ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Cyclic Organosilicon Compounds. I. Synthesis of Compounds Containing the Dibenzosilole Nucleus

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Several functional dibenzosilole compounds, *i.e.*, compounds having a silicon–chlorine bond, as well as some non-functional dibenzosilole types, have been prepared by a cyclization reaction from 2,2′-biphenylenedilithium and appropriately substituted R_2SiCl_2 or $RSiCl_3$ compounds. Also, 5,5′-spirobi[dibenzosilole] and 5,5′-spirobi[dibenzogermole] have been synthesized in a similar fashion from silicon tetrachloride and germanium tetrachloride, respectively. The functional dibenzosilole derivatives have been treated with a variety of organolithium reagents to yield non-functional dibenzosilole compounds, some of which appear to possess favorable thermal stability characteristics.

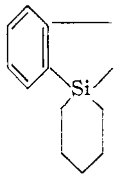
Only a few aromatic heterocyclic systems in which silicon is the only or one of the hetero atoms have been reported. Some compounds containing the phenoxasilin nucleus, a system containing both silicon and oxygen, have been prepared. Also, various derivatives of phenothiasilin-5,5-dioxide, a heterocyclic system containing silicon and sulfur, have been synthesized. These compounds were obtained by treating the dimetalated product of diphenyl ether and diphenyl sulfone with appropriately substituted chlorosilanes.[1]

The first dibenzosilole[2] compound was synthesized by treating 2,2′-biphenylenedilithium (I) with diphenyldichlorosilane to give a low yield of 5,5-diphenyldibenzosilole and an unidentified material. The by-product was thought originally to be bis-(2-biphenylyl)-diphenylsilane on the basis of the analytical data; however, comparison of its melting point and infrared spectrum with an authentic sample prepared by a less ambiguous method showed the two to be different.[3]

In these studies the syntheses of dibenzosilole compounds by a cyclization reaction between I and a di- or trichloro-substituted organosilicon compound have been more thoroughly investigated and have been broadened to include both functional and non-functional types.

Prior to syntheses of additional cyclic organosilicon compounds, the preparation of the intermediate I was further examined in view of the excellent yield of this organodilithium compound obtained by Wittig and Herwig[4] from 2,2′-diiodobiphenyl and lithium metal in diethyl ether. When this same method was tried with 2,2′-dibromobiphenyl, only a 46% yield of the benzophenone adduct was obtained subsequent to treatment of the reaction mixture with benzophenone Previously, preparation of I *via* an halogen–metal interconversion reaction, *i.e.*, reaction of 2,2′-dibromobiphenyl with *n*-butyllithium, gave 81% of the benzophenone adduct.[3] Thus, in this present investigation the halogen–metal interconversion method has been used again for the preparation of I.

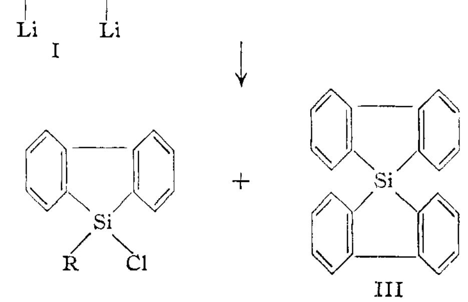
When di-*n*-dodecyldichlorosilane and diethyldichlorosilane were treated with I, low yields of 5,5-di-*n*-dodecyl- and 5,5-diethyldibenzosilole, respectively, were obtained. Likewise, a low yield of spiro[dibenzosilole-5,1′-silacyclohexane] (II), in addition to a small amount of 1,1-bis-(2-biphenylyl)-silacyclohexane, was isolated when 1,1-dichlorosilacyclohexane was allowed to react with I.



II

These low yields are not too surprising inasmuch as West[5] observed that in preparing alicyclic organosilicon compounds *via* a cyclization reaction, the yield of cyclic product increased as the number of chlorine atoms attached to silicon was increased. Apparently the higher polarity of a silicon–chlorine bond as compared to a carbon–silicon bond renders the silicon atom more susceptible to attack by nucleophilic reagents. One might suspect, therefore, that functional dibenzosilole compounds, *i.e.*, compounds containing a silicon–chlorine bond, should be obtained in higher yields than non-functional types. Indeed, this was found to be true but for one exception which will be mentioned later.

Methyl-, *n*-dodecyl- and phenyltrichlorosilane all coupled with I to give excellent yields of 5-chloro-5-methyl-, 5-chloro-5-*n*-dodecyl- and 5-chloro-5-phenyldibenzosilole, respectively, in addition to small but varying amounts of 5,5′-spirobi[dibenzosilole] (III). Only the *n*-dodecyl and



III

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[1] K. Oita and H. Gilman, THIS JOURNAL, **79**, 339 (1957); K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957).

[2] The nomenclature and the numbering system employed herein were recommended by the editorial staff of *Chemical Abstracts*.

[3] H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 6380 (1955).

[4] G. Wittig and W. Herwig, *Ber.*, **87**, 1511 (1954).

[5] R. West, THIS JOURNAL, **76**, 6012 (1954).

phenyl derivatives were analytically pure. The latter was obtained in a pure state and in a good yield only when refluxing was employed during the addition of I to phenyltrichlorosilane. The main impurity in 5-chloro-5-methyldibenzosilole appeared to be biphenyl. In order to minimize the formation of III, it was essential to use a large excess of alkyl- or aryltrichlorosilane. Another factor influencing the yield was the concentration of I. The yield of III increased with an increasing concentration of I.

A mediocre yield of 5,5-dichlorodibenzosilole, which was not analytically pure, was obtained by the ring closure method. Always accompanying the desired product, even when employing a large excess of silicon tetrachloride, was an appreciable amount of III. The latter compound was prepared in a good yield from two moles of I and one mole of silicon tetrachloride. The germanium analog, 5,5′-spirobi[dibenzogermole], was prepared in essentially the same manner but in lower yield.

Several unsymmetrically substituted dibenzosilole derivatives were synthesized from 5-chloro-5-*n*-dodecyldibenzosilole and appropriate organolithium compounds. 5-*n*-Dodecyl-5-phenyldibenzosilole, 5-(3-biphenylyl)-5-*n*-dodecyldibenzosilole, 5-[(dibenzylmethylsilyl)-methyl]-5-*n*-dodecyldibenzosilole (IV) and 5-*n*-dodecyl-5-*n*-hexadecyldibenzosilole (V) were prepared in good yields in this fashion. An isomer of the last compound, 5,5-di-*n*-tetradecyldibenzosilole (VI) was obtained from the reaction of 5,5-dichlorodibenzosilole with *n*-tetradecyllithium.

Both 5-chloro-5-phenyldibenzosilole and 5,5-dichlorodibenzosilole, when treated with phenyllithium, gave 5,5-diphenyldibenzosilole in yields exceeding 70%. This not only gives firmer support to the structure of the compound, prepared originally from diphenyldichlorosilane and I, but it reflects the superiority of a two-step method over a one-step cyclization reaction for preparing symmetrically substituted dibenzosilole types. In addition, this is an excellent method for obtaining unsymmetrical high molecular weight molecules.

Compounds IV, V and VI, which are liquids and volatilize at approximately 450°, may prove to be useful as lubricants or hydraulic fluids at elevated temperatures.

Experimental[6]

2,2′-Biphenylenedilithium.—To a stirred suspension of 2.38 g. (0.344 g. atom) of finely cut lithium wire in 50 ml. of dry ether was added, during 25 minutes, a solution of 2.22 g. (0.007 mole) of 2,2′-dibromobiphenyl (purchased from Reaction Products, Inc., Painesville, Ohio) in 25 ml. of ether. The reaction mixture was refluxed for 6.5 hours after stirring at room temperature for 20 minutes. A solution of 2.6 g. (0.014 mole) of benzophenone in 20 ml. of ether was added to the reaction mixture which was then worked up as described previously[3] to yield 1.68 g. (46%) of 2,2′-bis-(diphenylhydroxymethyl)-biphenyl, m.p. 254–256°, identified by mixed melting point.

5,5′-Spirobi[dibenzosilole].—Seventy-two milliliters of an ethereal solution containing 0.024 mole of 2,2′-biphenylenedilithium[3] was added, during 1 hour, to a rapidly stirred solution of 1.87 g. (0.011 mole) of silicon tetrachloride in 30 ml. of ether. The reaction mixture was stirred at room temperature for 1.5 hours and was refluxed for 3 hours. Subsequently, 50 ml. of benzene was added and the mixture was refluxed at 46° for 2 hours. Hydrolysis was effected with water. The organic layer was separated, dried over sodium sulfate, and filtered. Most of the ether was distilled and the remaining solution, on cooling, deposited 1.45 g. of product, m.p. 222–225°. The filtrate was concentrated to give an additional 0.6 g. of material; total yield, 2.05 g. (56%). Crystallization from ethanol raised the melting point of 5,5′-spirobi[dibenzosilole] to 226–227.5°.

Anal. Calcd. for $C_{24}H_{16}Si$: C, 86.72; H, 4.85; Si, 8.44; mol. wt., 332. Found: C, 86.83, 86.90; H, 4.87, 5.09; Si, 8.33; mol. wt., 344, 348.

The compound volatilized at about 460° with no apparent decomposition.[7]

5,5′-Spirobi[dibenzogermole].—An ethereal solution containing 0.05 mole of 2,2′-biphenylenedilithium was allowed to react with 5.35 g. (0.025 mole) of germanium tetrachloride as described in the preceding experiment. Following hydrolysis, 1.7 g. of ether-insoluble material together with 2.45 g. of crude product obtained from the organic layer were crystallized from ethyl acetate to give 2.77 g. (29%) of white prisms, m.p. 244.5–246°. The compound volatilized at about 470° with no apparent decomposition.

Anal. Calcd. for $C_{24}H_{16}Ge$: Ge, 19.23; mol. wt., 377. Found: Ge, 18.88; mol. wt., 418, 407.

5-Chloro-5-*n*-dodecyldibenzosilole.—Three hundred and forty-eight milliliters of an ethereal solution containing 0.10 mole of 2,2′-biphenylenedilithium[3] was diluted to 425 ml. with additional ether and was added, during 2.5 hours, to a rapidly stirred solution of 45 g. (0.148 mole) of *n*-dodecyltrichlorosilane in 600 ml. of ether. When the addition was complete, the mixture was stirred at room temperature overnight, after which the ether was distilled until the distillation temperature rose to 60°; 300 ml. of petroleum ether (b.p. 60–70°) was added and the mixture was refluxed for 1 hour before filtering, while hot, in a moisture-free atmosphere. The lithium salt was washed with several portions of petroleum ether. The solvents, together with *n*-butyl bromide, were distilled from the filtrate and the residual material was distilled at 0.012 mm. in an electrically heated air-oven to first yield 15.57 g. of *n*-dodecyltrichlorosilane, b.p. 93–96°. The main fraction distilled at 180–182° to give 33.16 g. (86%) of pale yellow liquid.

Anal. Calcd. for $C_{24}H_{33}ClSi$: Cl, 9.21; Si, 7.29. Found: Cl, 8.96, 8.94; Si, 7.25, 7.27.

In four other runs the yields varied between 73 and 85%. The run yielding 73% of product also deposited 0.5 g. of 5,5′-spirobi[dibenzosilole], m.p. 225–227°, identified by mixed melting point.

5,5-Dichlorodibenzosilole (Impure).—Two hundred and fifty-two grams (1.48 moles) of silicon tetrachloride and 0.078 mole of 2,2′-biphenylenedilithium[3] were allowed to react in the same manner as described in the preceding experiment. Following the previously described work-up of the reaction mixture, concentration and cooling of the filtrate resulted in the precipitation of 3.5 g. of material which was crystallized from ethyl acetate to give 2.89 g. (22%) of 5,5′-spirobi[dibenzosilole], m.p. 227–229°, identified by mixed melting point. The remaining petroleum ether was removed and the residual oil was distilled at 0.01 mm. to give a small amount of biphenyl followed by 7.41 g. (38%) of slightly impure 5,5-dichlorodibenzosilole, b.p. 108–110°, which crystallized on cooling. The material was very soluble in inert solvents which might have served as crystallization media. Sublimation did not result in any further purification.

Anal. Calcd. for $C_{12}H_8Cl_2Si$: Cl, 28.3; Si, 11.33. Found: Cl, 26.5; Si, 10.75.

5-Benzyl-5-chlorodibenzosilole (Impure).—The reaction of 16 g. (0.071 mole) of benzyltrichlorosilane[8] with 0.05 mole of 2,2′-biphenylenedilithium was carried out as described in the preparation of 5-chloro-5-*n*-dodecyldibenzo-

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(6) All melting points are uncorrected and all reactions involving organolithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents.

(7) Volatility was determined by inserting a melting point capillary containing a small amount of a sample into a copper block which was heated by means of a Bunsen burner. The volatilization point or range was that temperature at which either all of the liquid disappeared from the bottom of the capillary or that temperature at which rapid refluxing was observed in the top of the tube.

(8) A. Bygden, *Ber.*, **45**, 707 (1912).

silole. Distillation of the crude product at 0.01 mm. afforded two fractions; b.p. 150–160° and b.p. 160–171°. Redistillation of the two fractions gave 7.25 g. (47%) of impure product, b.p. 150–157° (0.01 mm.).

Anal. Calcd. for $C_{19}H_{15}ClSi$: Cl, 11.6. Found: Cl, 12.3.

5-Chloro-5-phenyldibenzosilole.—To a stirred, refluxing solution of 23.45 g. (0.111 mole) of phenyltrichlorosilane in 450 ml. of ether was added, during 80 minutes, 234 ml. of an ethereal solution containing 0.07 mole of 2,2′-biphenylenedilithium. Following work-up of the mixture as described for 5-chloro-5-*n*-dodecyldibenzosilole, the solvent-free residue was distilled to give phenyltrichlorosilane followed by 15 g. (73%) of pale yellow liquid, b.p. 172–175° (0.005 mm.), which crystallized and melted over the range 69–72°. Attempts to recrystallize the product were unsuccessful due to its extreme solubility in inert solvents.

Anal. Calcd. for $C_{18}H_{13}ClSi$: Cl, 12.11; Si, 9.58. Found: Cl, 11.78; Si, 9.68, 9.47.

Refluxing during the addition of the organodilithium compound seemed essential, since in two runs made at room temperature the crude yields were 55 and 58%, and the product could not be purified.

In another run in which 25.86 g. (0.122 mole) of phenyltrichlorosilane was allowed to react with 0.08 mole of 2,2′-biphenylenedilithium, while refluxing, there was obtained 1.89 g. (14%) of 5,5′-spirobi[dibenzosilole].

5-Chloro-5-methyldibenzosilole (Impure).—The procedure from the above experiment was followed for the reaction of 0.065 mole of 2,2′-biphenylenedilithium with 19.22 g. (0.128 mole) of methyltrichlorosilane. After the usual work-up, the excess methyltrichlorosilane was distilled at atmospheric pressure and the crude product was distilled at 0.007 mm. to give 12.45 g. (83%) of colorless liquid, b.p. 98–100°, which crystallized on standing to give a solid, m.p. 63–68°.

Anal. Calcd. for $C_{13}H_{11}ClSi$: Si, 12.16. Found: Si, 11.18, 11.30.

The residue from the distillation was crystallized from a mixture of benzene and ethanol to give 0.4 g. of material, m.p. 230–231°, which showed no depression in melting point when admixed with an authentic sample of 5,5′-spirobi[dibenzosilole].

When the addition of the organodilithium compound was carried out at room temperature, the yields dropped to about 60% and the product was less pure than the material obtained when refluxing was employed.

Spiro[dibenzosilole-5,1′-silacyclohexane].—One hundred milliliters of an ethereal solution containing 0.025 mole of 2,2′-biphenylenedilithium was added, during 40 minutes, to a stirred solution of 3.38 g. (0.02 mole) of 1,1-dichlorosilacyclohexane[5] in approximately 50 ml. of ether. Benzene was added and ether was distilled until the temperature rose to 50°. After stirring at this temperature for 1 hour, more ether was distilled until the temperature rose to 60°. Stirring was continued at this temperature for 16 hours. Hydrolysis was effected with water. The organic layer was separated, dried, and the solvents were distilled. The residue was chromatographed on alumina. Three fractions whose melting points ranged from 120 to 175° were collected and sublimed *in vacuo* to give 1.03 g. of sublimate melting over the range 134–140°. Recrystallization of the sublimate from petroleum ether (b.p. 60–70°) raised the melting point to 144–145.5°. The infrared spectrum of the compound in carbon disulfide solution showed a band at 8.9 μ characteristic of the dibenzosilole nucleus.

Anal. Calcd. for $C_{17}H_{18}Si$: C, 81.15; H, 7.24. Found: C, 81.03, 81.25; H, 7.37, 7.19.

The residue, 0.66 g., m.p. 180–182°, was crystallized from petroleum ether (b.p. 60–70°) to give a product melting at 183–184°. The infrared spectrum showed a band at 9.0 μ characteristic of an aryl–silicon linkage but no band at 8.9 μ. An *o*-disubstitution band was present at 13.2 μ. Infrared analysis coupled with the analytical data indicate the compound to be 1,1-bis-(2-biphenylyl)-silacyclohexane.

Anal. Calcd. for $C_{29}H_{28}Si$: C, 86.08; H, 6.97; Si, 6.95. Found: C, 86.27; H, 6.65; Si, 7.03.

5,5-Diethyldibenzosilole.—A solution of 5.02 g. (0.032 mole) of diethyldichlorosilane in 20 ml. of ether was added, during 15 minutes, to 100 ml. of a stirred ethereal solution containing 0.032 mole of 2,2′-biphenylenedilithium; 90 ml. of benzene was added and ether was distilled until the temperature reached 63°. After refluxing at this temperature for 4.5 hours, hydrolysis was effected with water. The crude product was distilled to give a material which boiled between 95–105° (0.02 mm.). Crystallization from a mixture of ethanol and water gave, after drying *in vacuo*, 1.76 g. (23%) of white needles, m.p. 60–61°.

Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.63; H, 7.61. Found: C, 80.56, 80.69; H, 7.76, 7.51.

5,5-Di-*n*-dodecyldibenzosilole.—An ethereal solution containing 0.034 mole of 2,2′-biphenylenedilithium and 13.1 g. (0.03 mole) of di-*n*-dodecyldichlorosilane was allowed to react in the manner described in the preceding experiment. Following hydrolysis and work-up of the organic layer, the oily residue was distilled under reduced pressure to give a small amount of forerun followed by a fraction boiling between 250–265° (0.02 mm.). Redistillation of this fraction yielded 4.36 g. (28%) of 5,5-di-*n*-dodecyldibenzosilole, b.p. 240–243° (0.01 mm.), $n^{20}\mathrm{D}$ 1.5246, d^{20}_{20} 0.923.

Anal. Calcd. for $C_{36}H_{58}Si$: C, 83.33; H, 11.26; *MR*, 171.5. Found: C, 83.17, 83.06; H, 11.46, 11.43; *MR*, 171.9.

5-*n*-Dodecyl-5-phenyldibenzosilole.—An ethereal solution containing 0.02 mole of phenyllithium and 5 g. (0.013 mole) of 5-chloro-5-*n*-dodecyldibenzosilole was allowed to react at room temperature. Hydrolysis and work-up of the organic layer was carried out as described in the preceding experiments. The crude product was distilled under reduced pressure to give, after collecting a small amount of forerun, 4.06 g. (73%) of pale yellow liquid, b.p. 196–198° (0.012 mm.), $n^{20}\mathrm{D}$ 1.5718, d^{20}_4 0.995.

Anal. Calcd. for $C_{30}H_{38}Si$: Si, 6.58; *MR*, 140.5. Found: Si, 6.59, 6.60; *MR*, 140.8.

5-(3-Biphenylyl)-5-*n*-dodecyldibenzosilole.—Reaction of 0.017 mole of 3-biphenylyllithium, prepared according to the method used for 2-biphenylyllithium,[9] with 6.0 g. (0.0155 mole) of 5-chloro-5-*n*-dodecyldibenzosilole was carried out as described previously. The crude product was distilled under reduced pressure to give 6.4 g. (82%) of pale yellow liquid, b.p. 242–247° (0.008 mm.), $n^{20}\mathrm{D}$ 1.5992. The compound volatilized between 430–440° with no sign of decomposition.

Anal. Calcd. for $C_{36}H_{42}Si$: Si, 5.58. Found: Si, 5.72.

5-*n*-Dodecyl-5-*n*-hexadecyldibenzosilole.—*n*-Hexadecyllithium,[10] prepared from 12.2 g. (0.04 mole) of *n*-hexadecyl bromide and 1.4 g. (0.20 g. atom) of lithium, was allowed to react with 6.0 g. (0.0155 mole) of 5-chloro-5-*n*-dodecyldibenzosilole. Following the usual work-up, the crude product was distilled at 0.005 mm. to give 5.9 g. (66%) of product, b.p. 255–260°. Redistillation yielded a yellow liquid, b.p. 230–232° (0.005 mm.), $n^{20}\mathrm{D}$ 1.5170, d^{20}_4 0.918. The compound volatilized at about 460°.

Anal. Calcd. for $C_{40}H_{66}Si$: C, 83.35; H, 11.57; Si, 4.88; *MR*, 189.9. Found: C, 83.02; H, 11.57; Si, 4.93; *MR*, 189.4.

5,5-Di-*n*-tetradecyldibenzosilole.—An ethereal solution containing 0.043 mole of *n*-tetradecyllithium[10] and 4.75 g. (0.019 mole) of impure 5,5-dichlorodibenzosilole were allowed to react as described in previous experiments. Following the usual work-up, the crude product was distilled to give several small fractions followed by 3.95 g. (36%) of pale yellow liquid, b.p. 245–250° (0.003 mm.), $n^{20}\mathrm{D}$ 1.5168, d^{20}_4 0.914. The liquid volatilized between 440–450° with slight decomposition.

Anal. Calcd. for $C_{40}H_{66}Si$: Si, 4.88; *MR*, 189.9. Found: Si, 4.73, 4.85; *MR*, 190.2.

5-[(Dibenzylmethylsilyl)-methyl]-5-*n*-dodecyldibenzosilole.—(Dibenzylmethylsilyl)-methyllithium,[11] prepared from 6.43 g. (0.0234 mole) of dibenzyl-(chloromethyl)-methylsilane and 3.15 g. (0.455 g. atom) of lithium ribbon in *n*-pentane, was allowed to react with 6.0 g. (0.0155 mole) of 5-chloro-5-*n*-dodecyldibenzosilole in 20 ml. of benzene. After refluxing the mixture for 9 hours, it was worked up as described in preceding experiments. Distillation of the

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(9) H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).

(10) Prepared in accordance with the procedure for *n*-butyllithium; H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

(11) H. Gilman and R. D. Gorsich, unpublished studies.

crude product gave 2.6 g. of forerun, b.p. up to 238° (0.005 mm.), followed by 7.3 g. (80%) of colorless liquid, b.p. 250–251° (0.005 mm.), n^{20}_{D} 1.5750, d^{20}_{4} 1.005. The compound volatilized between 460–470° with no sign of decomposition.

Anal. Calcd. for $C_{40}H_{52}Si_2$: C, 81.60; H, 5.91; Si, 9.53; *MR*, 192.9. Found: C, 81.60; H, 5.94; Si, 9.69, 9.52; *MR*, 193.7.

5,5-Dimethyldibenzosilole.—An ethereal solution containing 0.068 mole of methyllithium and 15.67 g. (0.068 mole) of 5-chloro-5-methyldibenzosilole was allowed to react at room temperature. Following work-up of the mixture, the crude product was crystallized from methanol to give 9.93 g. (70%) of colorless plates, m.p. 58–59°. The analytical sample melted at 60–61°.

Anal. Calcd. for $C_{14}H_{14}Si$: C, 79.93; H, 6.72. Found: C, 80.30, 80.45; H, 6.64, 6.66.

5,5-Diphenyldibenzosilole. (a) **From 5-Chloro-5-phenyldibenzosilole.**—A solution of 1.35 g. (0.0046 mole) of 5-chloro-5-phenyldibenzosilole in 25 ml. of ether was allowed to react with 0.008 mole of phenyllithium. The mixture was hydrolyzed with water. The crude product was crystallized from ethanol to give 1.1 g. (72%) of 5,5-diphenyldibenzosilole, m.p. 147–148°, which showed no depression in melting point when admixed with a sample prepared from diphenyldichlorosilane and 2,2'-biphenylenedilithium.[3]

(b) **From 5,5-Dichlorodibenzosilole.**—To 1.23 g. (0.0049 mole) of impure 5,5-dichlorodibenzosilole dissolved in 20 ml. of dry ether was added 18 ml. of a 0.87 *M* phenyllithium solution. The mixture was hydrolyzed and worked up as described previously to yield 1.21 g. (74%) of 5,5-diphenyldibenzosilole, m.p. 148–149°, identified by mixed melting point.

5-(2-Biphenylyl)-5-methyldibenzosilole.—2-Biphenylyllithium,[9] 0.0098 mole, and 2.86 g. (0.0124 mole) of 5-chloro-5-methyldibenzosilole were allowed to react at room temperature. The mixture was worked up in the usual fashion. The crude product was crystallized from ethanol to yield 2.8 g. (65%) of white needles, m.p. 115–116°.

Anal. Calcd. for $C_{25}H_{20}Si$: C, 86.22; H, 5.74. Found: C, 86.34; H, 5.83.

Infrared Absorption Spectra.—All of the infrared spectra of dibenzosilole compounds in carbon disulfide, in carbon tetrachloride or as liquids showed an absorption band at 8.9 μ which appears to be characteristic of the dibenzosilole nucleus. In addition, the 5,5-diaryldibenzosiloles exhibited a split band at 9.4 μ, while the 5,5-dialkyldibenzosiloles had only one band at 9.4 μ. The 5-alkyl-5-aryldibenzosiloles had sharp bands at 9.3 and 9.4 μ.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Isomerism of Some α-Hydroxysilanes to Silyl Ethers

BY A. G. BROOK

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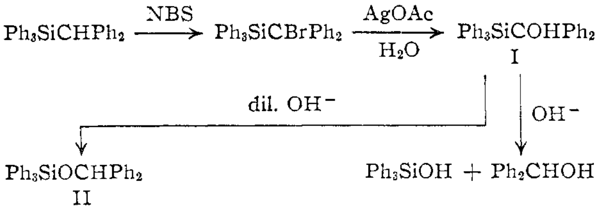
Triphenylsilyldiphenylcarbinol (I), prepared from benzhydryltriphenylsilane *via* the bromide, was found to rearrange to the isomeric ether benzhydryloxytriphenylsilane (II) in refluxing pyridine, or when treated with catalytic amounts of sodium hydroxide, sodium or sodium–potassium alloy or with sodium hydride at room temperature. The possible rearrangement of other similar α-silylcarbinols was investigated, but only diphenylcarbinols appear to rearrange under these conditions. When Compound I was treated with excess phenyllithium only tetraphenylsilane and benzhydrol were isolated.

In connection with an investigation of the reaction of triphenylsilylmetallics with benzophenone, to be reported in a forthcoming paper, it became necessary to prepare triphenylsilyldiphenylcarbinol (I). This compound, prepared from α-bromobenzhydryltriphenylsilane by treatment with aqueous silver acetate, was found to be extremely sensitive to alkali. While brief refluxing in dilute alcoholic aqueous sodium hydroxide caused complete hydrolysis to triphenylsilanol and benzhydrol, when the compound was treated briefly at room temperature with extremely dilute alkali (about 0.01 *M* for 1 minute) it was converted into the isomeric ether benzhydryloxytriphenylsilane (II) in high yield.



Subsequently it was found that compound I was converted to II more conveniently by refluxing briefly in pyridine where a practically quantitative yield was obtained, or by treating I in ether with catalytic amounts of sodium or sodium–potassium alloy or with an excess of sodium hydride.

Undoubtedly the ether II is an intermediate in the hydrolysis of I to triphenylsilanol and benzhydrol, since compound I may be converted to II under conditions where no hydrolysis occurs, although II itself is hydrolyzed readily to triphenylsilanol and benzhydrol with dilute alkali.

The generality of this reaction was studied by investigating related carbinols. Methyldiphenylsilyldiphenylcarbinol (III) readily was converted by refluxing pyridine to benzhydryloxymethyldiphenylsilane (IV) in good yield, and in view of the similar behavior of methyldiphenylsilyl- and dimethylphenylsilyl derivatives[1] it seems probable that dimethylphenylsilyldiphenylcarbinol could be similarly isomerized.

$MePh_2SiCOHPh_2$	$MePh_2SiOCHPh_2$
III	IV

However, triphenylsilyldimethylcarbinol, prepared from triphenylsilyllithium and acetone, could not be rearranged either with refluxing pyridine or when treated with sodium–potassium alloy.

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(1) We are indebted to Dr. Henry Gilman, Iowa State College, for unpublished information about these compounds.