions of the alkoxyasilanes appear to involve reaction at the silicon-oxygen bond, since the configuration of an alkyl group asymmetric at the point of attachment through oxygen to silicon survives the reactions unchanged.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Preparation and Some Properties of Hydrides of Elements of the Fourth Group of the Periodic System and of their Organic Derivatives

BY A. E. FINHOLT, A. C. BOND, JR., K. E. WILZBACH AND H. I. SCHLESINGER¹

Although the hydrides of silicon, of germanium and of tin have been known for some time, their preparation has been difficult. The most satisfactory method for the silicon and germanium compounds has been the treatment of magnesium silicide or germanide with acidic reagents. In the earlier work, aqueous hydrochloric acid was employed to liberate silane² or germane³; the substitution of ammonium bromide in liquid am-

monia for the aqueous acids constituted a marked improvement in the preparation of these hydrides.⁴ But even these improved procedures are troublesome. The preparation of the magnesium compounds has to be carried out under rigid conditions; the hydrides are likely to contain impurities which must be removed by low temperature fractionations or by a series of chemical treatments, and the use of liquid ammonia as a solvent requires special techniques. Furthermore, these methods are not applicable to the preparation of the alkyl or aryl derivatives of the hydrides; for

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(2) Stock and Somieski, *Ber.*, **49**, 111 (1916).

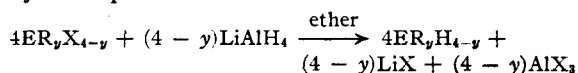
(3) Dennis, Corey and Moore, *THIS JOURNAL*, **46**, 657 (1924).

(4) Kraus and Carney, *ibid.*, **56**, 765 (1934), for germane, and Johnson and Isenberg, *ibid.*, **57**, 1349 (1935), for silane.

the latter no general, convenient method has, hitherto, been available.

Special difficulty has been encountered in the preparation of stannane. Paneth and his co-workers⁵ treated magnesium stannide with hydrochloric acid, but later found that it is unnecessary to prepare the alloy, since they obtained better results either by using a mixture of magnesium and tin, or by reducing a sulfuric acid solution of tin sulfate with magnesium. At best, their yields were extremely small and irregular; for that reason they preferred the cathodic reduction of tin sulfate at lead electrodes.⁶ That this method is also highly inefficient is seen from the fact that eight electrolytic cells operating for over a week produced only a few cubic centimeters of gaseous tin hydride.

Except for the precautions necessary when the products are spontaneously inflammable, *e.g.*, silane, these hydrides and their alkyl and aryl derivatives may now be easily obtained by the reaction of lithium aluminum hydride⁷ on the appropriate halide in ether solution, as illustrated by the equation



in which E represents silicon, germanium or tin, X represents a halogen, and R an alkyl or an aryl radical; *y* may vary from zero to three. Diethyl ether is employed except in cases in which its separation from the desired product is difficult, or in which a temperature higher than is attainable with this solvent is to be used. In such instances other ethers of suitable physical properties are employed. Such halides as hexachlorodisilane may also be used, as in the preparation of disilane.

Application of the general reaction to organolead halides resulted in what appeared to be partial reduction to metallic lead and to the formation of unstable, volatile lead compounds, thus far isolated in quantities too small for identification. The preparation of hydrocarbons through the use of lithium aluminum hydride will be described by W. G. Brown and his co-workers, who have been exploring the application of the reagent to problems of organic chemistry.

In some instances, *e.g.*, in the preparation of some of the silicon compounds, lithium hydride was used in place of lithium aluminum hydride, but in others, *e.g.*, in the preparation of tin compounds, lithium hydride did not give the desired products. Even in those cases in which the simple hydride could be used, the reactions were much slower, and the yields were satisfactory only when a large excess of the hydride was employed.

The reactions with lithium aluminum hydride proceed smoothly, usually at room temperature, to produce products of high purity, provided the

(5) Paneth and Furth, *Ber.*, **52B**, 2020 (1919); Paneth, Johansen and Matthies, *ibid.*, **55**, 769 (1922).

(6) Paneth and Rabinowitsch, *ibid.*, **57B**, 1877-1890 (1924).

(7) Finholt, Bond and Schlesinger, *THIS JOURNAL*, **69**, 1199 (1947).

starting materials are pure.⁸ The great convenience of the procedure is best illustrated by the case of the inherently unstable stannane of which 50 cc. of the pure gas was prepared in small scale apparatus in two to three hours.

In the course of this investigation a considerable number of compounds, some of them not described in the literature, have been prepared. The latter are briefly discussed in a later portion of this paper.^{8a}

Experimental

Apparatus and Procedure.—Except in cases in which larger quantities of the reaction products were desired for other purposes, time was saved by carrying out the preparation in a vacuum system such as described by Stock.⁹ Quantities thus obtained were adequate to identify and characterize the compounds prepared, and to judge of the yields obtainable. For larger quantities the reaction was carried out in a three-necked flask, equipped with a mercury sealed stirrer, a reflux condenser and a dropping funnel; openings to the air were protected by calcium chloride tubes. Although the spontaneously inflammable hydrides, such as silane, were among those prepared in the vacuum system, there is no reason why they could not be successfully made in the larger scale apparatus in an atmosphere of nitrogen.

In the description of preparations, quantities are given in terms of volumes only for materials measured in the gaseous state, and these volumes have been referred to standard conditions.

Materials.—The silicon tetrachloride was a commercial sample redistilled. Hexachlorodisilane was obtained from the General Electric Company through the courtesy of Dr. E. G. Rochow. The ethylchlorosilanes were Dow-Corning products; the other alkyl and aryl chlorosilanes were prepared by the Grignard procedure.¹⁰ J. T. Baker analyzed stannic chloride, and germanium tetrachloride, secured from A. D. Mackay Co., were used without further treatment. The methylchlorostannanes were prepared by the method of Kozeschkow,¹¹ but were not purified.⁸ In most cases, the lithium aluminum hydride was not isolated, but the diethyl ether solution obtained in the preparative procedure⁷ was used after the concentration of an aliquot had been determined. Anhydrous "peroxide-free" diethyl ether was employed; dioxane was dried over sodium hydride, and distilled.

Typical Examples of the Preparatory Procedure.—The following examples of the use of lithium aluminum hydride in preparing hydrogen compounds of fourth main group elements illustrate the procedures sufficiently well to make unnecessary recital of details in the cases of the nine additional compounds prepared. Of the latter, all but one have hitherto not been described, and physical constants and other data which characterize them are assembled in Table I.

The compounds, the preparation of which is to be described, were selected either because they illustrate some particular aspect of the procedure, or because the fact that they were previously known permits comparison of the new

(8) In the case of some of the tin compounds, a mixture of mono-, di- and tri-alkyl chlorostannanes was treated directly with lithium aluminum hydride, because the hydrogen compounds are easier to separate from each other than are the chloro derivatives.

(8a) Since this paper was submitted for publication, Whitmore, Pietrusza and Sommer, *THIS JOURNAL*, **69**, 2108 (1947), have described the preparation of dialkylsilanes, *e.g.*, diethylsilane, by a hydrogen-halogen exchange reaction. The product obtained by them had properties in fairly close agreement with those described herein.

(9) "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(10) Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904); Dilthey, *Ber.*, **37**, 319 (1904).

(11) Kozeschkow, *ibid.*, **66**, 1661 (1933).

TABLE I
 PHYSICAL PROPERTIES OF THE ORGANO-SILANES AND STANNANES

Formula	Vapor pressure equation constants ^a		Calcd. b. p., °C. (760 mm.)	Calcd. heat of vapn., cal./mole	Trouton const., cal./mole-deg.	Ref. index n_{D}^{20}	d_{4}^{20} , g./ml.	Mol. ref.		Mol. wt.		Silicon, %	
	A	B						Calcd.	Found	Calcd.	Found	Calcd.	Found
1 C ₂ H ₅ SiH ₃	-1189	7.471	-14	5450	21.0	60.1	60.5
2 (C ₂ H ₅) ₂ SiH ₂	-1619	7.836	54	7410	22.7	1.3918	0.6832	30.80	30.73	88.2	88.3	31.83	31.97
3 n-C ₃ H ₇ SiH ₃	-1390	7.582	23	6370	21.5	1.3759	.6434	26.43	26.44	74.2	73.7
4 (n-C ₃ H ₇) ₂ SiH ₂	-1867	7.738	111	8550	22.2	1.4112	.7194	40.06	40.13	116.2	117.1	24.14	24.15
5 n-C ₄ H ₉ SiH ₃	-1603	7.765	55	7340	22.4	1.3929	.6764	31.06	31.11	88.2	...	31.98	31.83
6 C ₆ H ₅ SiH ₃	-1814	7.496	120	8310	21.1	1.5125	.8681	36.99	37.03	108.2	...	26.06	25.94
7 CH ₃ SnH ₃	-1255	7.475	0	5750	21.0	136.7	135.9
8 (CH ₃) ₂ SnH ₂	-1482	7.697	35	6790	22.1	1.4480	1.4766	...	36.17	150.8	150.4
9 (CH ₃) ₃ SnH ^b	-1581	7.641	59	7240	21.8	164.8	164.0

^a Constants for the equation $\log p = -A/T + B$. ^b Kraus and Greer¹⁸ reported a b. p. of 60°.

reaction with those formerly available. The first four of the following preparations were carried out in the vacuum system; the remainder in the larger scale apparatus. In several instances the results obtained when lithium hydride replaced the lithium aluminum hydride are also described.

(a) **Silane.**—A solution of 0.348 g. (9.19 mmoles.) of lithium aluminum hydride in 12.5 g. of diethyl ether was placed in a reaction vessel connected with the vacuum system by a standard ground glass joint. Somewhat less than the equivalent amount of silicon tetrachloride, 175.2 cc. (7.82 mmoles.) was condensed into the flask after the latter had been cooled with liquid nitrogen and evacuated. The mixture was allowed to warm slowly to about 0°, at which temperature rapid evolution of gas and the formation of a white precipitate occurred.

The volatile material was fractionated through an isopentane bath (-159°) and the silane collected at liquid nitrogen temperature. A 99% yield (175.0 cc.), based on the amount of silicon tetrachloride used, was obtained. The molecular weight of the product was 31.9 (calcd. 32.1), the vapor tension at -111.9° was 781 mm., or somewhat higher than the 760 mm. value reported by Stock and Somieski.²

Silicon tetrachloride also reacts with lithium hydride in the presence of ether to produce silane, but the reaction is much slower than the corresponding one with the aluminum compound, and the best yield (89%) was obtained only when a three to four-fold excess of the simple hydride was used.

(b) **Disilane.**—This preparation illustrates a slight modification of the procedure just described in that the solution of lithium aluminum hydride in diethyl ether was slowly added at 0° *in vacuo* to an ether solution of hexachlorodisilane. The resulting disilane was passed through a -100° bath and collected at -130°. A small amount of monosilane was also obtained, probably because of slight contamination of the hexachloride with the tetrachloride of silicon. A yield of 87% of disilane (based on the quantity of chloride used) was obtained when a 15% excess of the lithium aluminum hydride was used. The molecular weight of the product was 62.4 (calcd. 62.2), and the vapor tensions at four temperatures agree with the values of Stock and Somieski.²

(c) **Germane.**—Germanium tetrachloride (125.0 cc. gas, or 5.5 mmoles.) was distilled in the vacuum system into a flask containing a liquid nitrogen cooled solution of 0.388 g. (10.2 mmoles.) of lithium aluminum hydride in 4.7 g. of ether. The excess of the lithium compound was unquestionably larger than necessary. The reaction proceeded smoothly as the mixture warmed to room temperature. The germane, separated from ether by fractional condensation through a -111.9° bath, had a vapor tension of 182 mm. at that temperature and of 8 mm. at -146°. The molecular weight was 76.8 (calcd., 76.6)

(12) Paneth and Rabinowitsch, *Ber.*, **58**, 1143 (1925), reported vapor tensions of 191 and 8 mm., respectively, at these temperatures.

and the yield (34.8 cc.) of germane corresponded to 27.7% of the chloride used. Formation of germanium was probably responsible for the small yield; no efforts were made to ascertain whether alteration of temperature or concentration would cause improvement.

(d) **Stannane.**—Stannic chloride (0.746 g., or 2.86 mmoles.) was distilled *in vacuo* into a reaction vessel attached to the vacuum system, and was solidified in a liquid nitrogen bath. After admitting gaseous nitrogen to the apparatus, a solution of 0.470 g. (12.4 mmoles.) of lithium aluminum hydride in 7 g. of diethyl ether was added. The mixture was allowed to warm without stirring. At about -30° the reaction proceeded vigorously. Volatile material was removed from the reaction zone at ten-minute intervals. The mixture thus removed was immediately condensed and solidified in a liquid nitrogen bath. After one hour the volatile material seemed to consist entirely of ether, and the residue in the vessel was a black solid, probably containing finely divided tin, suspended in residual ether.

The volatile materials were fractionated through a -111.9° bath several times. The gas not condensed thereby had a vapor tension of 18.5 mm. at -111.9° and 182 mm. at -80°, values which agree with the vapor tensions previously reported for stannane.¹³ The yield was 13.1 cc. or 20.4%. After standing for twelve hours at room temperature, the stannane had completely decomposed with the formation of a tin mirror on the walls of the vacuum line. This rate of decomposition is considerably greater than was described by Paneth, Haken and Rabinowitsch.¹³ These authors, however, point out that rough spots on glass surfaces initiate decomposition, which is further accelerated by impurities (*e. g.*, metals), as well as autocatalytically by tin itself. Since we took no precautions to avoid roughnesses in the glass apparatus, or to prevent contamination with the mercury usually present in vacuum systems such as those we employed, the somewhat more rapid decomposition of the product is not surprising. Attention should be called to the highly poisonous character of stannane.¹⁴

Use of lithium hydride in place of lithium aluminum hydride produced only traces of stannane, less than 1% of the quantity theoretically obtainable.

(e) **Di-n-propylsilane.**—To a solution of 10.0 g. (0.264 mole) of lithium aluminum hydride in 22.5 g. of diethyl ether, contained in the large scale apparatus, which had previously been flushed with nitrogen, 77.8 g. (0.421 mole) of di-n-propyldichlorosilane was added with constant stirring at a rate to keep the mixture refluxing gently. After completion of the addition, the mixture was maintained at refluxing temperature for one hour, and was then filtered. Most of the volatile material was distilled from the filtrate at atmospheric pressure until the temperature of the vapor reached 110°; the remaining portion was removed at 70° and 1 mm. pressure. The distillate was

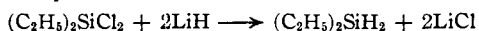
(13) Paneth, Haken and Rabinowitsch, *ibid.*, **57**, 1898 (1924).

(14) Paneth and Joachimoglu, *ibid.*, **57B**, 1925 (1924).

fractionated to obtain 39.1 g. (80% yield) of di-*n*-propylsilane, b. p. 110–112° (uncor.).

(f) **Diethylsilane.**—Diethylsilane has been prepared in the vacuum system by the reaction between the corresponding chloro derivative and lithium aluminum hydride, but the preparative procedure involves no features different from those described in other cases and need not be described. The reaction between diethyldichlorosilane and lithium hydride, on the other hand, is of interest in that it permits a comparison of the behavior of this hydride with sodium hydride. It is to be noted that the preparation of alkyl silanes through the use of lithium hydride requires higher temperatures than when the aluminum compound is employed; for this reason dioxane was the solvent used.

A suspension of 18.0 g. (2.26 moles) of lithium hydride in 250 g. of anhydrous dioxane was heated to reflux temperature in the larger scale apparatus which had been flushed out with nitrogen. Diethyldichlorosilane was then added dropwise until about 10 g. of the latter had been added. Refluxing was continued until definite evidence of reaction was noticed; the mixture was then rapidly cooled with an ice-bath, since the reaction is likely to become so vigorous that the mixture may be ejected into and out of the condenser. Thereafter further addition of the chloro derivative was continued at a rate to keep the mixture refluxing gently. After the total quantity of the reagent, 157 g. (1.00 mole), had been added, the mixture was maintained at gentle reflux for another hour. The volatile material was distilled from the reaction vessel and fractionated to obtain 58.3 g. (0.66 mole) of diethylsilane, b. p. 53–57° (uncor.). The yield thus was 66% of that expected from the reaction.



When diethyldichlorosilane (16 g. or 0.10 mole) was treated in similar fashion with 14 g. (0.58 mole) of sodium hydride suspended in 200 g. of dioxane, there was no evidence of reaction, even after the mixture had been refluxed for several hours and had been allowed to stand overnight. To the mixture 44 g. (0.33 mole) of aluminum chloride was added, and refluxing was again continued for several hours. The resulting mixture was then distilled; the fraction boiling between 60 and 100°, at which temperature diethylsilane should all have been removed, was collected and amounted to about 30 g. This product was refractionated through a Vigreux column to give 4 g. of a sample boiling between 50 and 55°. After re purification of the material in the vacuum system, a 2 g. (0.023 mole) sample having a molecular weight of 88.8 (calcd. 88.2) was isolated. The yield was only 23%, but it is possible that longer refluxing of the mixture might have brought about an improvement.

The influence of aluminum chloride on the reaction indicates that sodium aluminum hydride is formed as an intermediate in the reaction. This compound has now been prepared in quantity and isolated, as will be described in a later paper.

(g) **Dimethylstannane.**—The product obtained by the interaction of 60 g. (0.33 mole) of tetramethyltin and 87 g. (0.33 mole) of tin tetrachloride according to the method already mentioned¹¹ was melted. It was gradually added without further purification⁸ to a suspension of 12 g. (0.316 mole) of lithium aluminum hydride in 250 g. of dioxane at 15° in the large scale apparatus. After all of the chloro derivative had been added, the temperature was raised to 25°, and there maintained for one hour. The volatile material was distilled from the reaction vessel at room temperature and 10 mm. pressure. The distillate, originally collected at liquid nitrogen temperature, was redistilled through a small, vacuum jacketed Vigreux column. A 72-g. fraction (72% yield) of crude dimethylstannane of b. p. 33–40° was collected.

No dimethylstannane was obtained when lithium hydride was used in place of the aluminum compound.

Physical Properties of Organo-silanes and Stannanes.—Six alkyl or arylsilanes and three alkylstannanes, of which all but trimethylstannane are described for the first time¹⁵

herein, are listed in Table I with some of their physical properties. All of the compounds were carefully fractionated before the measurements were made; the data given are in themselves criteria of the purity of the samples. Molecular weight determinations were made by the vapor density method with an accuracy of about 1%. The equations of the type, $\log p = -A/T + B$, for the vapor pressure curves were derived from five or more points covering the range between 10 and 760 mm. The values found conform to the equations with an average error which, for any one compound, did not exceed 1.1%. The normal boiling points, the heats of vaporization, and the Trouton constants were calculated from the empirical equations. Refractive indices were determined by means of an Abbe type refractometer with a precision of about ± 0.0002 unit. The densities were measured with a precision of ± 0.0005 g./ml. The temperature was controlled in all measurements of refractive indices and densities to $\pm 0.05^\circ$. Molecular refractions were calculated by the system of organosilicon bond refractions developed by Warrick.¹⁵ The observed refractions agreed almost equally well with values calculated according to Sauer.¹⁶ In the analyses, silicon was determined as dioxide after fusion of the silane derivatives with sodium peroxide.

Chemical Properties of the Organo-silanes and Stannanes.—The properties of the new silane derivatives are, in general, like those of the methyl silanes described by Stock and Somieski.¹⁷ All of the new organo-silanes are liquids or gases at room temperature, not spontaneously inflammable in air. They react very slowly with water and somewhat more rapidly with aqueous alkali. They are soluble in solvents such as diethyl ether or benzene. No measurable decomposition has been noticed in samples which have stood for over a year *in vacuo* in glass tubes.

The methylstannanes are less stable than the alkylsilanes, although considerably more stable than stannane itself. A few observations confirmed the hypothesis of Kraus and Greer¹⁸ that stability in these hydrides increases with the number of alkyl groups attached to the metal. Monomethylstannane formed a slight metallic deposit in a glass tube after standing a few hours at room temperature, although the amount of material decomposed was small. In sixteen days the decomposition was less than 2%. Dimethylstannane did not undergo any appreciable change in three weeks at room temperature in a glass tube, but at the end of three months, 15% had decomposed. Trimethylstannane did not change in three months. At temperatures higher than 25° the rate of decomposition increased markedly, and for this reason the preparation and purification of these stannanes were carried out at temperatures as low as conveniently possible. The products of decomposition were not studied; it was observed, however, that disproportionation did not occur.

Like the alkylsilanes, the alkylstannanes are not spontaneously inflammable in air. They react slowly with water to form white gels.

Acknowledgment.—It gives us pleasure to acknowledge the financial support of the Naval Research Laboratory in this investigation.

Summary

1. The interaction of lithium aluminum hydride with the appropriate halides of silicon, of germanium and of tin in the presence of ethers has been shown to be a convenient, efficient method for preparing the corresponding hydrides and their alkyl or aryl derivatives.

2. In some instances, though not in all, lithium

(15) Warrick, *THIS JOURNAL*, **68**, 2455 (1946).

(16) Sauer, *ibid.*, **68**, 954 (1946).

(17) Stock and Somieski, *Ber.*, **52**, 605 (1919).

(18) Kraus and Greer, *THIS JOURNAL*, **41**, 2629 (1922).

hydride, suspended in ethers, may be used in place of lithium aluminum hydride, but the latter in general reacts more rapidly and at lower temperatures to give better yields.

3. In the one instance investigated, sodium hydride did not undergo the analogous reaction un-

less aluminum chloride was added to the reaction mixture.

4. Physical and chemical properties of six new organosilanes and two new methyl stannanes are briefly described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anhydrous Lower Bromides of Hafnium

BY WALTER C. SCHUMB AND CLARENCE K. MOREHOUSE

Although the remarkably close resemblance in properties of hafnium to zirconium is commonly recognized, the existence of lower valence halides of hafnium, analogous to the tri- and divalent halides of zirconium, seems not to have been established. Employing procedures similar to those used by R. C. Young¹ in preparing zirconium tribromide and dibromide, we have been able to demonstrate that hafnium forms analogous lower valence compounds with closely similar properties.

Hafnium dioxide obtained from a commercial laboratory was found to contain 99.9% of combined hafnium and zirconium oxides by the selenious acid method,² and the hafnium to zirconium ratio in the mixed oxides was determined by the procedure of Claassen,³ later modified by Schumb and Pittman.⁴ In this manner the hafnium oxide was found to contain 97.2% hafnium dioxide and the rest essentially zirconium dioxide. A qualitative spectroscopic analysis confirmed these conclusions.

Experimental

Preparation of Hafnium Tetrabromide.—Five-gram portions of the hafnium dioxide were converted into the tetrabromide by the method described by Hönigschmid, Zintl and Gonzalez,⁵ with slight modifications, in which the oxide, in an intimate mixture with 15 g. of dry sugar charcoal, was heated in a graphite boat in a Pyrex apparatus at 700–800° in an atmosphere of pure nitrogen saturated with bromine vapor. The product was thrice re-sublimed and sealed off in a glass tube in a dry nitrogen atmosphere. Eleven grams of the tetrabromide was obtained from each five grams of oxide; the purity of the product was not less than 95.5% hafnium tetrabromide. It was a white, crystalline solid, which sublimed readily at 400° at ordinary pressure, or at 280° at 1 mm. pressure. It is estimated that not over 25° separate the sublimation temperatures of hafnium and zirconium tetrabromides.

Reduction of the Tetrabromide.—The sublimed, anhydrous hafnium tetrabromide was subsequently reduced to the tribromide in the apparatus shown in the accompanying figure, which consisted essentially of a 19 mm. "hot-cold" tube of Vycor glass, sealed at each end to standard taper quartz joints and thence connected to the rest of the

apparatus, which was made of Pyrex glass. A closely-wound aluminum coil (99.9% aluminum), 5-cm. long, was placed with one end 3 cm. from the end of the cold element of the "hot-cold" tube. The sample of hafnium tetrabromide, introduced through joint C, with as little access to the air as possible, was shaken down to a position between G and S. When the apparatus was filled with dry, oxygen-free hydrogen, the tetrabromide was slowly sublimed, in the hydrogen atmosphere, through a filter plug, S, of glass wool, and thus over the aluminum coil, T, which had been heated to 600°, as indicated by a chromel-alumel thermocouple placed outside the Vycor tube in the furnace, U.

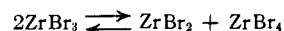
A blue-black mass collected on the end of the "cold finger," consisting of aluminum bromide and hafnium tri- and tetra-bromides. Twenty to thirty minutes were required for this operation, during which the temperature of the reaction tube remained at 600–650°, or just below the melting point of the aluminum wire. After the volatilization of the tetrabromide had been completed, the furnace was cooled to room temperature and pure, dry nitrogen was substituted for the hydrogen in the apparatus.

The rest of the procedure followed closely in principle that previously described in the preparation of zirconium tribromide: the transfer of the products from the "cold finger" to tube, E, through constriction, J; sealing at J; complete sublimation *in vacuo* of aluminum bromide and unchanged hafnium tetrabromide over a period of twelve to fifteen hours at a maximum temperature of 290°; finally transfer of the blue-black tribromide to the small side-tube, K, and sealing off in an atmosphere of nitrogen.

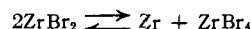
An analysis of a sample of the product thus obtained gave 42.02% Hf; 60.54% Br; corresponding to an atomic ratio of Br: Hf = 3.2.

In the preparation of this substance, and in its properties, so far as they were examined, the phenomena observed closely paralleled those reported for zirconium tribromide. The blue-black solid reacted immediately with water with evolution of hydrogen; ammonium hydroxide added to this solution precipitated hydrous hafnium dioxide.

A sample of the tribromide contained in an evacuated 8-mm. Pyrex tube, 16 cm. long, was heated very gradually in an electric sleeve furnace so as to observe its decomposition at elevated temperatures. It is well known that zirconium tribromide on heating disproportionates into di- and tetrabromide



the white tetrabromide sublimes leaving the non-volatile, black dibromide. Similarly, at higher temperatures the dibromide decomposes, forming zirconium metal and the tetrabromide



In precisely analogous manner, the sample of hafnium tribromide, heated *in vacuo* to slightly above 300° gave a deposit of white tetrabromide at the cold end of the reaction tube and the color of the residue became jet black. The

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