[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Organosilicon Compounds Derived from Aryl Ethers

KATASHI OITA AND HENRY GILMAN

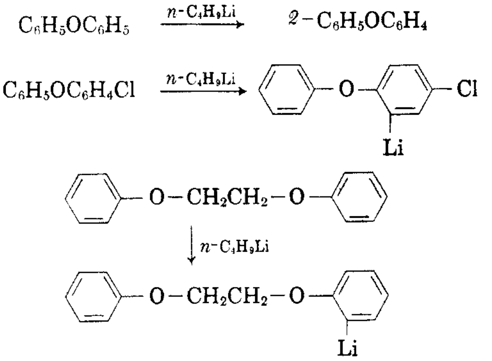
Received April 2, 1956

1. Seven new aromatic silicon compounds containing one or more ether groups were prepared. These were 2-phenoxyphenyltriphenylsilane, bis(2-phenoxyphenyl)diphenylsilane, tris(2-phenoxyphenyl)phenylsilane, tetrakis(2-phenoxyphenyl)silane, 2-phenoxy-5-chlorophenyltriphenylsilane, bis(2-phenoxy-5-chlorophenyl)diphenylsilane, and ethylene glycol phenyl *o*-triphenylsilylphenyl ether.

2. The organolithium intermediates were prepared by the metalation of aryl ethers with *n*-butyllithium. The metalation product from ethylene glycol diphenyl ether was converted to ethylene glycol phenyl *o*-carboxyphenyl ether.

3. The volatilization temperatures were determined for the organosilicon compounds synthesized.

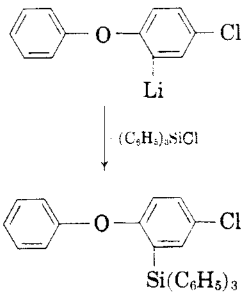
In connection with the preparation of organosilicon compounds with low melting points, high volatilization temperatures, and good thermal stabilities, the syntheses of some tetrasubstituted silanes derived from aryl ethers were effected. The ethers employed as starting materials were diphenyl ether, 4-chlorodiphenyl ether, and ethylene glycol diphenyl ether. Metalation of these ethers with *n*-butyllithium provided a convenient and an inexpensive route for the introduction of a silyl group into a position *ortho* to the ether linkage.



2-Phenoxyphenyltriphenylsilane, bis(2-phenoxyphenyl)diphenylsilane, tris(2-phenoxyphenyl)phenylsilane, and tetrakis(2-phenoxyphenyl)silane were prepared from the reaction of 2-phenoxyphenyllithium with triphenylchlorosilane, diphenyldichlorosilane, phenyltrichlorosilane, and silicon tetrachloride, respectively.

The identification of the compounds is based upon their infrared spectra and upon the structure of the reactive intermediate, 2-phenoxyphenyllithium. All of the infrared spectra had an *ortho*-disubstituted benzene band and a mono-substituted benzene band. The product from the monometalation of diphenyl ether with *n*-butyllithium has been carbonated to yield 2-phenoxybenzoic acid,[1] thereby proving that the metalated product was 2-phenoxyphenyllithium. The thermal stabilities and volatilization temperatures of 2-phenoxyphenyl substituted silanes were approximately the same as those for the analogous 4-phenoxyphenyl compounds,[2] but the melting points of the 2-isomers were higher than those of the 4-isomers.

In the 2-phenoxy-5-chlorophenyl series the compounds prepared were 2-phenoxy-5-chlorophenyltriphenylsilane and bis(2-phenoxy-5-chlorophenyl)diphenylsilane. The identity of the intermediate prepared by the metalation of 4-chlorodiphenyl ether with *n*-butyllithium has been established as 2-phenoxy-5-chlorophenyllithium by its conversion to 2-phenoxy-5-chlorobenzoic acid.[3] The melting point of 2-phenoxy-5-chlorophenyltriphenylsilane (163–163.5°) was higher than that of 2-phenoxyphenyltriphenylsilane (145–146°), but its volatilization temperature (450°) was the same. However, bis (2-phenoxy-5-chlorophenyl)diphenylsilane had a melting point of 151–152° as compared to 164–165° for bis(2-phenoxyphenyl)diphenylsilane. The volatilization temperature (500°) of bis(2-phenoxy-5-chlorophenyl)diphenylsilane, on the other hand, was higher than that (470°) for bis (2-phenoxyphenyl)diphenylsilane. The thermal stability of these compounds was very good.



The metalation of ethylene glycol diphenyl ether did not give a good yield of ethylene glycol phenyl *o*-lithiophenyl ether although Color Test II[4] became

---

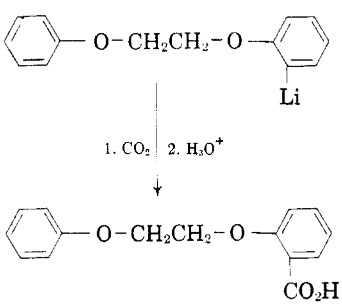
(1) Gilman and Bebb, *J. Am. Chem. Soc.*, **61**, 109 (1939).

(2) Unpublished studies by Jack J. Goodman.

(3) Langham, Brewster, and Gilman, *J. Am. Chem. Soc.*, **63**, 545 (1941).

(4) Gilman and Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

negative after stirring for 90 minutes at room temperature. Carbonation of the metalation product, followed by acidic hydrolysis, gave a monocarboxylic acid of ethylene glycol diphenyl ether which is designated as ethylene glycol phenyl *o*-carboxyphenyl ether because its infrared spectrum showed a strong absorption band at 13.3 μ, characteristic of an *ortho*-disubstituted benzene. The *ortho*-directing influence the ether linkage has in metalation reactions with *n*-butyllithium[5] supports the assigned structure. The infrared spectrum of ethylene glycol phenyl *o*-triphenylsilylphenyl ether obtained from the reaction of triphenylchlorosilane and the organolithium intermediate also indicates that metalation occurred in the *ortho* position. Absorption bands were present at 13.3 and 13.5 μ, characteristic of an *ortho*-disubstituted benzene and a monosubstituted benzene. The thermal stability of ethylene glycol phenyl *o*-triphenylsilylphenyl ether was not as good as that for 2-phenoxyphenyltriphenylsilane, but its low melting point (112–113.5°) and its volatilization temperature of 430° warrant the investigation of similar compounds.



EXPERIMENTAL[6]

2-Phenoxyphenyllithium. A slight modification[7] of the previously reported procedure[1] was employed in the preparation of 2-phenoxyphenyllithium from diphenyl ether. To a solution of 34.0 g. (0.2 mole) of diphenyl ether in 300 ml. of diethyl ether was added 0.21 mole of *n*-butyllithium in 163 ml. of an ethereal solution. The reaction mixture was stirred at ether-reflux temperature for 24 hours. Color Test II[4] was negative at the end of this period.

2-Phenoxyphenyltriphenylsilane. Into a 500-ml. flask containing 22.8 g. (0.08 mole) of triphenylchlorosilane was added 0.08 mole of 2-phenoxyphenyllithium in 233 ml. of diethyl ether. After 48 hours of stirring at the ether-reflux temperature the reaction mixture was hydrolyzed with 200 ml. of dilute hydrochloric acid, filtered, washed with water, and air-dried to yield 26.1 g. of a product melting over the range 130–138°. From two fractional recrystallizations from a mixture of benzene and petroleum ether (b.p. 77–115°) there was obtained 23.2 g. (67.4%) of 2-phenoxyphenyltriphenylsilane melting at 143.5–145°. The analytical sample obtained by recrystallization from ethyl acetate melted at 145–146°.

Anal. Calc'd for $C_{30}H_{24}OSi$: Si, 6.55. Found: Si, 6.54, 6.57.

The infrared spectrum measured as a Nujol mull had absorption bands at 8.2, 13.1, and 13.5μ, characteristic of an aryl ether, an *ortho*-disubstituted benzene, and a monosubstituted benzene, respectively.

The volatilization temperature[8] of this compound was 450°. At 480° the compound volatilized completely, leaving no residue.

Bis(2-phenoxyphenyl)diphenylsilane. Into a dry flask containing 9.75 g. (0.0384 mole) of diphenyldichlorosilane was added slowly 0.09 mole of 2-phenoxyphenyllithium in 309 ml. of diethyl ether. The reaction mixture was vigorously stirred at the ether-reflux temperature for 24 hours, hydrolyzed with 100 ml. of dilute acid, and filtered. The residue remaining after removing the ether from the ethereal phase was dissolved in a mixture of benzene and petroleum ether (b.p. 77–115°), dried over sodium sulfate, and filtered. The filtrate was concentrated, cooled, and filtered to yield 10.47 g. of white product melting at 120–121°. Fractional recrystallizations from a mixture of benzene and petroleum ether (b.p. 77–115°) gave 7.75 g. (39.5%) of bis(2-phenoxyphenyl)diphenylsilane melting at 162.5–164.5°. One recrystallization from ethyl acetate yielded an analytical sample melting at 164–165°.

Anal. Calc'd for $C_{36}H_{18}O_2Si$: Si, 5.49. Found: Si, 5.51, 5.45.

The infrared spectrum of this compound differed from that for 2-phenoxyphenyltriphenylsilane only in the position of the absorption bands attributed to an *ortho*-disubstituted benzene and a monosubstituted benzene. The absorption bands were present at 13.2 and 13.6μ.

A 1:1 mixture of bis(2-phenoxyphenyl)diphenylsilane and bis(4-phenoxyphenyl)diphenylsilane[9] (m.p. 161–162°) melted over the range 143–157°.

The volatilization temperature of the analytical sample, m.p. 164–165°, was 470°. At 500° some darkening of both the condensate and the residue was observed.

Tris(2-phenoxyphenyl)phenylsilane. Into a flask containing 4.23 g. (0.02 mole) of phenyltrichlorosilane was added carefully 0.06 mole of 2-phenoxyphenyllithium in 170 ml. of an ethereal solution. The mixture was stirred at the ether-reflux temperature for 72 hours, hydrolyzed with 100 ml. of water, filtered, washed with water, and air-dried to give 7.13 g. of white material melting over the range 150–170°. Four fractional recrystallizations, twice from a mixture of benzene and petroleum ether (b.p. 77–115°) and twice from a mixture of ethyl acetate and benzene, yielded 1.68 g. (13.7%) of pure tris(2-phenoxyphenyl)phenylsilane melting at 192–193°.

Anal. Calc'd for $C_{42}H_{32}O_3Si$: Si, 4.56. Found: Si, 4.41, 4.35.

The infrared spectrum measured as a Nujol mull had absorption bands at 13.3 and 13.5μ, indicating the presence of an *ortho*-disubstituted benzene and a nonosubstituted benzene. The band at 13.5μ was weak.

The volatilization temperature of this compound was 510°. At 540° some decomposition was observed on the capillary wall and there was a slight amount of glassy residue.

---

(5) Gilman and Morton in *Org. Reactions*, 8, 276–282 (1954).

(6) All melting points reported herein are uncorrected and all reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

(7) Gilman and Eidt, Unpublished results.

(8) Volatility was determined by inserting an unsealed melting point capillary containing a small amount of a sample into a copper block which was heated with a Bunsen flame. The volatilization temperature was arbitrarily taken as the temperature at which approximately one-eighth of an inch of condensate appeared in the capillary tube above the block.

(9) Kindly supplied by J. J. Goodman of this laboratory.

A 1:1 mixture of tris(2-phenoxyphenyl)phenylsilane with tris(4-phenoxyphenyl)phenylsilane (m.p. 149–150°)[8] melted over the range 180–190°.

Tetrakis(2-phenoxyphenyl)silane. To 3.40 g. (0.02 mole) of silicon tetrachloride were added 403 ml. of an ethereal solution containing approximately 0.083 mole of 2-phenoxyphenyllithium. The reaction mixture was stirred at the ether-reflux temperature for 72 hours, hydrolyzed with 100 ml. of water, filtered, washed with water, and air-dried to yield 3.74 g. of white powder melting at about 250°. When this material was recrystallized successively from benzene and a mixture of benzene and ethyl acetate, 1.73 g. (12.3%) of pure tetrakis(2-phenoxyphenyl)silane (m.p. 284–285°) was obtained.

Anal. Calc'd for $C_{48}H_{36}O_4Si$: Si, 3.98. Found: Si, 3.98, 3.94.

The infrared spectrum measured as a Nujol mull was practically identical with that for tris(2-phenoxyphenyl)-phenylsilane.

The volatilization temperature of this compound was 540°. No appreciable decomposition occurred until the sample was heated to 570°.

A 1:1 mixture of tetrakis(2-phenoxyphenyl)silane with tetrakis(4-phenoxyphenyl)silane (m.p. 204°)[9] melted over the range 190–240°.

2-Phenoxy-5-chlorophenyllithium. 2-Phenoxy-5-chlorophenyllithium was prepared in accordance with the previously reported procedure[3] by the reaction of 4-chlorodiphenyl ether, b.p. 125–128° (4 mm.), with *n*-butyllithium.

2-Phenoxy-5-chlorophenyltriphenylsilane. To a cooled, orange-colored, ethereal solution of 2-phenoxy-5-chlorophenyllithium prepared from 20.45 g. (0.1 mole) of 4-chlorodiphenyl ether in 300 ml. of diethyl ether and 0.1 mole of *n*-butyllithium in 82 ml. of diethyl ether was added 29.5 g. (0.1 mole) of triphenylchlorosilane. The reaction mixture was stirred at room temperature for 18 hours, and then it was hydrolyzed and an insoluble material was filtered to yield 11.3 g. of a product melting over the range 161–165°. This material was dissolved in benzene and chromatographed on activated alumina with benzene as an eluant. The solid obtained on removing the solvent from the eluate was recrystallized from petroleum ether (b.p. 77–115°) to give 7.97 g. (17.4%) of 2-phenoxy-5-chlorophenyltriphenylsilane melting at 161–162.5°. The ethereal layer from the filtrate of the hydrolyzed mixture was separated, concentrated, and filtered to yield 9.3 g. of material melting over the range 154–162°. Successive recrystallizations from a petroleum ether (b.p. 60–70°)–benzene mixture and petroleum ether (b.p. 77–115°) gave 8.83 g. (19.1%) of an analytical sample melting at 163–163.5°. A mixture melting point of the analytical sample and the material melting at 161–162.5° showed no depression.

Anal. Calc'd for $C_{30}H_{24}OSi$: Si, 6.06. Found: Si, 6.21, 6.28.

The infrared spectrum measured in a carbon disulfide solution had absorption bands at 8.2, 12.3, and 13.6μ, indicating the presence of an aryl ether, a 1,2,4-trisubstituted benzene, and a monosubstituted benzene, respectively.

This compound formed a clear, colorless melt which volatilized at 450° without any observable decomposition.

Bis(2-phenoxy-5-chlorophenyl)diphenylsilane. Into a flask containing 0.1 mole of 2-phenoxy-5-chlorophenyllithium in 250 ml. of an ethereal solution cooled to 0° was added 13.9 g. (0.055 mole) of diphenyldichlorosilane in 35 ml. of diethyl ether. The reaction mixture was stirred at room temperature for 18 hours; then it was hydrolyzed with 100 ml. of water. The ethereal layer was separated, dried over sodium sulfate, and chromatographed on activated alumina with ether as an eluant. The sticky residue left upon removing the solvent was digested with petroleum ether (b.p. 60–70°) and filtered through a sintered glass Büchner funnel to yield 3.87 g. of white powder melting at 145–148°. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 2.36 g. (7.34%) of pure bis(2-phenoxy-5-chlorophenyl)diphenylsilane melting at 151–152°.

Anal. Calc'd for $C_{36}H_{26}Cl_2O_2Si$: Si, 4.84. Found: Si, 4.81, 4.70.

The infrared spectrum of this compound determined in a carbon disulfide solution was the same as that of 2-phenoxy-5-chlorophenyltriphenylsilane with respect to the presence and position of the absorption bands.

The volatilization temperature of this compound was 500°. At 510° the sample was completely volatilized and there was no apparent decomposition.

Ethylene glycol phenyl o-carboxyphenyl ether. To a stirred solution of 5.35 g. (0.025 mole) of ethylene glycol diphenyl ether (m.p. 97–98°) in 100 ml. of diethyl ether was added over a period of 15 minutes 0.026 mole of *n*-butyllithium in 29 ml. of diethyl ether. After 90 minutes of stirring at room temperature Color Test II[4] became negative; therefore, the mixture was cooled to −72° and carbonated by pouring it jetwise upon a slurry of ether and Dry Ice. The carbonated mixture was worked up in the usual manner by adding water, stirring, separating the two phases, heating to remove the residual ether from the aqueous layer, treating with Norit-A, filtering, cooling, acidifying, filtering, and air-drying. The product which weighed 1.25 g., m.p. 50–52°, was recrystallized from a mixture of petroleum ether (b.p. 28–38°) and ether to yield 0.92 g. (14.3%) of pure ethylene glycol phenyl *o*-carboxyphenyl ether melting at 80–80.5°. The melting point did not change upon recrystallization from a mixture of petroleum ether (b.p. 60–70°) and tetrahydrofuran.

Anal. Calc'd for $C_{15}H_{14}O_4$: C, 69.5; H, 5.46; Neut. equiv., 258. Found: C, 69.79, 69.20; H, 5.67, 5.43; Neut. equiv., 258.

The infrared spectrum measured in a carbon disulfide solution had sharp absorption bands at 5.8 and 13.3μ, indicating the presence of a carbonyl group and an *ortho*-disubstituted benzene, respectively.

The ethereal layer from the carbonation was evaporated to dryness, and the resulting residue was recrystallized from petroleum ether (b.p. 60–70°) to yield 3.86 g. (72% recovery) of ethylene glycol diphenyl ether melting at 97–98°. A mixture melting point with an authentic specimen melting at 97–98° showed no depression.

Ethylene glycol phenyl o-triphenylsilylphenyl ether. Triphenylchlorosilane (29.5 g., 0.1 mole) was added to a cooled solution of ethylene glycol phenyl *o*-lithiophenyl ether prepared from 21.4 g. (0.1 mole) of ethylene glycol diphenyl ether in 400 ml. of ether and 82 ml. of an ethereal solution containing 0.1 mole of *n*-butyllithium. The reaction mixture was stirred at a room temperature for 18 hours; then it was hydrolyzed with 200 ml. of water and filtered. The ethereal phase was separated and the ether was removed. The remaining residue was digested with petroleum ether (b.p. 60–70°), filtered, and air-dried to yield 14.99 g. of white product melting over the range 75–78°. This material could not be purified by three fractional recrystallizations from petroleum ether (b.p. 60–70°) and two from ethanol. The filtrate from the original petroleum ether (b.p. 60–70°) digestion, upon concentration, yielded 9.06 g. of a material melting over the range 93–107°. This was dissolved in benzene and chromatographed on activated alumina with benzene as an eluant. The main fraction obtained from the eluates weighed 5.99 g. and melted over the range 109–114°. Three recrystallizations from petroleum ether (b.p. 60–70°) and one from ethanol gave 3.10 g. (6.55%) of pure ethylene glycol phenyl *o*-triphenylsilylphenyl ether, m.p. 112–113.5°.

Anal. Calc'd for $C_{32}H_{28}O_2Si$: Si, 5.95. Found: Si, 6.00, 6.05.

The infrared spectrum determined in a carbon disulfide solution had absorption bands at 3.3, 3.45, 13.3, and 13.5μ, characteristic of an aromatic C—H, an aliphatic C—H, an *ortho*-disubstituted benzene, and a monosubstituted benzene, respectively.

This compound volatilized at 430° with the only sign of decomposition being a slight yellowish color in the residue. At 440° volatilization was complete, but the orange color of the condensate indicated some decomposition.

Acknowledgment. The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance. They are grateful also to the Institute for Atomic Research, Iowa State College, and Dr. V. A. Fassel and Mr. R. McCord for the actual determination of the spectra.

AMES, IOWA