ing over the range 77–82°. Repeated crystallization of this material from methanol gave no pure products. An infrared spectrum of this mixture showed absorption peaks at 1090 cm.$^{-1}$ and 1070 cm.$^{-1}$, which a large number of spectra have shown to be indicative of the phenyl-germanium and phenyl-tin bonds. The melting point of the mixture is consistent with what one might expect from a mixture of triphenyl-*n*-propylgermane and triphenyl-*n*-propyltin.

With phenyllithium. To an ether solution of phenyllithium prepared from 7.85 g. (0.05 mole) of bromobenzene there was added 3.27 g. (0.005 mole) of triphenylgermyltriphenyltin. After stirring overnight the mixture was hydrolyzed by the addition of water. Filtration then gave 3.52 g. of solid melting over the range 217–223°. From the ether layer there was obtained an additional 0.65 g. of solid melting over the range 222–226°. Repeated crystallization of these materials from benzene gave no pure products. It is believed a mixture of tetraphenylgermane and tetraphenyltin is present. The infrared spectrum of this mixture also showed absorption peaks at 1090 cm.$^{-1}$ and 1070 cm.$^{-1}$ indicative of the phenyl-germanium and phenyl-tin bonds. The melting point of the mixture is consistent with the melting point that Drew and Landquist[8] found for a mixture of tetraphenylgermane and tetraphenyltin in their studies on mixture melting points of the tetraphenyls of the Group IV-B elements; they reported a melting point of 223–224° for their synthetic mixture.

With butyllithium. To a suspension of 3.27 g. (0.005 mole) of triphenylgermyltriphenyltin in 20 ml. of ether there was added rapidly 10 ml. of a 0.1*N* solution of *n*-butyllithium. After stirring 24 hr. Color Test I[9] was positive and Color Test II[10] was negative. The mixture was then carbonated by pouring it into an ether–Dry-Ice slurry, and after warming to room temperature water was added and the alkaline layer was separated. The ether layer was extracted twice with 50 ml.-portions of 5% sodium hydroxide solution, and then the combined alkaline layers were acidified by the addition of concentrated hydrochloric acid. There precipitated a solid weighing 0.6 g. which was recrystallized from ethanol to give 0.16 g. (9%) of triphenylgermanecarboxylic acid melting at 186° with the evolution of carbon monoxide. The ether layer above was filtered to give 0.75 g. of solid melting over the range 300–320°. Recrystallization of this material from benzene gave 0.35 g. of hexaphenyldigermane melting at 338–340°. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed by distillation to leave a residue which was washed with methanol to give 0.4 g. of material melting over the range 210–230°. Recrystallization of this material gave no pure products.

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[8] H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1480 (1935).

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Synthesis of Some Derivatives of Phenothiasilin, A Silicon Analog of Thiaxanthene

KATASHI OITA AND HENRY GILMAN

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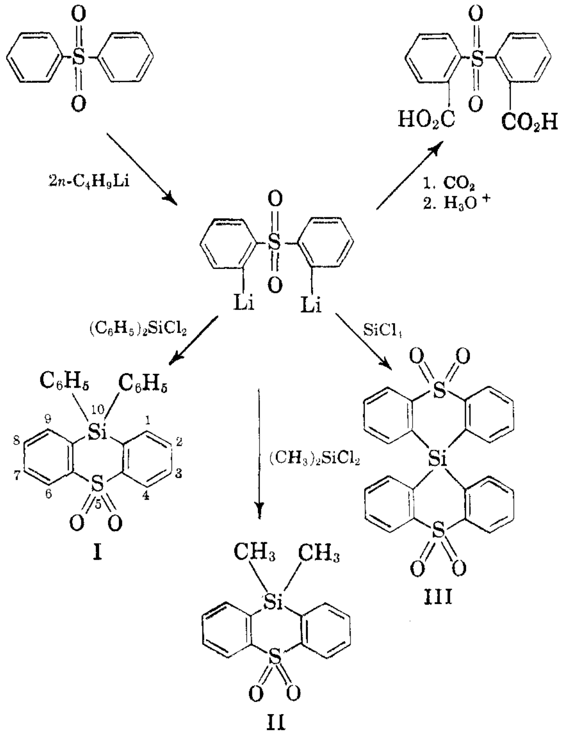
In view of the success attained in the preparation of several derivatives of phenoxasilin,[1] a silicon analog of xanthene, the synthesis of a new heterocyclic system in which silicon and sulfur were present as hetero atoms was undertaken. The compounds prepared were 10,10-diphenylphenothiasilin-5,5-dioxide (I) and 10,10-dimethylphenothiasilin-5,5-dioxide[2] (II), silicon analogs of 10,10-diphenylthiaxanthene-5,5-dioxide and 10,10-dimethylthiaxanthene-5,5-dioxide, respectively. A Fisher-Hirschfelder-Taylor model of phenothiasilin-5,5-dioxide indicated very little strain.

These phenothiasilin derivatives were prepared from the reaction of 2,2′-dilithiodiphenyl sulfone with the corresponding dichlorosilane. The dimetalation of diphenyl sulfone was carried out in accordance with the previously reported low-temperature procedure.[3] The identity of 2,2′-dilithiodiphenyl sulfone has been confirmed by its conversion to 2,2′-dicarboxydiphenyl sulfone.[3]



As in the syntheses of phenoxasilin derivatives[1]

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[1] K. Oita and H. Gilman, *J. Am. Chem. Soc.*, 79, 339 (1957).

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

[3] H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, **75**, 278 (1953).

the optimum yields are obtained if the reaction of the dilithium intermediate and the dichlorosilane is carried out under the conditions that would keep the concentration of either one or both of the reactants in the reaction mixture low. The method of simultaneous addition of the two reactants to a vigorously stirred, refluxing, reaction mixture[1] was not used with 2,2′-dilithiodiphenyl sulfone because it is stable only at a relatively low temperature. Therefore, the dichlorosilane solution was slowly added to a cooled (0° or less), extremely dilute, ethereal suspension of 2,2′-dilithiodiphenyl sulfone, and this temperature was maintained until most of the reaction had occurred. Chromatographic separation was employed to remove silanols or silanediols formed upon the hydrolysis of the unreacted or partially reacted diphenyl- and dimethyldichlorosilane.

The structure of 10,10-diphenylphenothiasilin-5,5-dioxide was supported by its infrared spectrum which showed aromatic-substitution bands at 13.1 and 13.5 μ, characteristic of an *ortho*-disubstituted benzene and a monosubstituted benzene, respectively.

An attempt was made to prepare 10,10′-spirobiphenothiasilin-5,5,5′,5′-tetroxide (III) from the reaction of two equivalents of 2,2′-dilithiodiphenyl sulfone and one of silicon tetrachloride. The desired product has not been isolated as yet.

EXPERIMENTAL[4]

10,10-Diphenylphenothiasilin-5,5-dioxide (I). To a well stirred, ethereal suspension (1156 ml.) containing 0.1 mole of 2,2′-dilithiodiphenyl sulfone prepared in accordance with the published procedure[3] was added over a period of 70 min. a solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane in 100 ml. of ether. The reaction mixture was maintained at 0° during the addition and then at an ether-reflux temperature for 12 hr. The chocolate-brown suspension was hydrolyzed with 200 ml. of water, stirred, and filtered. The ethereal layer of the filtrate was separated, dried over anhydrous sodium sulfate, and chromatographed on activated alumina with ether as an eluant. The sticky paste obtained on removing the ether from the eluate was digested with petroleum ether (b.p. 77–115°), cooled, and filtered. The resulting white solid was recrystallized once from a mixture of petroleum ether (b.p. 77–115°), once from ethyl acetate, and twice from a mixture of petroleum ether (b.p. 77–115°) and benzene to yield 3.34 g. (8.4%) of 10,10-diphenylphenothiasilin-5,5-dioxide melting at 208–209°. The analytical sample obtained by another recrystallization from a mixture of petroleum ether (b.p. 77–115°) and benzene melted at 208.5–209°.

Anal. Calcd. for $C_{24}H_{18}O_2SSi$: S, 8.05; Si, 7.05. Found: S, 8.10, 7.94; Si, 7.06, 7.20.

The infrared spectrum measured in a carbon disulfide solution had sulfone bands at 7.6 and 8.6 μ, an *ortho* disubstituted benzene band at 13.1 μ, and a monosubstituted benzene band at 13.5 μ.

The analytical sample melted at 208.5–209° to form a clear, colorless melt and volatilized[5] at 450° with some decomposition. At 490° the decomposition appeared to be complete.

10,10-Dimethylphenothiasilin-5,5-dioxide (II). To a yellow suspension of 2,2′-dilithiodiphenyl sulfone prepared from 12.6 g. (0.058 mole) of diphenyl sulfone in 580 ml. of ether and 0.116 mole of *n*-butyllithium (1.21*M* ethereal solution) was added over a period of 90 min. a solution of 7.34 g. (0.058 mole) of dimethyldichlorosilane in 50 ml. of ether. During the addition period the temperature of the reaction mixture was maintained at −20°. After stirring at approximately 0° overnight Color Test I[6] was still positive; therefore, it was stirred at room temperature for 8 hr. The reaction mixture which now gave a negative Color Test I was hydrolyzed with 150 ml. of water, stirred, filtered, and the ethereal phase was separated. This ethereal solution was dried over anhydrous sodium sulfate and chromatographed on activated alumina using ether as an eluant. The eluate upon removing the solvent yielded 12.4 g. of a white material melting over the range 78–150°. Successive recrystallizations from ethanol and from a mixture of ethanol and petroleum ether (b.p. 77–115°) gave 8.12 g. of white plates melting over the range 103–140°. When this product was recrystallized from excess ethanol, there was obtained 3.81 g. (24%) of 10,10-dimethylphenothiasilin-5,5-dioxide (m.p. 160.5–161.5°) in a form of square, platelike crystals.

Anal. Calcd. for $C_{14}H_{14}O_2SSi$: C, 61.2; H, 5.15. Found: C, 61.1, 61.2; H, 5.30, 5.11.

The infrared spectrum determined in a carbon disulfide solution and the assigned structure were compatible.

This compound upon melting formed a clear, colorless liquid which volatilized completely without decomposition at 400°. At 420° refluxing of the condensate in the capillary tube occurred but no discoloration was observed.

Attempted preparation of 10,10′-spirobiphenothiasilin-5,5,-5′,5′-tetroxide (III). The crude product from the reaction of 0.1 mole of 2,2′-dilithiodiphenyl sulfone and 0.05 mole of silicon tetrachloride was extracted with methyl ethyl ketone in a Soxhlet extraction apparatus. The extract was concentrated and the solid obtained was digested with petroleum ether (b.p. 60–70°), filtered and air-dried to yield 6.35 g. of a white powder melting over the range 230–290° with decomposition. This material was insoluble in benzene, xylene, petroleum ether (b.p. 77–115°), ethylene glycol dimethyl ether, chloroform, carbon tetrachloride, ethanol, dioxane, and glacial acetic acid. Recrystallization from a mixture of methyl ethyl ketone and petroleum ether (b.p. 77–115°) has not resulted yet in any significant amount of purification.

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[4] All melting points reported are uncorrected and all reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

(5) Volatility was determined by inserting a 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.

(6) H. Gilman and F. Schulze, *J. Am. Chem. Soc.* **47**, 2002 (1925).