[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

p-Phenylenedisilanes[1]

L. W. BREED, WILLIAM J. HAGGERTY, JR., AND FRED BAIOCCHI

Received January 6, 1960

A series of *p*-phenylenedisilanes with two or four silicon-attached alkoxy groups has been prepared. When these compounds were prepared through the intermediate bifunctional Grignard reagents, the over-all yield was determined by the choice of solvent, the presence of various reactants which can act as cosolvents, and the reactivity of the condensing silane. Methods for preparing the following *p*-phenylenedisilanes are discussed: *p*-Phenylenebis(diethoxymethylsilane), *p*-phenylenebis(ethoxydimethylsilane), *p*-phenylenebis(ethoxymethylvinylsilane), *p*-phenylenebis(diethoxyvinylsilane), *p*-phenylenebis(*p*-chlorophenyldiethoxysilane), *p*-phenylenebis(*p*-anisyldiethoxysilane), *p*-phenylenebis(diethoxyphenylsilane), *p*-phenylenebis[diethoxy-*p*-(*N*,*N*-dimethylaminophenyl)silane], and 1-diethoxymethylsilyl-4-diethoxyphenylsilylbenzene.

Although a variety of totally alkylated or arylated derivatives of *p*-phenylenedisilane are described in the literature,[2-8] little is reported on the synthesis of *p*-phenylenedisilanes that can be hydrolyzed in aqueous media to yield hybrid arylenesiloxane polymers.

Condensation of trisubstituted silanes with benzene in the presence of aluminum trichloride or boron trichloride gave isomeric mixtures of the *meta* and *para* derivatives, particularly when the silane was present in large excess. The isolation of pure *p*-phenylenebis(trichlorosilane), *p*-phenylenebis(dichloromethylsilane,) and *m*-phenylenebis(trichlorosilane) from the crude reaction products has been described.[9-11]

p-Phenylenebis(chlorodimethylsilane) and *p*-phenylenebis(chlorodiphenylsilane) were obtained by Sveda from the Grignard reagent of *p*-dibromobenzene in ether and the corresponding chlorosilanes, but no yields were reported.[12,13] From triethoxymethylsilane and the same Grignard reagent, Gainer obtained 9% of *p*-phenylenebis(ethoxydimethylsilane) and 42% of *p*-bromophenyldiethoxymethylsilane.[14] Also, he condensed the Grignard reagent of *p*-bromophenyldimethylethoxysilane with triethoxymethylsilane to obtain 39% of 1-diethoxymethylsilyl-4-dimethylethoxysilylbenzene. Lewis prepared *p*-phenylenebis(ethoxydimethylsilane) from the Grignard reagent of *p*-dibromobenzene in ether and diethoxydimethylsilane. Although he did not report the yield of the pure material, repetition of the procedure in this laboratory gave a 31% yield of the phenylenedisilane. The synthesis of 1-trichlorosilyl-4-triethylsilylbenzene from *p*-triethylsilylphenylmagnesium bromide has also been reported.[2]

A series of *p*-phenylenedisilanes, each with two or four silicon-attached ethoxy groups, has been prepared (see Table I) in our laboratory. Because their preparation required the condensation of a bifunctional metallo-organic intermediate with a polyfunctional silane, reaction conditions were selected to avoid the formation of polymeric materials.

Grignard Syntheses. Yields of 30–40% of *p*-phenylene (diethoxymethylsilane) were obtained when the Grignard reagent of *p*-dibromobenzene was prepared in tetrahydrofuran, when this Grignard reagent was coupled with chlorodiethoxymethylsilane, and when the silane and bromide were added concomitantly to the magnesium.

The over-all yield of the various phenylenedisilanes from *p*-bromobenzene, as well as the identity of the by-products, was not limited by the ability of the dihalide to form the intermediate Grignard reagent, particularly when the dihalide and the silane are added concomitantly to the magnesium. The yield depended on factors that include the identity of the solvent, the presence of the various reactants that can act as cosolvents, and the reactivity of the condensing silane.

In ether the maximum yield of the Grignard reagent of *p*-dibromobenzene that may be expected is about 12%, unless entrainment procedures are used.[14-19] Also in ether, up to 70% of the mono-

(1) This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) G. Gruttner and M. Cauer, *Ber.*, **51**, 1283 (1918).

(3) H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

(4) H. A. Clark, U. S. Patent **2,268,242** (1953); Brit. **671,553** (1952).

(5) H. Gilman, B. J. Gaj, D. K. Aoki, M. V. George, O. R. Marrs, W. J. Trepka, and E. A. Zuech, WADC TR 53-426, Part VII, ASTIA Document No. 215,444.

(6) H. Gilman, A. G. Brook, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4531 (1953).

(7) H. A. Clark, U. S. Patent **2,507,514** (1950); Brit. **669,178** (1952).

(8) H. A. Clark, U. S. Patent **2,507,515** (1950); Brit. **669,179** (1952).

(9) A. J. Barry, U. S. Patent **2,557,931** (1951); Brit. **682,835** (1952).

(10) A. J. Barry, D. E. Hook, and L. De Pree, U. S. Patent **2,511,820** (1950); Brit. **635,645** (1950).

(11) L. De Pree, A. J. Barry, and D. E. Hook, U. S. Patent **2,580,159** (1951).

(12) M. Sveda, U. S. Patent **2,561,429** (1951).

(13) M. Sveda, U. S. Patent **2,562,000** (1951).

(14) G. C. Gainer, U. S. Patent **2,709,692** (1955).

(15) L. H. P. Weldon and C. C. Wilson, *J. Chem. Soc.*, 235, (1946).

(16) R. Quelet, *Bull. Soc. Chim.*, **41**, 933 (1927).

TABLE I

p-PHENYLENEDISILANES

Compound	Method of Preparation[a]	Yield, %
p-Phenylenebis(diethoxymethylsilane)	1. A and triethoxymethylsilane	11.5
	2. B and chlorodiethoxymethylsilane	
	a. Concomitant addition	33.3
	b. Normal addition	32–38
	3. *p*-Bromophenyldiethoxymethylsilane, chlorodiethoxymethylsilane, and sodium	27
1-Diethoxymethylsilyl-4-diethoxyphenylsilylbenzene	*p*-Bromophenyldiethoxymethylsilane, chlorodiethoxyphenylsilane, and sodium	6
p-Phenylenebis(ethoxydimethylsilane)	1. A and diethoxydimethylsilane	31
	2. B and chlorodiethoxymethylsilane	20
p-Phenylenebis(ethoxymethylvinylsilane)	B and diethoxymethylvinylsilane	9
p-Phenylenebis(diethoxyvinylsilane)	B and triethoxyvinylsilane	15
p-Phenylenebis(diethoxyphenylsilane)	B and chlorodiethoxyphenylsilane	
	a. Normal addition	29
	b. Concomitant addition	28
p-Phenylenebis(*p*-chlorophenyldiethoxysilane)	B and chloro(*p*-chlorophenyl)diethoxysilane	27
p-Phenylenebis(*p*-anisyldiethoxysilane)	B and *p*-anisylchlorodiethoxysilane	44
p-Phenylenebis[diethoxy-*p*-(*N*,*N*-dimethylaminophenyl)silane]	B and triethoxy-*p*-dimethylaminophenylsilane	44

[a] A = Grignard reagent of *p*-dibromobenzene in ether. B = Grignard reagent of *p*-dibromobenzene in tetrahydrofuran. Concomitant addition unless otherwise specified.

Grignard reagent is usually obtained. The reaction of *p*-dibromobenzene and magnesium in the presence of ethyl ether and diethoxydimethylsilanes gave, unexpectedly, about 30% of the *p*-phenylenebis(ethoxydimethylsilane), which was greater than the yield of the bifunctional Grignard reagent that is normally obtained in the absence of the silane. Substitution of the triethoxymethylsilane for diethoxydimethylsilane in the latter procedure gave the disilane in about the same proportion that would be predicted from the yield of the Grignard reagent formed in the absence of the silane. The cosolvent effect was apparently lost.

Although the conversion to the bifunctional Grignard reagent was higher in tetrahydrofuran,[20] the Grignard-tetrahydrofuran complex is less reactive toward alkoxysilanes than the Grignard-ethyl ether complex. When an attempt was made to react the bifunctional Grignard-tetrahydrofuran complex and triethoxymethylsilane, the complex was sufficiently stable that no condensation occurred. In tetrahydrofuran, it was necessary that the more reactive chlorodiethoxymethylsilane be substituted for the triethoxymethyl silane. With this change in the procedure, yields of 30–40% were obtained consistently in the preparation of *p*-phenylenebis(diethoxymethylsilane).

The presence of the chlorodiethoxymethylsilane did not materially affect the formation of the Grignard reagent. Similar yields were obtained when the silane was added concomitantly to the magnesium with the *p*-dibromobenzene or when the performed Grignard reagent was precipitated as the Grignard-tetrahydrofuran complex by external cooling, treated with the silane, and heated to effect condensation. In the latter procedure the reactivities of the various condensing groups permitted a mode of addition that would ordinarily be expected to yield only highly polymeric materials. This disilane was sufficiently stable against hydrolysis that the product could be worked up by pouring the reaction mixture over water.

The reactivity of the alkoxysilanes or the alkoxychlorosilanes was also increased by introducing groups into the condensing silane that could contribute a net increase in the electron density on silicon. Although triethoxymethylsilane and the phenylene-Grignard reagent failed to condense, diethoxymethylvinylsilane, whose structure is analogous to an allyl ether, gave a 9% yield of *p*-phenylenebis(ethoxymethylvinylsilane) and triethoxyvinylsilane gave 15% of the corresponding product.

Similarly, in the *p*-phenylenebis(diethoxyphenylsilane) series, substitution of a strong negative group *para* to silicon increased the yields, presumably through an increased reactivity of the silicon-attached chlorine. Yields of about 30% were obtained when chlorodiethoxyphenylsilane and chloro(*p*-chlorophenyl)diethoxysilane were condensed with the Grignard reagent of *p*-dibromobenzene in tetrahydrofuran. *p*-Anisylchlorodiethoxysilane gave 44% *p*-phenylenebis(*p*-anisyldiethoxysilane), and *p*-(triethoxysilyl)-*N*,*N*-dimethylamiline[21] gave 44% *p*-phenylenebis[diethoxy-*p*-(*N*,*N*-dimethylaminophenyl)silane]. The latter compounds are analogous to *p*-methoxy- and *p*-dimethylaminobenzyl derivatives in the carbon series.

(17) J. Pink, *J. Chem. Soc.*, **123**, 3418 (1923).
(18) Y. S. Zal'kind and P. V. Ragovina, *J. Russ. Phys. Chem. Soc.*, **59**, 1013 (1927).
(19) H. Gilman, H. J. Beaber, and H. L. Jones, *Rec. trav. chim.*, **48**, 597 (1929).
(20) D. R. Nielson and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 3081 (1957).

Aside from the improved yield, the Grignard-tetrahydrofuran procedure offers another advantage for the preparation of *p*-phenylenebis(diethoxymethylsilane). In ether, considerable unchanged *p*-dibromobenzene was recovered, as well as the *p*-bromophenyldiethoxymethylsilane. Avoiding the recovery of the solid and obtaining essentially a single volatile reaction product permitted the use of simpler distillation procedures. The chief products other than the *p*-phenylenedisilane were nondistillable polymeric products.

Sodium Condensations. Consistent with the results published by Clark, *et al.*,[22] *p*-dibromobenzene failed to condense with chlorodiethoxymethylsilane in the presence of sodium, either with toluene or diethyl ether as the reaction medium. When one bromine atom was replaced with the diethoxymethylsilyl group, however, *p*-phenylenebis(ethoxydimethylsilane) was obtained in a 27% yield. This yield is not significantly different from that reported for the condensation of *p*-bromophenyltrimethylsilane with chlorotrimethylsilane under similar conditions (30%).[22] The presence of silicon-attached alkoxy groups does not interfere with the normal course of the reaction, demonstrating the preferential reactivity of the arylsodium toward chlorine.[23]

The unsymmetrical compound, 1-diethoxymethylsilyl-3-diethoxyphenylsilylbenzene, was obtained in only a 6% yield when *p*-bromophenyldiethoxymethylsilane and chlorodiethoxyphenylsilane were condensed in the presence of sodium in refluxing toluene. Interaction with the solvent, always an important consideration in arylations with sodium in toluene, gave considerable diethoxymethylphenylsilane with the consequent loss in yield of the product.

Lithium intermediate. Although the dilithium derivatives form in good yields by an interchange reaction between *p*-dibromobenzene and butyllithium in petroleum ether,[24] these intermediates were not convenient for the preparation of polyfunctional phenylenedisilanes. Because of their great reactivity for both silicon-attached chloro and alkoxy groups, inverse addition of the preformed dilithium compound to the silane was required. Preparation of the lithium reagent by exchange precludes the formation of the intermediate in the presence of the silane. *p*-Phenylenedilithium is a gummy solid, insoluble in petroleum ether, and is not conveniently added to the silane.

EXPERIMENTAL

Alkoxychlorosilanes. Chlorodiethoxymethylsilane, prepared by the ethanolysis of trichloromethylsilane and subsequent fractional distillation, contained little dichloroethoxymethylsilane but some triethoxymethylsilane.[25] The chlorine equivalent was calculated on the basis of titration of a hydrolyzed aliquot of the silane.

Chloroethoxydimethylsilane was prepared by treating 903 g. (7.0 moles) of dichlorodimethylsilane with 323 g. (7.0 moles) of anhydrous alcohol and distilling the 32 g. of product that distilled below 72°. The residue, which had a neutralization equivalent of 139.1 (calcd. for $C_4H_{11}ClSiO$, 138.7), was used directly in the condensation with the Grignard reagent.

The syntheses of chlorodiethoxyphenylsilane, chloro-*p*-chlorophenyldiethoxysilane, and *p*-anisylchlorodiethoxysilane by ethanolysis of the chlorosilanes followed by fractional distillation were described earlier.[25] Pure *p*-(chlorodiethoxysilyl)-*N*,*N*-dimethylaniline was not obtained in the corresponding alcoholysis reaction, but the product which was mostly *p*-(triethoxysilyl)-*N*,*N*-dimethylaniline, was used in the Grignard synthesis.

A stirred mixture of 91 g. (0.36 mole) of *p*-(trichlorosilyl)-*N*,*N*-dimethylaniline 218 g. (2.16 moles) of triethylamine, and 600 ml. of toluene was treated with 32.7 g. (0.71 mole) of anhydrous ethanol by dropwise addition. The amine salts were removed by filtration and washed with a little toluene. Fractional distillation of the combined filtrate and washings gave 46 g. (45%) of the impure product boiling 135–143° at 2 mm. (164–165° at 5 mm.).

Anal. Calcd. for $C_{12}H_{20}ClNO_2Si$ *p*-(chlorodiethoxysilyl)-*N*,*N*-dimethylaniline: C, 52.63; H, 7.36; Si, 10.26; neut. equiv., 274. For $C_{14}H_{25}NO_3Si$ *p*-(triethoxysilyl)-*N*,*N*-dimethylaniline: C, 59.32; H, 8.89; Si, 9.91. Found: C, 57.95; H, 8.86; Si, 9.94, 9.76, neut. equiv., 2440.

p-Phenylenebis(diethoxymethylsilane) and p-bromophenyldiethoxymethylsilane. Grignard procedure in ethyl ether. In a series of experiments the best yields that were obtained following Gainer's procedure[14] were 11.5% of *p*-phenylenebis(diethoxymethylsilane) and 30.1% of *p*-bromophenyldiethoxymethylsilane. In this procedure, 4 moles of *p*-dibromobenzene, 5 g.-atoms of magnesium and 6 moles of triethoxymethylsilane were allowed to react. When most of the ether was not removed by distillation prior to filtering the product, unchanged Grignard reagent was collected in the filtration residue. Distillation of the product gave unchanged *p*-dibromobenzene in the forerun making it necessary to disassemble and clean the distillation apparatus before the products were collected. Redistillation of the higher boiling product from these experiments through an Oldershaw column with 15 plates gave *p*-phenylenebis(diethoxymethylsilane) boiling 128° at 2 mm., n_D^{25} 1.4614, d_4^{25} 0.9828.

Anal. Calcd. for $C_{16}H_{30}O_4Si_2$: C, 56.10; H, 8.83; Si, 16.40; MR_D, 95.24. Found: C, 56.08; H, 8.65; Si, 16.21; MR_D, 95.74.

The lower boiling fraction, 4-bromophenyldiethoxymethylsilane, was collected at 111–115° at 2.0 mm., n_D^{25} 1.4983.

Anal. Calcd. for $C_{11}H_{17}BrO_2Si$: C, 45.66; H, 5.94; Si, 9.71. Found: C, 45.94; H, 6.02; Si, 9.96.

Changing the stoichiometry of the reactants to 0.4 mole of *p*-dibromobenzene, 0.8 g.-atom of magnesium, and 1.0 mole of triethoxymethylsilane did not significantly alter the yields of either product.

p-Phenylenebis(diethoxymethylsilane). Grignard method in tetrahydrofuran. Concomitant addition of reactants. Magnesium, 53.5 g. (2.2 g.-atoms) and 16 g. of *p*-dibromobenzene,

(21) An attempt was made to prepare the *p*-(chlorodiethoxysilyl-*N*,*N*-dimethylaniline by the ethanolysis of *p*-(trichlorosilyl)-*N*,*N*-dimethylaniline in the presence of triethylamine, which was used as an acid acceptor. The triethylamine-chlorosilane complex was insoluble, even in a fairly large excess of toluene, and the low concentration of silane in solution gave mostly the trialkoxy product.

(22) H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798, 3803 (1951).

(23) K. Hizdua, *et al.*, Japanese Patent **1,282** (1953).

(24) H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

(25) L. W. Breed and W. J. Haggerty, Jr., *J. Org. Chem.*, **25**, 126 (1960).

covered with 100 ml. of tetrahydrofuran and activated with a crystal of iodine, were treated with a solution of 220 g. (1 mole, total) of *p*-dibromobenzene, 338 g. (2 moles) of chlorodiethoxymethylsilane, and 450 ml. of tetrahydrofuran by dropwise addition over 2.5 hr. After the mixture was refluxed 3 hr., it was cooled and filtered. Several additional filtrations were required to remove salts that separated when the filtrate was concentrated by distillation. The product, fractionally distilled at 5.5 mm., gave 114 g. (33.3%) of *p*-phenylenebis(diethoxymethylsilane) at 164°. Between 100–108°, 15.4 g. of a material was collected which could not be purified by additional distillation. Analysis by vapor phase chromatography showed that this fraction contained about 67% diethoxymethylphenylsilane, n_D^{25} 1.4664 (for an authentic sample, n_D^{20} 1.4684). The conversion was 4%.

When triethoxymethylsilane was substituted for chlorodiethoxymethylsilane, the product obtained from 5.3 g. (0.22 g.-atom) of magnesium, 23.4 g. (0.1 mole) of *p*-dibromobenzene, 28.5 g. (0.24 mole) of triethoxymethylsilane, and 90 ml. of tetrahydrofuran was refluxed for 8 hr. Distillation of a part of the tetrahydrofuran from the mixture gave two liquid phases. After 100 ml. of toluene was added, solvents were again distilled from the mixture. The residue, which gave a positive Gilman Color Test I, yielded only decomposition products during an attempted distillation.

Addition of silane to preformed Grignard reagent. The Grignard reagent, prepared in the usual manner from 10.6 g. (0.44 g.-atom) of magnesium, 100 ml. of tetrahydrofuran, and 47.2 g. (0.2 mole) of *p*-dibromobenzene, was diluted with 25 ml. of tetrahydrofuran and cooled to 20° to crystallize the Grignard-tetrahydrofuran complex. To the cold solution was added 75 ml. (0.44 mole) of chlorodiethoxymethylsilane in rapid drops. After the product was refluxed 2 hr., procedure A or B was used for purification. No *p*-bromophenyldiethoxymethylsilane was collected during the distillations.

A. The salts were removed by filtration and the filtrate was concentrated by distillation. Fractional distillation of the residue gave 26.6 g. (38%) of *p*-phenylenebis(diethoxymethylsilane).

B. The product was poured into a mixture of 200 ml. of water, 200 ml. of toluene, 25 g. of sodium bicarbonate, and ice. The organic phase, separated, and washed with three 100-ml. portions of water, was filtered and dried with Drierite. After the solvents were removed, 21.8 g. (32%) of *p*-phenylenebis(diethoxymethylsilane) was obtained by fractional distillation.

In larger scale experiments (for example, with 2.4 moles of *p*-dibromobenzene) formation of the Grignard reagent required 24 hr. The temperature could not be maintained at 20° during the addition of the silane because adequate stirring of the thick mixture was not obtained. The average yield for two batches was 11.8%.

Substitution of *p*-dichlorobenzene for *p*-dibromobenzene gave only the monosilane. From 29.4 g. (0.2 mole) of *p*-dichlorobenzene was obtained 16.0 g. (32.7%) of *p*-chlorophenyldiethoxymethylsilane boiling 74–76° at 0.1 mm. n_D^{22} 1.4841, d_4^{28} 1.069, when the product was purified by method A.

Anal. Calcd. for $C_{11}H_{17}ClO_2Si$: Si, 11.47; MR_D, 65.66. Found: Si, 12.19, 12.16; MR_D, 65.48.

p-Phenylenebis(diethoxymethylsilane). Sodium method. A mixture of 5.5 g. (0.24 g.-atom) of sodium and 30 ml. of toluene was heated to 112°, and then stirred at 600 r.p.m. to disperse the sodium. Dropwise addition of a mixture of 28.0 g. (0.093 mole) of *p*-bromophenyldiethoxymethylsilane and 20.0 g. (0.118 mole) of chlorodiethoxymethylsilane gave an exothermi reeaction which maintained a refluxing mixture without external heating. The cooled product was filtered to remove the sodium halides and distilled at atmospheric pressure to remove the toluene and unchanged chlorodiethoxymethylsilane. Fractional distillation of the residue at 0.3 mm. gave 8.6 g. (27.0%) of phenylenebis(diethoxymethylsilane) boiling at 124–127°, n_D^{25} 1.4536.

When 13.0 g. (0.5 g.-atom) of sodium in 50 ml. of toluene was treated with a mixture of 29.5 g. (0.125 mole) of *p*-dibromobenzene, 42.3 g. (0.25 mole) of chlorodiethoxymethylsilane, and 50 ml. of toluene, a self-sustaining reaction could not be initiated even with the addition of small quantities of ethyl acetate. The results were the same when a threefold excess of the silane was used.

After 35.5 g. (0.15 mole) of *p*-dibromobenzene, 53 g. (0.30 mole) of chlorodiethoxymethylsilane, 15.2 g. (0.60 g.-atom) of sodium pressed into 1 mm. diameter wire, and 125 ml. of absolute ether were heated under reflux and stirred for 24 hr., the mixture became dark purple but an exothermic reaction could not be initiated. No *p*-phenylenebis(diethoxymethylsilane) was obtained when the product was fractionally distilled under reduced pressure.

1-Diethoxymethylsilyl-4-diethoxyphenylsilylbenzene. Sodium method. In a similar experiment, 5.1 g. (0.22 g.-atom) of sodium in 30 ml. of toluene, treated with 21.4 g. (0.11 mole) of chlorodiethoxyphenylsilane and 27.0 g. (0.093 mole) of *p*-bromophenyldiethoxymethylsilane, gave two materials when the product was fractionally distilled at 0.1 mm. One fraction, mostly *diethoxymethylphenylsilane*, was collected at 54–56°, n_D^{25} 1.4602, d_4^{25} 0.993.

Anal. Calcd. for $C_{11}H_{18}O_2Si$: C, 62.80; H, 8.62; Si, 13.35. Found: C, 61.95, 62.05; H, 7.95, 7.79; Si, 12.08, 121.15.

1-Diethoxymethylsilyl-4-diethoxyphenylsilylbenzene. 2.0 g. (5.7%) was obtained at 143–145°, n_D^{25} 1.4973, d_4^{25} 1.034.

Anal. Calcd. for $C_{21}H_{32}Si_2O_4$: C, 62.33; H, 7.97; Si, 13.89; MR_D, 115.0. Found: C, 61.95, 62.05; H, 7.95, 7.79; Si, 13.88, 14.10; MR_D, 114.6.

p-Phenylenebis(dichloromethylsilane). Attempted by the lithiation of p-dibromobenzene. A mixture of 0.122 mole of butyllithium in petroleum ether (b.p. 33–55°) and 14.4 g. (0.061 mole) of *p*-dibromobenzene, stirred at reflux for 24 hr., yielded a solid product. The liquid phase gave a negative Gilman Color Test I. Carbonation of the product gave 63% of the theoretical acids (calculated as terephthalic acid) with a neutralization equivalent 127.

When a similar lithium derivative, prepared from 0.115 mole of *p*-dibromobenzene, was added to a solution of 0.46 mole of trichloromethylsilane in 100 ml. of petroleum ether, distillation of the product gave 9.3 g. of an unidentified material boiling 150–153° at 26 mm.

Anal. Found: C, 62.59, 62.48; H, 7.57, 7.61; Si, 5.07, 5.14; neut. equiv., 309.

p-Phenylenebis(ethoxydimethylsilane). Grignard procedure in ether. Magnesium, 80.2 g. (3.3 g.-atoms), covered with 100 ml. of ether, was treated with a solution of 353.9 g. (1.5 moles) of *p*-dibromobenzene, 444.6 g. (3.0 moles) of diethoxydimethylsilane, and 500 ml. of anhydrous ether by dropwise addition over 2.5 hr. The product was heated and stirred for 15 hr., and then 400 ml. of ether was removed by downward distillation. After 400 ml. of heptane was added to the mixture, the salts were removed by filtration and the solvents were distilled from the mixture. Fractional distillation of the residue at 3.5 mm. gave four fractions: A, b.p. 64–123°, 49 g.; B, b.p. 123–125°, 26 g., n_D^{25} 1.4752; C, b.p. 127–128°, 131 g.; n_D^{25} 1.4752, d_4^{25} 0.9354; and D, b.p. 128–135°. Fraction C represented a 31% yield of the product.

Anal. Calcd. for $C_{14}H_{26}O_2Si_2$: Si, 19.88; MR_D, 84.46. Found: Si, 19.24, 19.14; MR_D, 85.19.

Grignard method in tetrahydrofuran. Addition of a mixture of 565 g. (5.0 moles, total) of *p*-dibromobenzene, 694 g. (5.0 moles) of chloroethoxydimethylsilane, and 1125 ml. of tetrahydrofuran to 134 g. (5.5 g.-atoms) of magnesium, which had been previously activated with 25 g. of *p*-dibromobenzene in 200 ml. of tetrahydrofuran, gave 139 g. (19.7%) of *p*-phenylenebis(ethoxydimethylsilane) boiling at 132–134°, n_D^{25} 1.4763, when the product was filtered and fractionally distilled at 4.5 mm.

p-Phenylenebis(ethoxymethylvinylsilane). When a mixture of 358 g. (1.56 moles) of *p*-dibromobenzene, 500 g. (3.12 moles) of diethoxymethylvinylsilane, and 400 ml. of tetrahydrofuran was added dropwise over 4 hr. to 83.4 g. (3.43

TABLE II

OTHER *p*-PHENYLENEDISILANES

Compound	B.P., Mm.	M.P.	Yield, %	Analysis Calcd. C	Calcd. H	Calcd. Si	Found C	Found H	Found Si
p-[$C_6H_5Si(OC_2H_5)_2$]$_2C_6H_4$[a]	188–197 (0.30–0.07)	—	27.9	66.91	7.34	12.04	67.45	7.15	12.10
p-[4-$ClC_6H_4Si(OC_2H_5)_2$]$_2C_6H_4$	210–246 (0.25–0.8) 239–239 (1)	54–55[b]	26.5	58.30	6.02	10.49	58.14	5.82	10.35
p-[4-$(CH_3)_2NC_6H_4Si(OC_2H_5)_2$]$_2C_6H_4$	*ca.* 270 (0.1)	104–105[b]	43.5	65.17	8.02	10.16	65.57	7.83	10.56 10.16
				N = 5.07			N = 5.09		
p-[4-$CH_3OC_6H_4Si(OC_2H_5)_2$]$_2C_6H_4$	230–250 (0.2–0.6)	55–56[b]	43.9	63.84	7.27	10.67	63.52	7.21	10.68 10.74

[a] n_D^{25} 1.5345. [b] From anhydrous ethanol.

g.-atoms) of magnesium turnings, and the mixture was stirred at reflux for 7 hr., a negative Gilman Color Test I was obtained. After 500 ml. of heptane was added to the mixture, 400 ml. of the solvents were removed by distillation, and the salts were removed by filtration. When the product, containing 1 wt. % hydroquinone, was fractionally distilled at 3.3 mm. three fractions were obtained: A, b.p. 74–139°, 25 g.; B, b.p. 139–144°, 42 g.; n_D^{25} 1.4930, d_4^{25} 0.9605; C, b.p. 144–155°, 5 g., n_D^{25} 1.4958, d_4^{25} 0.9587. Fraction B represented a 9% yield of the product.

Anal. Calcd. for $C_{16}H_{26}O_2Si_2$: Si, 18.33; MR_D, 92.78. Found: Si, 18.75, 18.81; MR_D, 92.75.

p-Phenylenebis(diethoxyvinylsilane). Similarly, 5.3 g. (0.2 g.-atom) of magnesium, 23.6 g. (0.1 mole) of *p*-dibromobenzene, 38 g. (0.2 mole) of triethoxyvinylsilane, and 160 ml. of tetrahydrofuran gave 5.6 g. (15%) of *p*-phenylenebis(diethoxyvinylsilane), b.p. 125–129° at 0.15 mm.; n_D^{25} 1.4743; d_4^{25} 0.9852, MR_D calcd., 103.56, found, 104.63.

Other p-phenylene(disilanes). Compounds listed in Table II were prepared by the concomitant addition of mixtures of *p*-dibromobenzene and the appropriate dialkoxyarylchlorosilane in tetrahydrofuran to magnesium and were purified by fractional distillation.

p-Phenylenebis(diethoxyphenylsilane), prepared by treating a cooled, preformed Grignard reagent with chlorodiethoxyphenylsilane, was purified by method B. The product, 26.5 g. (28.5%), boiled at 160–170° at 0.1 mm.

When the reaction products were purified directly by filtration and distillation, the crude reaction mixtures were treated with an equal volume of heptane, and a large part of the tetrahydrofuran was removed by distillation. More complete precipitation of the magnesium halides was obtained, eliminating the necessity for several filtrations.

KANSAS CITY 10, MO.

[CONTRIBUTION FROM THE CORNING GLASS WORKS AND DOW CORNING CORP. MULTIPLE FELLOWSHIP AT MELLON INSTITUTE AND THE DOW CORNING CORP.]

Dehydration of 1,3-Bis(hydroxyalkyl)tetramethyldisiloxanes

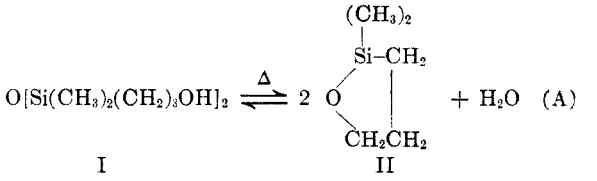
JOHN L. SPEIER,[1] MARY P. DAVID, AND BENJAMIN A. EYNON[1]

Received February 16, 1960

Three 1,3-bis(hydroxyalkyl)tetramethyldisiloxanes of the formula $[(CH_3)_2Si(CH_2)_nOH]_2O$ were prepared in which n = 1, 2, or 3. When subjected to dehydration, each reacted differently. When n = 1, dehydration in the presence of sulfuric acid caused the formation of ethers having the formula, $[-(CH_3)_2SiCH_2OCH_2(CH_3)_2SiO-]_{1,2,\ldots x}$. The cyclic compound in which x = 1 was isolated. In the presence of lime, a product was obtained having the formula, $[-(CH_3)_2SiCH_2O-]_{2,3,\ldots x}$. Under either alkaline or acidic conditions, when n = 2, ethylene, water, and polydimethylsiloxanes formed. When n = 3, a reactive cyclic compound was formed having the formula $(CH_3)_2Si(CH_2)_3O$.

The synthesis of a series of three *sym*-(hydroxyalkyl)tetramethyldisiloxanes of the formula $[HO(CH_2)_n(CH_3)_2Si]_2O$ has recently been completed with n = 1, 2 or 3, and the dehydration of these three structures has been studied. Although these three compounds form an homologous series, each loses water in a different manner.

1,3-Bis(hydroxypropyl)tetramethyldisiloxane, (I), prepared by the methanolysis of 1,3-bis(acetoxypropyl)tetramethyldisiloxane[2] lost water on distillation to form a cyclic structure (II) according to equation A:



I II

(1) Present address, Dow Corning Corporation, Midland, Michigan.