

40–100° obtained during the working up of the reaction mixture. This material was carefully fractionated to yield 1.10 g. of material boiling at 77–83°. The identity of this material as cyclohexene was confirmed by preparation of the 1-chloromercuri-2-methoxycyclohexane derivative.²⁰ The material isolated weighed 4.0 g. (corresponding to 22%)

(20) J. Romeyn and G. F. Wright, *THIS JOURNAL*, **69**, 697 (1947).

cyclohexene) and melted at 113–114°; the mixed melting point with an authentic specimen was not depressed.

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TORONTO, CANADA

[CONTRIBUTION NO. 747 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

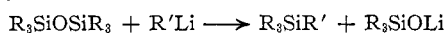
The Cleavage of *sym*-Diphenyldisiloxane by Organometallic Compounds

BY MACK C. HARVEY, WILLIAM H. NEBERGALL AND JOHN S. PEAKE

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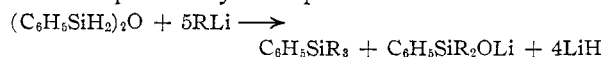
The cleavage of *sym*-diphenyldisiloxane by organolithium compounds, Grignard reagents and lithium aluminum hydride has been accomplished. With organolithium compounds the products are a tetrasubstituted silane and the lithium salt of a silanol. With Grignard reagents two reactions occur. The products from reaction I are an alkylphenylsilane and the halomagnesium salt of phenylsilanol, and from reaction II the products are phenylsilane and the halomagnesium salt of an alkylphenylsilanol. The latter reaction involves the alkylation of a silicon-hydrogen group and the reduction of the silicon-oxygen bond. *sym*-Diphenyldisiloxane is reduced by lithium aluminum hydride to phenylsilane.

It has been reported¹ that when a symmetrical hexasubstituted disiloxane is cleaved by an organolithium compound, one obtains as the products a tetrasubstituted silane and the lithium salt of a silanol.



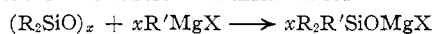
These authors likewise found that hexaphenyldisiloxane and hexa-*p*-tolylidisiloxane were cleaved by phenyllithium but not by methylolithium.

In the present investigation the cleavage of *sym*-diphenyldisiloxane by both phenyllithium and methylolithium was accomplished. Because an excess of these organolithium compounds was employed, the hydrogen atoms attached to silicon were replaced by alkyl groups, and the net reaction can be expressed by the equation

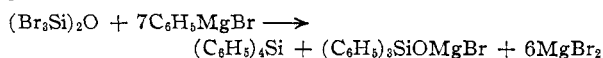


Subsequent hydrolysis of the lithium salt of the silanol gave triphenylsilanol when $R = C_6H_5$, and *sym*-tetramethyldiphenyldisiloxane, $[C_6H_5(CH_3)_2Si]_2O$, when $R = CH_3$.

Kipping and Hackford² found that Grignard reagents cleave cyclic siloxanes of the type $(R_2SiO)_x$, but not hexasubstituted disiloxanes

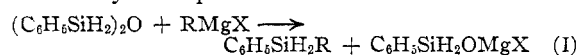


Similarly, Sauer³ found that dimethylsilicone, $[(CH_3)_2SiO]$, reacted with methylmagnesium iodide to form trimethylsilanol (after hydrolysis). Schumb and Saffer⁴ reported that no cleavage was observed in the reaction between hexachlorodisiloxane and phenylmagnesium bromide, but that when hexabromodisiloxane was treated in a similar manner, some cleavage of the silicon-oxygen bond resulted.



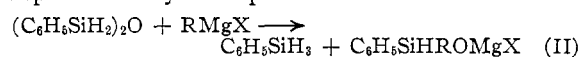
In the present work it was discovered that two reactions take place concurrently between Grignard reagents and *sym*-diphenyldisiloxane. One of these

is the expected cleavage reaction, which is described by the equation

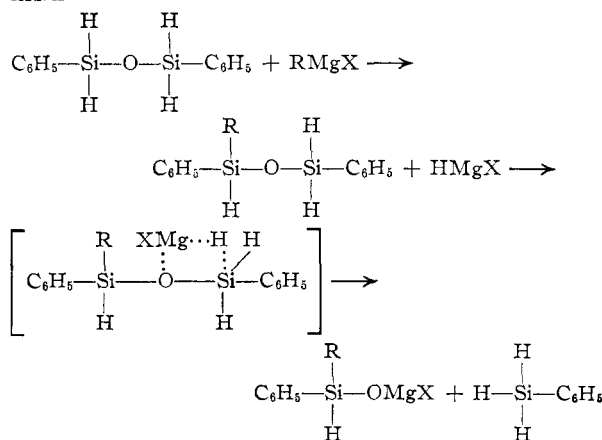


Hydrolysis of the magnesium salt should give rise to the original disiloxane. However it appears that one of the hydrogen atoms attached to silicon in the salt is hydrolyzed off, giving rise to high polymers of the type $(C_6H_5SiHO)_x$. In fact a considerable quantity of the trimer was isolated in an experiment in which phenylmagnesium bromide was the Grignard reagent employed.

The second reaction occurring between *sym*-diphenyldisiloxane and Grignard reagents may be represented by the equation



Hydrolysis converts the magnesium salt to the corresponding tetrasubstituted disiloxane, $(C_6H_5SiHR)_2O$. This reaction is the first reported example of the alkylation of the Si-H group by Grignard reagents. It may be that the alkylation step in this reaction results in the formation of halomagnesium hydride,⁵ $HMgX$, which then proceeds to reduce the Si-O bond, as indicated in the mechanism



(1) H. Gilman, H. N. Benedict and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954).

(2) F. Kipping and J. Hackford, *J. Chem. Soc.*, **99**, 138 (1911).

(3) R. Sauer, *THIS JOURNAL*, **66**, 1707 (1944).

(4) W. Schumb and C. Saffer, *ibid.*, **61**, 363 (1939).

(5) C. Miles, U. S. Patent 2,432,921, June 20, 1944; *C. A.*, **42**, 2278 (1948).

Because it is well-established that the silicon atom in organosilicon compounds assumes a pentavalent state in certain nucleophilic displacement reactions,⁶ it is not unreasonable to assume the existence of the intermediate complex indicated above.

The Grignard reagents used and the products which were successfully isolated and identified in this study are listed in Table I.

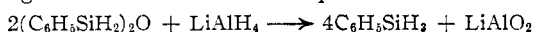
TABLE I

THE REACTIONS OF *sym*-DIPHENYLDISILOXANE WITH GRIGNARD REAGENTS

Reactant with (C ₆ H ₅ SiH ₂) ₂ O	Products isolated and identified
CH ₃ MgI	C ₆ H ₅ SiH ₃ , C ₆ H ₅ SiH ₂ CH ₃ , (C ₆ H ₅ SiHCH ₃) ₂ O
C ₂ H ₅ MgBr	C ₆ H ₅ SiH ₃ , C ₆ H ₅ SiH ₂ C ₂ H ₅ , (C ₆ H ₅ SiHCH ₂ C ₂ H ₅) ₂ O
C ₆ H ₅ MgBr	C ₆ H ₅ SiH ₃ , (C ₆ H ₅) ₂ SiH ₂ , (C ₆ H ₅ SiHO) ₃
C ₆ H ₅ CH ₂ MgCl	C ₆ H ₅ SiH ₃ , C ₆ H ₅ SiH ₂ C ₆ H ₅ CH ₂

Attempts to isolate and identify *sym*-tetraphenyldisiloxane and *sym*-dibenzoyldiphenyldisiloxane from the corresponding high-boiling hydrolytic residues were unsuccessful.

Schumb, *et al.*,⁷ and Fittz⁸ recently reported independently that the Si-O bonds of hexachlorodisiloxane are cleaved by lithium aluminum hydride with silane being formed. In the present work it was found that *sym*-diphenyldisiloxane is cleaved by lithium aluminum hydride with phenylsilane being formed as the reduction product



Experimental

All reactions involving an organolithium compound or lithium anhydride were carried out in an atmosphere of oxygen-free, dry nitrogen. The ether used as a solvent was previously dried over sodium. All melting points and boiling points are uncorrected.

sym-Diphenyldisiloxane.—Phenylsilane was prepared by adding dropwise a solution of 1692 g. (8 moles) of phenyltrichlorosilane in one liter of ether to a solution of 300 g. (8 moles) of lithium aluminum hydride in six liters of ether. The reaction mixture was allowed to stand overnight and then hydrolyzed with crushed ice and dilute sulfuric acid. The ether layer was separated, dried over Drierite, and the ether removed by distillation. The residue gave 573 g. (67%) of phenylsilane, boiling at 120° (750 mm.).⁹

Phenylbromosilane was then prepared by passing anhydrous hydrogen bromide through a solution of 108 g. (1 mole) of phenylsilane in 50 ml. of ether for 13.5 hours.¹⁰ After removal of the ether, the phenylbromosilane was purified by distillation under reduced pressure. The product distilled at 70° (17 mm.), yield 187 g. (95%).

A 187-g. (1 mole) sample of phenylbromosilane was dissolved in 300 ml. of ether and poured onto crushed ice. The resultant reaction was exothermic and hydrogen bromide was evolved. After the hydrolysis appeared to be complete, the organic layer was separated and washed twice with water. After drying over Drierite, the ether was removed and the residual liquid distilled under reduced pressure. *sym*-Diphenyldisiloxane, (C₆H₅SiH₂)₂O, distilled at 86–90° (0.15 mm.), *n*_D²⁰ 1.541, yield 73 g. (78%), mol. wt. calcd. 230, found 227.

Anal. Calcd. for C₁₂H₁₄OSi₂: C, 62.6; H, 6.13; Si, 24.4. Found: C, 62.4; H, 6.19; Si, 24.1.

A second fraction identified as 2,4,6-triphenylcyclotrisiloxane, (C₆H₅SiHO)₃, distilled at 140–150° (0.07 mm.), *n*_D²⁵ 1.566, yield 9.6 g. (8%); mol. wt. calcd. 366; found

357. The infrared spectrum of this compound was identical with that¹¹ of an authentic sample of 2,4,6-triphenylcyclotrisiloxane prepared in this Laboratory.

Cleavage of *sym*-Diphenyldisiloxane by Methylolithium.—A 10.0-g. (0.044 mole) sample of *sym*-diphenyldisiloxane in 50 ml. of ether was added dropwise to a 400-ml. ether solution of methylolithium, which had been made from 44 g. (0.33 mole) of methyl iodide and an excess of lithium metal. A white precipitate formed immediately, and refluxing of the solvent resulted from the heat of reaction. After the addition was completed, the reaction mixture was stirred for three hours. After pouring the reaction mixture onto cracked ice, the organic layer was separated, washed three times with water, and dried over Drierite. The ether was then removed and the residual liquid fractionated under reduced pressure. Trimethylphenylsilane, C₆H₅Si(CH₃)₃, distilled at 30° (1.5 mm.) and boiled at 166–167° (749 mm.), yield 2.8 g. (43%).

Anal. Calcd. for C₆H₇Si: C, 71.9; H, 9.38; Si, 18.6. Found: C, 71.7; H, 9.66; Si, 18.6.

A second fraction identified as *sym*-tetramethyldiphenyldisiloxane, [C₆H₅Si(CH₃)₂]₂O, distilled at 110° (2 mm.), yield 2.5 g. (38%).

Anal. Calcd. for C₁₆H₂₂OSi₂: C, 67.1; H, 7.75; Si, 19.6. Found: C, 67.4; H, 7.78; Si, 19.8.

Cleavage of *sym*-Diphenyldisiloxane by Phenylolithium.—A 1.5-g. (0.007 mole) sample of *sym*-diphenyldisiloxane in 10 ml. of ether was added dropwise to 150 ml. of a solution of phenylolithium, which had been made from 15.7 g. (0.1 mole) of bromobenzene and an excess of lithium metal. A white precipitate formed immediately, and the heat of reaction caused refluxing of the solvent. The reaction mixture was refluxed for one hour and then poured onto a mixture of cracked ice and dilute hydrochloric acid to hydrolyze the excess phenylolithium. A white crystalline solid, tetraphenylsilane, insoluble in water and ether, was collected, and the ether layer evaporated, leaving white crystals of triphenylsilanol. The tetraphenylsilane melted at 234°, yield 1.9 g. (87%). The triphenylsilanol melted at 150°, yield 1.2 g. (79%). The melting point of tetraphenylsilane has been reported¹² to be 234°, and that of triphenylsilanol¹³ to be 150°.

Cleavage of *sym*-Diphenyldisiloxane by Methylmagnesium Iodide.—A 46-g. (0.20 mole) sample of *sym*-diphenyldisiloxane in 50 ml. of ether was added dropwise to a 200-ml. ether solution of methylmagnesium iodide, which had been made from 71 g. (0.50 mole) of methyl iodide and 12 g. (0.50 g. atom) of magnesium turnings. A reaction started immediately and refluxing of the solvent resulted. The reaction mixture was held at the reflux temperature for one hour, then allowed to stand overnight. A small sample of crystals which had formed in the reaction flask was removed and heated under reduced pressure to remove volatile material. An infrared spectrum of the solid showed it to contain the following groups¹⁴: Si-C₆H₅, Si-CH₃, Si-H and Si-O. Analysis showed the solid to contain 42.1% iodine; calculated for C₆H₅SiHCH₃OMgI: 44.0% iodine. The remainder of the reaction mixture was poured onto a mixture of cracked ice and dilute sulfuric acid. The organic layer was separated, dried over Drierite, and the ether evaporated. Fractional distillation of the residue gave 14 g. of a mixture of phenylsilane and methylphenylsilane distilling at 118–140°, and a residual liquid. This liquid was distilled under reduced pressure, giving 15.5 g. (0.06 mole) of crude *sym*-dimethyldiphenyldisiloxane, (C₆H₅SiHCH₃)₂O, distilling at 96–100° (0.25 mm.). This distillate was redistilled twice to obtain a pure sample for analysis, infrared spectrum and physical properties. The infrared spectrum of this compound was found to be identical with that¹⁵ of an authentic sample of *sym*-dimethyldiphenyldisiloxane. The compound distilled at 80° (0.12 mm.), *n*_D²⁵ 1.519.

Anal. Calcd. for C₂₄H₁₈OSi₂: C, 65.0; H, 7.02; mol. wt., 258. Found: C, 65.7; H, 7.20; mol. wt., 259.

The mixture of phenylsilane and methylphenylsilane men-

(6) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, *THIS JOURNAL*, **71**, 965 (1949).

(7) W. Schumb and D. Robinson, *ibid.*, **77**, 5294 (1955).

(8) G. Fittz, *Z. Naturforsch.*, **10b**, 423 (1955).

(9) W. H. Nebergall, *THIS JOURNAL*, **72**, 4702 (1950).

(10) Method to be published by J. S. Peake and I. Al-Refai.

(11) To be published by W. F. Mivelaz and W. H. Nebergall.

(12) F. Kipping, *J. Chem. Soc.*, **93**, 198 (1908).

(13) J. Sugden and L. Wilkens, *ibid.*, 126 (1931).

(14) M. C. Harvey, W. H. Nebergall and John S. Peake, *THIS JOURNAL*, **76**, 4555 (1954).

(15) Private communication, A. L. Smith, Dow Corning Corp., Midland, Michigan.

tioned above was added dropwise to a 300-ml. ether solution of phenyllithium, which had been made from 110 g. (0.70 mole) of bromobenzene and an excess of lithium metal. After refluxing for one hour, this reaction mixture was poured onto cracked ice and dilute sulfuric acid to destroy the excess phenyllithium. The ether was then removed by evaporation, leaving a white solid, which was collected and dried. This solid was placed in a Soxhlet extractor and extracted for one hour with 20–40° petroleum ether to dissolve the methyltriphenylsilane (derived from the methylphenylsilane). The yield of this compound was 7.9 g. (0.03 mole), m.p. 65–66°. The remaining solid was extracted with toluene for 12 hours to give 33.0 g. (0.10 mole) of tetraphenylsilane (derived from phenylsilane), m.p. 232–233°.¹²

Cleavage of *sym*-Diphenyldisiloxane by Ethylmagnesium Bromide.—A 46-g. (0.20 mole) sample of *sym*-diphenyldisiloxane in 50 ml. of ether was added dropwise to a 200-ml. solution of ethylmagnesium bromide, which had been made from 70 g. (0.50 mole) of ethyl bromide and 12 g. (0.50 g. atom) of magnesium turnings. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up as described in the above experiment. The phenylsilane and ethylphenylsilane obtained were converted to tetraphenylsilane and ethyltriphenylsilane, respectively. The yield of tetraphenylsilane was 24.6 g. (0.073 mole), m.p. 232–233°; that of triphenylethylsilane was 7.0 g. (0.024 mole), m.p. 72–73°. The liquid remaining after the separation of the phenylsilane and ethylphenylsilane was distilled under reduced pressure, giving 12.0 g. of crude *sym*-diethyldiphenyldisiloxane, (C₆H₅SiHC₂H₅)₂O, distilling at 140–200° (0.05 mm.). The crude product was redistilled at 107° (0.03 mm.) to obtain a sample for analysis and physical properties. The infrared spectrum of the compound was identical with that¹⁵ of an authentic sample of *sym*-diethyldiphenyldisiloxane, *n*_D²⁰ 1.523.

Anal. Calcd. for C₁₆H₂₂OSi₂: C, 67.2; H, 7.75; mol. wt., 286. Found: C, 67.0; H, 7.90; mol. wt., 282.

Cleavage of *sym*-Diphenyldisiloxane by Phenylmagnesium Bromide.—A 23-g. (0.10 mole) sample of *sym*-diphenyldisiloxane in 20 ml. of ether was added dropwise to a 200-ml. ether solution of phenylmagnesium bromide, which had been made from 63 g. (0.40 mole) of bromobenzene and 4.8 g. (0.40 g. atom) of magnesium turnings. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up in the usual way. The ether was removed, and the residual liquid fractionated. A 3.0-g. (0.03 mole) fraction composed of phenylsilane distilled at 118–120°. This compound was identified by its infrared spectrum¹⁴ and its boiling point. The residual liquid was distilled under reduced pressure, giving 11.7 g. (0.064 mole) of diphenylsilane, which distilled at 60° (0.6 mm.). The diphenylsilane was identified by its infrared spectrum.¹⁴ A fraction consisting of 5.0 g. (0.014 mole) of 2,4,6-triphenylcyclotrisiloxane, (C₆H₅SiHO)₃, distilled at 168° (0.02 mm.), *n*_D²⁰ 1.566; calcd. mol. wt. 366, found 352. The infrared spectrum of this compound was identical

with that of the sample of the trimer obtained by the hydrolysis of phenylbromosilane.

Anal. Calcd. for C₆H₆OSi: C, 59.0; H, 4.95. Found: C, 59.9; H, 5.20.

Cleavage of *sym*-Diphenyldisiloxane by Benzylmagnesium Chloride.—A 23-g. (0.10 mole) sample of *sym*-diphenyldisiloxane in 25 ml. of ether was added dropwise to a 200-ml. ether solution of benzylmagnesium chloride, which had been made from 63 g. (0.50 mole) of benzyl chloride and 12 g. (0.5 g. atom) of magnesium turnings. The reaction started immediately and refluxing of the solvent resulted. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up in the usual manner. The ether was distilled off and a 19-g. mixture of phenylsilane and toluene distilled at 120°, leaving a residue which was distilled later. The mixture of phenylsilane and toluene was treated with phenyllithium, which had been made from 94 g. (0.60 mole) of bromobenzene and an excess of lithium metal. The yield of tetraphenylsilane was 7.0 g. (0.03 mole), m.p. 232–233°. The residual liquid was distilled under vacuum, giving a 24-g. mixture of 1,2-diphenylethane and benzylphenylsilane, which distilled at 100–160° (0.43 mm.). This mixture was treated with an ether solution of phenyllithium, which had been made from 63 g. (0.40 mole) of bromobenzene and an excess of lithium metal. The reaction mixture was hydrolyzed and worked up in the usual manner. The ether was evaporated, and the residual liquid distilled under reduced pressure to remove the 1,2-diphenylethane. The residue was treated with 20–40° petroleum ether, which caused benzyltriphenylsilane to precipitate. This compound was recrystallized twice from 95% ethanol; yield 15 g. (0.04 mole), m.p. 96–97°.¹⁶

Cleavage of *sym*-Diphenyldisiloxane by Lithium Aluminum Hydride.—A 4.0-g. (0.02 mole) sample of *sym*-diphenyldisiloxane was added dropwise to 2.0 g. (0.7 mole) of lithium aluminum hydride in 250 ml. of ether. Slight refluxing of the solvent resulted, and a heavy white precipitate formed. The reaction mixture was allowed to stand for two hours and then it was poured onto a mixture of cracked ice and dilute hydrochloric acid. The ether layer was separated, washed first with dilute hydrochloric acid and then with water, and dried over Drierite. The ether was distilled off and the product (2.1 g., 59%) distilled at 119° (740.3 mm.). The product was identified as phenylsilane by its boiling point and infrared spectrum.¹⁴

Acknowledgments.—Analyses were by Miss J. Dickey of the Indiana University Microanalytical Laboratory. This paper is based upon work performed under contract Nonr-90802 NR 356-321 (Office of Naval Research).

(16) C. Hance and C. Hauser, *THIS JOURNAL*, **74**, 1856 (1952).

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Halogen Derivatives of Dibenzo-*p*-dioxin

BY HENRY GILMAN AND JOSEPH J. DIETRICH

RECEIVED OCTOBER 15, 1956

Direct preparations for 2-chloro- (II), 2,7-dichloro- (III), 2,7-dibromo- (VI) and 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin (VIII) from dibenzo-*p*-dioxin (I) are reported. The 1-bromo-dibenzo-*p*-dioxin (IV) and the 2-iodo-dibenzo-*p*-dioxin (IX) are obtained by indirect methods. II, IV, VI, VIII and IX are new compounds. Structure proofs for these and 2,8-dibromo-dibenzo-*p*-dioxin (VII) are included along with a brief theoretical discussion dealing with VI, VII and VIII. Brief instructions are given for the preparation of 2-bromo-dibenzo-*p*-dioxin (V) and of VII. I is formed from inexpensive *o*-chlorophenol in low yield.

Studies on the orientation of entering groups on the dibenzo-*p*-dioxin (I) nucleus have led to the

preparation of a number of halogen derivatives and confirmation of their structures.