

tetrahedral nature of silicon and the plentiful supply of coordination ions and molecules is considered. Then of the theoretically possible quartz species listed in Table III, SiO_3 , Si_2O_7 and $\text{Si}_n\text{O}_{3n+1}$ where n is greater than 2, would be eliminated from consideration. SiO_4 formed by either reaction (b) or (c) could account for all of the variables tested experimentally. The reversal of equation (a) could also account for all of the variables. However, since crystallization and growth can be accomplished by reaction (b) or (c) in systems (3) not containing F^- or SiF_6^{--} , reaction (a) is necessary only to provide the hydroxide ions in order that the silica may be converted to α -quartz *via* reactions (b) or (c).

Weitz, Franck and Schuchard¹⁰ have reported that orthosilicic acid occurs in river water up to 50 p.p.m. and in hot springs and geysers of New Zealand up to 1000 p.p.m. because of the high temperatures. The above suggested mechanisms postulating salts of orthosilicic acid as the interim compound between glass and α -quartz suggests that natural quartz may be formed by the same mechanism.

Acknowledgments.—The authors wish to acknowledge the help of David R. Swaney and Neil R. Fetter, who acted as technical assistants in this program.

(10) E. Weitz, H. Franck and M. Schuchard, *Chem.-Ztg.*, **74**, 256 (1951).

YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation and Characterization of Some Pure Organobromosilanes

BY PATRICK A. MCCUSKER AND EDWARD L. REILLY

RECEIVED DECEMBER 8, 1952

Phenyldibromosilane, phenylbromosilane and *p*-methoxyphenyltribromosilane, previously unreported, have been prepared, purified and characterized. Ethyltribromosilane and diethyldibromosilane have been purified and characterized, and some other organobromosilanes further characterized. A new reaction in silicon chemistry has been observed in the preparation of triphenylbromosilane by the reaction of silicon tetrabromide with triphenylsilanol. Replacement of chlorine by bromine, accompanied by extensive cleavage of the silicon-to-carbon bond, was observed to occur by the reaction of aluminum bromide on organochlorosilanes. With hydrogen bromide alone no replacement was observed.

For the purpose of obtaining electric moment data, which are to be reported in another paper,¹ a number of pure organobromosilanes were required. Some of the compounds obtained are new and further physical data were obtained for several others. In the present paper the new data are reported and some reactions of organohalogenosilanes are discussed.

Experimental

Trimethylchlorosilane, dimethyldichlorosilane, diethyldichlorosilane from the Dow Corning Corporation, diphenyldichlorosilane from Anderson Laboratories, Inc., Adrian, Michigan, phenyltrichlorosilane and hexamethyldisiloxane from the Linde Air Products Company, and *p*-bromanisole from the Matheson Company, were used as received without further purification. Triphenylchlorosilane from Anderson Laboratories, Inc., was vacuum distilled before use. Silicon tetrabromide was prepared and purified as previously described.²

The refractive indices of the compounds were measured with a calibrated Abbé refractometer at 25.0°. The densities were determined in an 8-ml. Ostwald pycnometer. Melting points, below room temperature, were determined in an apparatus previously described by Kennard and McCusker.²

The reaction apparatus consisted of a 3-necked flask equipped with sealed stirrer and reflux condenser and protected from atmospheric moisture. The products, with the exception of triphenylbromosilane, were purified by repeated fractional distillations through a 53" glass-helix packed column of about 15 theoretical plates. Small middle cuts were used for measurements. Analyses were carried out by titrating aqueous suspensions of the organobromosilanes with standard base. Molar refractions were calculated from the data of Warrick.³ The purity of the fractions used for measurements of physical constants was established by constancy of boiling point and melting point.

Methyltribromosilane, Dimethylbromosilane, Ethyltribromosilane and *p*-Methoxyphenyltribromosilane.—These compounds were prepared by the dropwise addition of an ether solution of 1 mole of Grignard reagent to an ether solution containing a 5% excess of silicon tetrabromide, at a rate sufficient to maintain reflux. After the reaction was complete separation into two layers occurred. The lower layer consisted essentially of magnesium bromide etherate and was discarded. Distillation of the upper layers was complicated by the separation of large quantities of solid magnesium bromide etherate after the ether had been distilled off. In later preparations this mechanical difficulty was greatly reduced by the addition of dry carbon tetrachloride to the liquid mixture, to cause precipitation of solid magnesium bromide etherate. The liquid was then decanted and fractionally distilled. Data on purified fractions are listed in Table I.

Diethyldibromosilane, Triethylbromosilane, Phenyltribromosilane and Diphenyldibromosilane.—These compounds were prepared in one mole quantities by the bromination of partially substituted silanes obtained by the reduction of the chloro compounds with lithium aluminum hydride.

The reductions of diethyldichlorosilane and triethylchlorosilane were performed according to the procedure described by Finholt, *et al.*,⁴ for the reduction of diethyldichlorosilane. The reductions of phenyltrichlorosilane and diphenyldichlorosilane were performed according to the procedure described by Benkeser, Landesman and Foster.⁵ The brominations were carried out according to the procedure described by Kraus and Nelson⁶ for the bromination of triethylsilane and by Nebergall⁷ for the bromination of phenylsilane. Properties of purified samples of these compounds are listed in Table I.

Phenylbromosilane and Phenyldibromosilane.—To 0.3 mole of phenylsilane dissolved in 120 ml. of ethyl bromide was added dropwise over a two-hour period a solution of 0.9 gram atoms of bromine in 120 ml. of ethyl bromide. The

(1) E. L. Reilly, C. Curran and P. A. McCusker, *THIS JOURNAL*, to be published.

(2) M. S. Kennard and P. A. McCusker, *ibid.*, **70**, 1039 (1948).

(3) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(4) A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2696 (1947).

(5) R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

(6) C. A. Kraus and W. K. Nelson, *ibid.*, **66**, 195 (1934).

(7) W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

TABLE I

Compound	$^{\circ}\text{C.}$ B.p.,	Mm.	M.p., $^{\circ}\text{C.}$	n_D^{25}	d_4^{25}	MR_D obsd.	MR_D calcd.	Br obsd., %	Br calcd. %
CH_3SiBr_3	131.2–131.3	744	–28.4–28.1 –39.5–39.2 ^a	1.5152	2.2130	38.37	38.17	84.5	84.8
$(\text{CH}_3)_2\text{SiBr}_2$	110.2–110.3	748	–58.5–58.0 –62.5–62.0 ^a	1.4696	1.6952	35.88	35.54	73.1	73.4
$(\text{CH}_3)_3\text{SiBr}$	77.3	735	–43.5–43.2	1.4211	1.1727	33.00	32.91	52.0	52.2
$\text{C}_2\text{H}_5\text{SiBr}_3^b$	160.1–160.2	750	–80.0–0.2	1.5155	2.0671	43.11	42.80	80.5	80.8
$(\text{C}_2\text{H}_5)_2\text{SiBr}_2^b$	166.2–166.3	744	–73.0–72.5	1.4850	1.5767	44.71	44.80	64.8	65.0
$(\text{C}_2\text{H}_5)_3\text{SiBr}$	163.2–163.3	737	–49.7–49.3	1.4544	1.1335	46.69	46.80	41.0	41.0
$\text{C}_6\text{H}_5\text{SiBr}_3$	178.3	80	–21.0–20.8	1.5970	2.0228	58.12	57.99	69.7	69.6
$(\text{C}_6\text{H}_5)_2\text{SiBr}_2$	192.2–192.3	1	+3.8–4.0 –1.0–0.8 ^a	1.6179	1.5869	75.41	75.18	46.7	46.8
$(\text{C}_6\text{H}_5)_3\text{SiBr}$	210–211	1	120–121				92.37	23.2	23.6
$\text{C}_6\text{H}_5\text{SiH}_2\text{Br}^b$	118.0–118.2	70	–30.0–29.8	1.5555	1.3632	44.09	43.99	42.5	42.8
$\text{C}_6\text{H}_5\text{SiHBr}_2^b$	146.7–147.0	58	–51.0–50.6	1.5778	1.7293	51.05	50.99	60.0	60.2
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{SiBr}_3^b$	147.0	1	+21.0–22.0	1.5958	1.9089	66.82	64.34	63.5	64.0

^a Metastable form. ^b New or previously unpurified compounds.

solution was refluxed until no more hydrogen bromide evolved and was then fractionally distilled. Pure fractions amounting to 0.1 mole of phenylbromosilane and 0.075 mole of phenyldibromosilane were obtained for a total yield of 60%. Properties of these compounds are listed in Table I.

Trimethylbromosilane.—This compound was prepared by a modification of the method of Gilliam, Meals and Sauer.⁸ The reaction was carried out by dropwise addition at room temperature of two moles of phosphorus tribromide to 1 mole of hexamethyldisiloxane followed by stirring for a two-hour period, and refluxing for a further 45-minute period. Separation of red phosphorus occurred during the reflux period. Distillation yielded 1.6 moles (80%) of impure trimethylbromosilane. A purified fraction, with properties listed in Table I, was obtained by repeated fractional distillations.

Triphenylbromosilane.—Triphenylsilanol was prepared by the hydrolysis of triphenylchlorosilane and tested for the absence of chlorine. To 0.3 mole of triphenylsilanol, dissolved in 200 ml. of ether, was added dropwise 0.15 mole of silicon tetrabromide. The heat of reaction was sufficient to maintain gentle reflux. During the addition of the silicon tetrabromide separation of solid occurred. The separated solid was dissolved by the addition of a further quantity of 200 ml. of ether and 200 ml. of benzene, leaving only a cloudiness due to silica formed in the reaction. The mixture was allowed to stand overnight and the settled silica was removed by filtration in an atmosphere of dry nitrogen. After removal of the solvents by distillation the residue was vacuum distilled, to give 0.15 mole (50% yield) of impure triphenylbromosilane. Repeated distillations in a Vigreux column gave a highly purified fraction whose properties are listed in Table I.

Attempted Reaction of Hydrogen Bromide with Trimethylchlorosilane.—Hydrogen bromide was bubbled through 25 g. of trimethylchlorosilane for a period of one-half hour. No evidence of reaction was observed and the starting material was recovered completely on distillation. Repetition of the procedure, using dimethyldichlorosilane with the addition of 5 g. of aluminum bromide, gave a similar result.

Reaction of Trimethylchlorosilane with Aluminum Bromide.—To 0.2 mole of freshly distilled aluminum bromide was added dropwise 0.5 mole of trimethylchlorosilane. A slight evolution of heat was observed. The reaction mixture was refluxed for four hours and then fractionally distilled. A number of fractions boiling between 57 and 101 $^{\circ}$ were collected, none of which contained any appreciable amount of trimethylbromosilane. The highest boiling fraction consisted of 3 g. of liquid distilling at 108.2–109.5 $^{\circ}$. This fraction, which had a boiling point close to the value for dimethyldibromosilane (110 $^{\circ}$), was analyzed and found to contain 71.0% bromine. The theoretical for dimethyldibromosilane is 73.4% bromine.

Discussion

The Grignard reaction has been used in only one

previous instance⁹ for the preparation of an organobromosilane. Our results indicate that the reaction of Grignard reagents with silicon tetrabromide is suitable in general for the preparation of mono- and dialkylbromosilanes where the boiling points of the products are not too close to one another. Reaction occurs readily as indicated by Anderson⁹ and contrary to the report of Wilkens, Brown and Stevens.¹⁰ Even in the case of the ethylbromosilanes, whose boiling points lie close together, ethyltribromosilane was readily obtained pure by the use of the Grignard reaction.

Because of anticipated separation difficulties some of the ethyl and phenyl bromosilanes were prepared by bromination of purified partially-substituted ethyl- and phenylsilanes. In the preparation of the partially substituted silanes direct volatilization of the low boiling compounds from the heated reaction mixtures occurred without difficulty. Attempts to separate the higher boiling silanes, phenyl- and diphenylsilane, from the reaction mixtures by volatilization led to decomposition and disproportionation and the liberation of spontaneously inflammable gases. It appears that, at the temperature necessary to volatilize phenyl- and diphenylsilane, the reaction products, lithium chloride and aluminum chloride, react with the arylsilanes to cause rapid decomposition and disproportionation. When the reaction mixtures were hydrolyzed with dilute hydrochloric acid,⁵ however, the lithium and aluminum chlorides were removed in the water layer and subsequent distillations occurred smoothly.

An attempt to effect the partial reduction of ethyltribromosilane with lithium aluminum hydride was unsuccessful. Addition of lithium aluminum hydride solution in ether to an excess of ethyltribromosilane gave no partially brominated silanes. It appears that under our experimental conditions, even in an excess of ethyltribromosilane, partially reduced silanes are preferentially attacked by lithium aluminum hydride to give completely reduced ethylsilane. In other attempts to partially brominate ethylsilane, in solution in ethyl bromide at –30 $^{\circ}$

(9) H. H. Anderson, *ibid.*, **73**, 5804 (1951).

(8) W. F. Gilliam, R. N. Meals and R. O. Sauer, *THIS JOURNAL*, **68**, 1161 (1946).

(10) C. J. Wilkens, N. P. H. Brown and A. D. Stevens, *J. Chem. Soc.*, 163 (1950).

and in a nitrogen atmosphere, explosions occurred which shattered the apparatus and caused fires. Apparently a vapor phase reaction between ethylsilane and bromine in diffuse daylight can occur explosively even at low temperatures.

The reaction of triphenylsilanol with silicon tetrabromide, used to prepare triphenylbromosilane, is a new reaction in silicon chemistry. The reaction occurred readily on simple mixing of the reactants in ether solution and gave good yields of product. While the generality of this reaction remains to be established it is interesting to note that similar reactions have been reported in carbon¹¹ and in boron chemistry.¹²

The failure of hydrogen bromide to cause replacement of chlorine by bromine in the chlorosilanes points up a difference between silicon halides and titanium halides. Titanium tetrachloride is readily converted to the tetrabromide by reaction with hydrogen bromide. The reaction of alumi-

num bromide on trimethylchlorosilane gave rise to a number of compounds which could not be separated by fractional distillation. The fact that one of the products was probably dimethyldibromosilane indicates that the reaction involves cleavage of the silicon-carbon bond as well as replacement of chlorine by bromine.

In the determination of the melting points of these compounds several were found to solidify readily in a metastable form, as indicated in Table I. The method² used for the melting point determinations is favorable for the separation and observation of metastable forms. A similar metastable form was previously observed² for silicon tetrabromide.

The calculated and observed molar refractions are in good agreement except for the *p*-methoxyphenyltribromosilane. In the case of this compound an exaltation of molar refraction results from electronic interaction between the *p*-methoxyphenyl and tribromosilyl groups.

NOTRE DAME, INDIANA

(11) W. Dilthey, *Ber.*, **36**, 923 (1903).

(12) A. B. Burg, *THIS JOURNAL*, **62**, 2232 (1940).

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Dialkylsilanediols¹

By PHILIP D. GEORGE, LEO H. SOMMER AND FRANK C. WHITMORE²

RECEIVED NOVEMBER 1, 1952

Diethylsilanediol, di-*n*-propylsilanediol and di-*n*-butylsilanediol have been synthesized, and their chemical and physical properties have been investigated. Methods are described for obtaining these labile compounds in good yields by hydrolysis of the corresponding dichlorosilanes. The diols are ordinary white solids, which are stable when pure; they exhibit typical silanol reactions.

Some years ago we reported³ the synthesis and some properties of diethylsilanediol. We now wish to give a more complete account of our work on dialkylsilanediols.⁴ While organosilanediols had been known for over forty years,⁵⁻⁷ no dialkylsilanediol had been reported. The non-isolation of this type compound had generally been attributed to rapidity of intermolecular condensation to form silicones.⁸ Hydrolysis studies on diethyl-

dichlorosilane had previously failed to give the diol.⁹

By careful control of conditions during the hydrolysis and the working up of the product we have prepared diethylsilanediol, di-*n*-propylsilanediol and di-*n*-butylsilanediol in good yield from the corresponding dichlorosilanes. Key features of the synthesis involve employment of dilute solutions, low temperatures and short reaction times. Best results were obtained with dilute alkali or saturated sodium bicarbonate solution; however, other media such as concentrated sodium chloride solution may also be used. One of the preferred methods is exemplified by the following synthesis of diethylsilanediol.

A 6% solution of diethyldichlorosilane in dry ether was added during five minutes with stirring to the theoretical amount of 1.5 *N* alkali at 0°. Immediate separation of the ether layer and ether extraction of the water layer were followed by drying over anhydrous potassium carbonate for a short time in the cold. The ether solution of the product was then concentrated at low temperature. Addition of an equal volume of pentane followed by cooling gave a 65% yield of diethylsilanediol. Similarly di-*n*-propylsilanediol and di-*n*-butylsilane-

(1) Paper 32 in a series on organosilicon chemistry; for paper 31, see *THIS JOURNAL*, **73**, 882 (1951).

(2) Deceased.

(3) (a) Communication to the Editor: P. D. George, L. H. Sommer and F. C. Whitmore, *THIS JOURNAL*, **68**, 344 (1946); (b) P. D. George, paper presented before the Division of Organic Chemistry at the 109th Meeting of the American Chemical Society at Atlantic City, N. J., April 10, 1946.

(4) Taken from a dissertation submitted by P. D. George to the Graduate School of the Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree, February, 1947.

(5) For references to diphenylsilanediol see C. A. Burkhard, *THIS JOURNAL*, **67**, 2173 (1945).

(6) For the preparation of the phenylethyl, benzylethyl, benzylphenyl and dibenzyl compounds see R. Robinson and F. S. Kipping, *J. Chem. Soc.*, **101**, 2148 (1912); R. Robinson and F. S. Kipping, *ibid.*, **101**, 2156 (1912).

(7) The isolation of dicyclohexylsilanediol in small yield as an unexpected by-product, N. W. Cusa and F. S. Kipping, *ibid.*, **121**, 2205 (1932), had been considered somewhat questionable until it was recently confirmed, C. Eaborn, *ibid.*, **141**, 2840 (1952).

(8) See for example E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger Geb., Berlin, 1937, p. 284; E. G. Rochow, *Chem. Eng. News*, **23**, 614 (1945).

(9) G. Martin and F. S. Kipping, *J. Chem. Soc.*, **95**, 313 (1909); J. F. Hyde and R. C. De Long, *THIS JOURNAL*, **63**, 1194 (1941); T. Alfrey, F. J. Honn and H. Mark, *J. Polymer Sci.*, **1**, 102 (1946).