

Trimethyl phosphate and styrene oxide with triphenylsilyllithium. To a solution of 7.00 g. (0.05 mole) of trimethyl phosphate, 6.01 g. (0.05 mole) of styrene oxide and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenylsilyllithium in tetrahydrofuran solution. The solution turned yellow, then orange, and became warm during the addition, which was completed in 1 hr. Color Test I was negative. The reaction mixture was hydrolyzed with concd. ammonium chloride solution and the usual chromatographic work-up was employed.

The products isolated were methyltriphenylsilane (46.0% crude, 38.3% pure) and 2-triphenylsilyl-1-phenylethanol (15.8% crude, 13.7% pure), both identified by mixture melting points.

Trimethyl phosphate and ethyl benzoate with triphenylsilyllithium. To a solution of 7.00 g. (0.05 mole) of trimethyl phosphate, 7.50 g. (0.05 mole) of ethyl benzoate, and 50 ml. of tetrahydrofuran was added slowly 0.05 mole of triphenyl-

silyllithium in tetrahydrofuran solution. The solution became warm during the addition, which was completed in 1.25 hr. Color Test I was negative. Aqueous hydrolysis followed by the usual chromatographic work-up gave methyltriphenylsilane (crude 40.1%, pure 28.8%); 0.30 g. of an unidentified solid, m.p. 183–185°; and triphenylsilanol (2.17%).

The infrared spectrum of the unknown solid showed bands to be expected for the addition-rearrangement product, phenyl(triphenylsilyl)triphenylsiloxymethane $(C_6H_5)-[(C_6H_5)_3Si][(C_6H_5)_3SiO]CH$. The silicon analysis also agrees with the structure.

Anal. Calcd. for $C_{43}H_{38}OSi_2$: Si, 8.99. Found: Si, 9.04, 8.83.

However, additional supporting evidence for the structure has not been obtained.

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

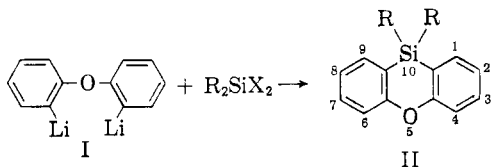
Preparation and Reactions of Some Unsymmetrical Phenoxasilin Compounds

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A number of unsymmetrical phenoxasilin compounds were prepared. The procedure involved the synthesis of the functional Si-H compound, 10-phenylphenoxasilin, from 2,2'-dilithiodiphenyl ether and phenylsilane. Reaction of the Si-H compound with a number of RLi reagents produced the desired unsymmetrical phenoxasilin compounds. The chemistry of the phenoxasilin system was explored briefly.

The first reported phenoxasilin compounds (II) were prepared by reaction of 2,2'-dilithiodiphenyl ether (I) with R_2SiX_2 or SiX_4 reagents.¹⁻³ Later



reports have described the preparation of phenoxasilin compounds by a Wurtz coupling of an *o,o'*-dibromodiphenyl ether with R_2SiX_2 ⁴ and by extended reaction of diphenylsilane with phenoxathiin.⁵

All of the compounds prepared previously contained like R groups on the silicon atom. Attempts had not been made to prepare unsymmetrically substituted phenoxasilin compounds, and it was toward this goal that the present investigation was directed. The inaccessibility of unsymmetrical

diorganosilicon halides negated the aforementioned routes to these compounds. An alternative approach was to prepare a phenoxasilin ring system containing either Si-X or Si-H at the bridge position which could then be coupled with an RLi reagent.

Such an approach was not new. 2,2'-Dilithiodiphenyl had been coupled with several monorganosilicon halides, such as methyltrichlorosilane, to produce 5-chloro-5-organodibenzosilole compounds.⁶ The reaction of these halides with organolithium reagents gave the appropriate unsymmetrical molecules. Since many difficulties were experienced in the handling and storing of the halo-silicon compounds, $RSiH_3$ reagents were substituted for $RSiX_3$ in reaction with *N*-ethyl-2,2'-dilithiodiphenylamine.⁷ The resulting cyclic Si-H compound could be handled with little risk of atmospheric hydrolysis, but still coupled readily with RLi reagents to give unsymmetrical phenoxasilin compounds. The latter reaction was chosen as the method for preparing the proposed unsymmetrical phenoxasilin compounds.

The dilithium intermediate employed for the phenoxasilin compounds had been prepared through the use of a halogen-metal interconversion reaction and was known to be of relatively high quality.

(1) C. H. S. Hitchcock, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 4537 (1957).

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

(3) H. Gilman and D. Miles, *J. Org. Chem.*, **23**, 1363 (1958).

(4) T. Yu, L. Hsu, and S. Wu, *Hua Hsueh Hsueh Pao*, **24**, 170 (1958); *Chem. Abstr.*, **53**, 6233 (1959).

(5) (a) H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957). (b) D. Wittenberg, H. A. McNinch, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 5418 (1958).

(6) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **80**, 1883 (1958).

(7) H. Gilman and E. A. Zuech, *J. Org. Chem.*, **26**, 2013 (1961).

The 2,2'-dilithiodiphenylether (I) employed in the following reactions was prepared by the dimetalation of diphenyl ether in a mixed ether-tetrahydrofuran solvent system as recently described,⁸ and some doubt still remained as to the ease of its reaction with silicon hydrides. However, this was removed with the isolation of the known compound, 10,10-diphenylphenoxasilin (III),¹ from reaction of the dilithium intermediate with diphenylsilane.

2,2'-Dilithiodiphenyl ether was allowed to react with phenylsilane to give the functional Si-H compound, 10-phenylphenoxasilin (IV). This was coupled with phenyllithium to give again the known 10,10-diphenylphenoxasilin (III) as proof of structure. Subsequent reactions of 10-phenylphenoxasilin with methyl-, *o*-tolyl-, *p*-tolyl-, *o*-biphenyl-, *p*-phenoxyphenyl-, and benzyl lithium gave the respective unsymmetrical phenoxasilin compounds V, VI, VII, VIII, IX, and X.

Only a trace of material, which gave a marginal analysis for 10-benzyl-10-phenylphenoxasilin (X), was isolated from the reaction of benzyl lithium with 10-phenylphenoxasilin. The major product isolated from the reaction was 10-hydroxy-10-

phenylphenoxasilin (XI) arising from hydrolysis of the Si-H bond. The silanol could also be prepared by direct reaction of the Si-H compound (IV) with alcoholic potassium hydroxide. Proof of structure for compound XI was obtained by warming in 98% formic acid to give the disiloxane, 10,10'-oxybis(10-phenylphenoxasilin) (XII).

10-Phenylphenoxasilin reacted spontaneously with *N*-bromosuccinimide at room temperature to give 10-bromo-10-phenylphenoxasilin (XIII) in good yield. The bromo compound did not fume in the atmosphere as does bromotriphenylsilane, possibly an indication of some steric interference in the cyclic system. However, the bromo compound was converted readily to the disilane (XIV) by refluxing with sodium in xylene.

The unsymmetrical cyclic silicon compound, 2-trimethylsilyl-10,10-diphenylphenoxasilin (XVI), was prepared by the dimetalation of 4-trimethylsilylphenyl phenyl ether (XV), followed by reaction with dichlorodiphenylsilane. As can be seen, the product was a silicon-substituted cyclic silicon compound.

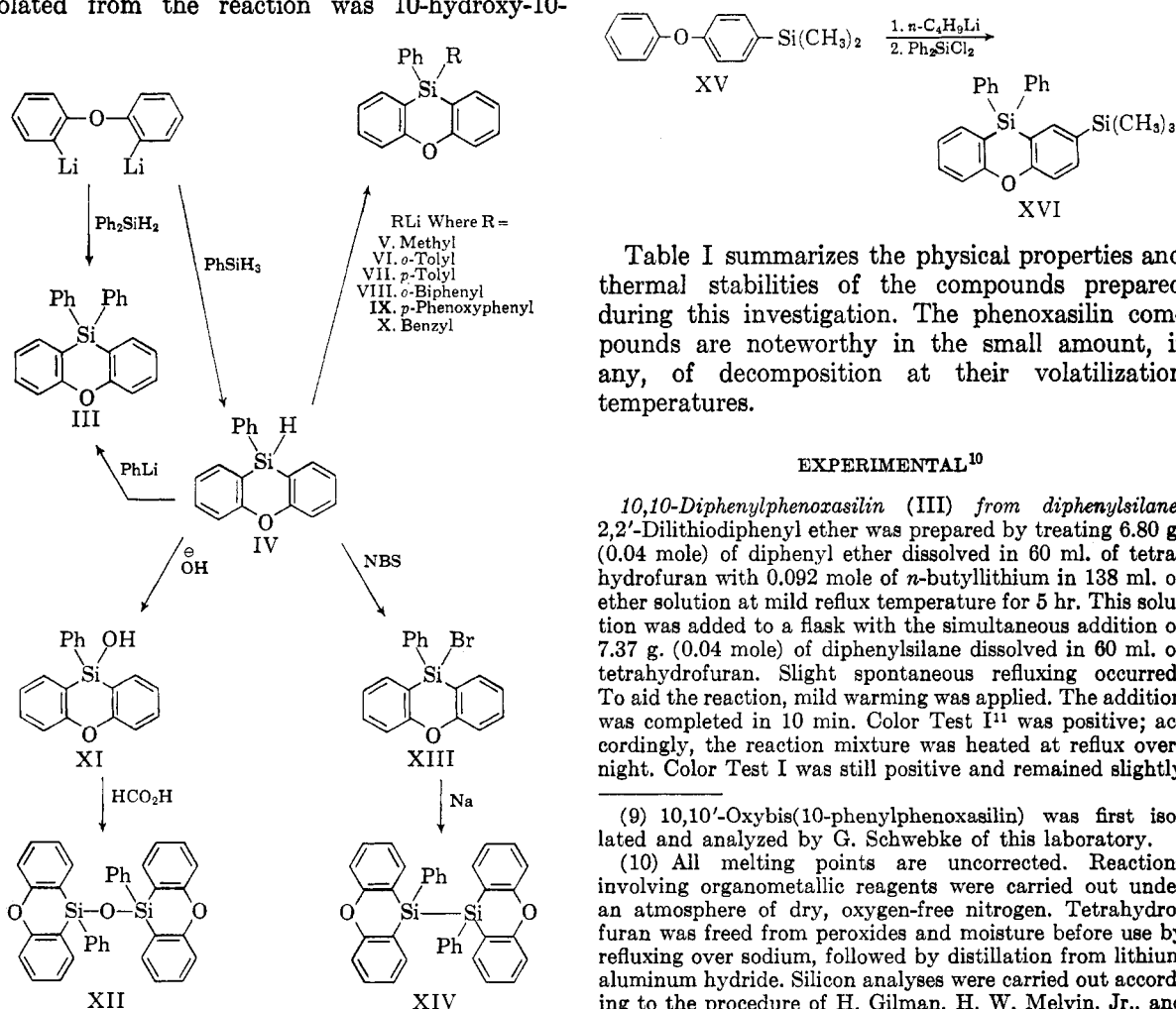


Table I summarizes the physical properties and thermal stabilities of the compounds prepared during this investigation. The phenoxasilin compounds are noteworthy in the small amount, if any, of decomposition at their volatilization temperatures.

EXPERIMENTAL¹⁰

10,10-Diphenylphenoxasilin (III) from diphenylsilane. 2,2'-Dilithiodiphenyl ether was prepared by treating 6.80 g. (0.04 mole) of diphenyl ether dissolved in 60 ml. of tetrahydrofuran with 0.092 mole of *n*-butyllithium in 138 ml. of ether solution at mild reflux temperature for 5 hr. This solution was added to a flask with the simultaneous addition of 7.37 g. (0.04 mole) of diphenylsilane dissolved in 60 ml. of tetrahydrofuran. Slight spontaneous refluxing occurred. To aid the reaction, mild warming was applied. The addition was completed in 10 min. Color Test I¹¹ was positive; accordingly, the reaction mixture was heated at reflux overnight. Color Test I was still positive and remained slightly

(9) 10,10'-Oxybis(10-phenylphenoxasilin) was first isolated and analyzed by G. Schwebke of this laboratory.

(10) All melting points are uncorrected. Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride. Silicon analyses were carried out according to the procedure of H. Gilman, H. W. Melvin, Jr., and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

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

(8) H. Gilman and W. J. Trepka, *J. Org. Chem.*, **26**, 5202 (1961).

TABLE I
 PHENOXASILIN COMPOUNDS

| Compound | Yield, % | M.P., °C. | Thermal Stability, ^a °C. |
|---|-------------|--------------|---|
| 10-Phenylphenoxasilin | 25.8 | 81-83 | Volatilizes 370-380, colorless condensate |
| 10-Methyl-10-phenylphenoxasilin | 60.0 | 56.5-58 | Volatilizes 360-370, colorless condensate |
| 10-Phenyl-10- <i>o</i> -tolylphenoxasilin | 47.2 | 116-117.5 | Microbubbles 320, volatilizes 438-444, clear distillate |
| 10-Phenyl-10- <i>p</i> -tolylphenoxasilin | 47.2 | 155-157 | Microbubbles 402, volatilizes 444-446, light yellow condensate |
| 10- <i>o</i> -Biphenyl-10-phenylphenoxasilin | 47.2 | 150-151 | Volatilizes 480-492, light brown distillate |
| 10- <i>p</i> -Phenoxyphenyl-10-phenylphenoxasilin | 19.3 | 136-137 | Volatilizes 526, light yellow distillate |
| 10-Benzyl-10-phenylphenoxasilin | Trace | 89-90 | Microbubbles 328, volatilizes 446-450, colorless distillate |
| 10-Hydroxy-10-phenylphenoxasilin | 77.4 | 124-125 | Occasional bubbles 270, rapid 310, apparent volatilization 416-418, light yellow distillate |
| 10,10'-Oxybis(10-phenylphenoxasilin) ^b | 37.3 | 189.5-191 | Volatilizes 554-556, light brown distillate |
| 10-Bromo-10-phenylphenoxasilin | 63.2 | 96-99 | — |
| 10,10'-Diphenyl-10,10'-bi(phenoxasilin) | 56.5 | 231-233 | Microbubbles 370, volatilizes 512-524, light yellow distillate |
| 2-Trimethylsilyl-10,10-diphenylphenoxasilin | 16.9 | 123-124 | Volatilizes 440-442, clear distillate |

^a 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 most of the material appeared as condensate in the capillary tube above the block. ^b See Ref. 9.

positive after another 6 hr. of refluxing. Hydrolysis was effected with water and the usual work-up was carried out. The ether extracts were evaporated under an air-jet to leave an oily solid. This was washed with petroleum ether (b.p. 60-70°) to give 5.65 g. (40.3%) of 10,10-diphenylphenoxasilin, melting range 165-173°. A recrystallization from petroleum ether (b.p. 80-110°) raised the melting point to 172-176.5°, 3.90 g. (27.8%); and a recrystallization from ethyl acetate gave 2.80 g. (20.0%) of pure product, m.p. 176-178°. A melting point of a mixture with an authentic sample¹ was undepressed.

10-Phenylphenoxasilin (IV). 2,2'-Dilithiodiphenyl ether, approximately 0.12 mole prepared by the dimetalation of diphenyl ether by *n*-butyllithium as described in the first reaction, was added to a flask with the simultaneous addition of a solution of 16.2 g. (0.15 mole) of phenylsilane¹² and 200 ml. of tetrahydrofuran. The rate of addition was adjusted in such a manner that there was always a slight excess of phenylsilane. Slight spontaneous refluxing occurred during the addition. Color Test I was deep violet. The reaction mixture was stirred overnight at room temperature; Color Test I was then a light violet. The solution was poured onto crushed ice acidified with sulfuric acid. The layers were separated, and the aqueous layer extracted several times with ether. After the ether extracts had been dried over anhydrous sodium sulfate, the solvent was stripped to leave a yellow oil, which was distilled under reduced pressure to give 2.30 g. (11.3%) of recovered diphenyl ether, b.p. 46-47° (0.08 mm.), n_D^{20} 1.5838, and another oil boiling over the range 119-127° (0.05 mm.). This oil solidified upon cooling in an ice bath. The solid was washed with methanol to give 10.9 g. (33.0%) of white solid, melting range 51-72°. A recrystallization from methanol gave 8.50 g. (25.8%) of pure 10-phenylphenoxasilin, m.p. 81-83°.

Anal. Calcd. for C₁₈H₁₄OSi: Si, 10.25. Found: Si, 10.14, 10.21. The infrared spectrum as a carbon tetrachloride solution showed the characteristic Si-H band at 4.65 μ in addition to the bands for Si-phenyl and diphenyl ether.

In order to obtain sufficient quantities of the silane for starting material, the reaction was repeated twice to give the cyclic silane in pure yields of 15.4 and 23.7%.

10,10-Diphenylphenoxasilin (III) from phenyllithium and *10-phenylphenoxasilin* (IV). An ether solution of 0.0073 mole of phenyllithium was added over a period of 10 min. to 2.00 g. (0.0073 mole) of 10-phenylphenoxasilin dissolved in 50 ml. of ether. Color Test I was slightly positive upon completion of addition, and after the solution had been stirred at room temperature for 4 hr.; however, after 1 hr. of refluxing the reaction mixture, the color test was negative. Hydrolysis was effected with water. The usual work-up gave 1.30 g. (50.6%) of 10,10-diphenylphenoxasilin melting over the range 164-178°. A recrystallization from petroleum ether (b.p. 80-110°) raised the melting point to 176-178°, 1.00 g. (39.0%) (mixture melting point identification).

10-Methyl-10-phenylphenoxasilin (V). Methylolithium, 0.0182 mole in ether solution, was brought into reaction with 5.00 g. (0.0182 mole) of 10-phenylphenoxasilin dissolved in 75 ml. of ether in essential accordance with the procedure described in the previous reaction. The product obtained, subsequent to several recrystallizations from ethanol, was 3.15 g. (60.0%) of 10-methyl-10-phenylphenoxasilin as white crystals, m.p. 56.5-58.0.

Anal. Calcd. for C₁₉H₁₆OSi: Si, 9.75. Found: Si, 9.77, 9.88. The infrared spectrum as a carbon disulfide solution was quite similar to those of the following 10-phenyl-10-tolylphenoxasilins except for a small peak at 8.14 μ which is characteristic of Si-methyl absorption.

*10-Phenyl-10-*o*-tolylphenoxasilin* (VI). The reaction of 0.0073 mole of *o*-tolyllithium¹³ with 2.00 g. (0.0073 mole) of 10-phenylphenoxasilin dissolved in 50 ml. of ether gave 1.25 g. (47.2%) of 10-phenyl-10-*o*-tolylphenoxasilin as white crystals, m.p. 116-117.5° after recrystallization from ethanol.

Anal. Calcd. for C₂₅H₂₀OSi: Si, 7.72. Found: Si, 7.58, 7.82. The infrared spectrum as a carbon disulfide solution

(12) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(13) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

showed the characteristic absorption bands for C-H aromatic and aliphatic, ether linkage, and Si-phenyl.

10-Phenyl-10-*p*-tolylphenoxasilin (VII). The reaction of an ethereal solution of 0.0073 mole of *p*-tolyllithium¹³ with a solution of 2.00 g. (0.0073 mole) of 10-phenylphenoxasilin and 50 ml. of ether in the usual manner gave 1.25 g. (47.2%) of 10-phenyl-10-*p*-tolylphenoxasilin, m.p. 155–157° after recrystallization from petroleum ether (b.p. 80–110°).

Anal. Calcd. for C₂₆H₂₀OSi: Si, 7.72. Found: Si, 7.73, 7.77.

10-(*o*-Biphenyl)-10-phenylphenoxasilin (VIII). An ethereal solution of 0.011 mole of 2-biphenyllithium was brought into reaction with 3.00 g. (0.011 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of ether to give 2.20 g. (47.2%) of 10-(*o*-biphenyl)-10-phenylphenoxasilin as a white crystalline solid, m.p. 150–151° after recrystallization from petroleum ether (b.p. 80–110°).

Anal. Calcd. for C₃₀H₂₂OSi: Si, 6.59. Found: Si, 6.47, 6.57.

10-(*p*-Phenoxyphenyl)-10-phenylphenoxasilin (IX). To 0.018 mole of *n*-butyllithium as an ethereal solution cooled to –20° was added slowly 4.53 g. (0.018 mole) of *p*-bromophenyl phenyl ether dissolved in 100 ml. of ether. The addition was adjusted at a rate to maintain the temperature at –20°. Upon completion of addition, the clear solution gave a negative Color Test II,¹⁴ but a positive Color Test I. Five grams (0.0182 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of ether was added rapidly to the cooled solution. The reaction mixture was allowed to warm to room temperature. Color Test I was mildly positive, and the reaction mixture was stirred at room temperature overnight. The color test was then negative. The solution was hydrolyzed with dilute aqueous ammonium chloride solution and the usual separation and ether extraction employed. Evaporation of the solvent left a colorless oil which solidified after standing for several days. The solid was washed with petroleum ether (b.p. 60–70°) and recrystallized several times from the same solvent to give 1.55 g. (19.3%) of 10-(*p*-phenoxyphenyl)-10-phenylphenoxasilin, m.p. 136–137°.

Anal. Calcd. for C₃₀H₂₂O₂Si: Si, 6.32. Found: Si, 6.11, 6.21.

10-Hydroxy-10-phenylphenoxasilin (XI). To 2.00 g. (0.0073 mole) of 10-phenylphenoxasilin suspended in 20 ml. of absolute ethanol was added slowly a solution of 1.51 g. (0.027 mole) of potassium hydroxide dissolved in 5 ml. of water and 15 ml. of absolute ethanol. A gas was given off during the addition, which was completed in 10 min. The reaction mixture was diluted with aqueous ammonium chloride solution. A white oil separated which was extracted with ether and the usual workup effected. Evaporation of the ether solvent left a white solid which was recrystallized several times from petroleum ether (b.p. 60–70°) to give 1.64 g. (77.4%) of 10-hydroxy-10-phenylphenoxasilin as a white crystalline solid, m.p. 124–125°.

Anal. Calcd. for C₁₈H₁₄O₂Si: Si, 9.66. Found: Si, 9.53, 9.61. The infrared spectrum as a carbon disulfide solution was quite similar to that of other phenoxasilin compounds except for an unassociated hydroxyl absorption peak at 2.70 μ .

10,10'-Oxybis(10-phenylphenoxasilin) (XII). One gram (0.0034 mole) of 10-hydroxy-10-phenylphenoxasilin was suspended in 20 ml. of 98% formic acid and the mixture was refluxed for 1 hr. Upon cooling to room temperature, the reaction mixture was filtered to leave a white solid. This was washed free of formic acid and dried to give 0.80 g. (85.1%) of crude 10,10'-oxybis(10-phenylphenoxasilin) melting over the range 167–183°. After trituration with ethanol and recrystallization from petroleum ether (b.p. 80–110°), the white solid melted at 189.5–191°, 0.35 g. (37.3%). The melting point of a mixture with a sample of solid isolated and analyzed previously in this laboratory⁹ was undepressed. The infrared spectra were superimposable.

10-Benzyl-10-phenylphenoxasilin (X). A tetrahydrofuran solution containing 0.011 mole of benzylolithium¹⁵ was added

to 3.20 g. (0.012 mole) of 10-phenylphenoxasilin dissolved in 50 ml. of ether. At first, the color of the benzylolithium solution was rapidly lost, but at the end of the addition the color of the solution was orange. Color Test I was mildly positive, but after the reaction mixture had stirred overnight at room temperature the color test was negative. Following hydrolysis with dilute aqueous ammonium chloride and the usual workup, evaporation of the ether solvent left a colorless oil which solidified upon standing. The oily solid was washed with petroleum ether (b.p. 60–70°) and recrystallized from the same solvent to give 0.95 g. (28.0%) of 10-hydroxy-10-phenylphenoxasilin, m.p. 124–125.5°. The melting point of a mixture with an authentic specimen was not depressed, and the infrared spectrum was superimposable with that of an authentic sample.

Evaporation of the mother liquor left a small amount of oil which crystallized upon standing. The solid was recrystallized from ethanol to give a trace of white crystals believed to be 10-benzyl-10-phenylphenoxasilin, m.p. 89–90°.

Anal. Calcd. for C₂₆H₂₀OSi: C, 82.30; H, 5.53. Found: C, 82.50, 82.60; H, 5.86, 6.01.

10-Bromo-10-phenylphenoxasilin (XIII). To a solution of 5.00 g. (0.018 mole) of 10-phenylphenoxasilin dissolved in 100 ml. of carbon tetrachloride was added, in small portions, 3.20 g. (0.018 mole) of *N*-bromosuccinimide. The solution became yellow in color and quite warm, a water-bath being used to control the temperature. The reaction mixture was stirred for 3 hr. at room temperature. At the end of that period, the mixture was filtered under nitrogen to give 1.50 g. (84.2%) of succinimide, m.p. 121–125° (mixture melting point). The red filtrate was distilled, using the reduced pressure of a water aspirator, to leave a brown residue. The solid was recrystallized from petroleum ether (b.p. 80–110°) to give 3.35 g. (52.6%) of 10-bromo-10-phenylphenoxasilin as a light yellow solid, m.p. 96–99°.

Anal. Calcd. for C₁₈H₁₃BrOSi: Si, 7.96. Found: Si, 8.18, 8.18. The infrared spectrum as a carbon tetrachloride solution was identical with that of the starting material except for the absence of the Si-H absorption peak.

The recrystallization solvent was hydrolyzed with water and worked up in the usual manner to give, after recrystallization from petroleum ether (b.p. 80–110°), 0.35 g. (6.68%) of 10-hydroxy-10-phenylphenoxasilin, m.p. 123–124° (mixture melting point).

The reaction was repeated to give a yield of 63.2% of 10-bromo-10-phenylphenoxasilin, m.p. 96.5–99.0°; and 24.9% of 10-hydroxy-10-phenylphenoxasilin.

To provide added proof for the structure of the bromo compound, 2.00 g. (0.0057 mole) was treated with an ethereal solution of 0.0057 mole of phenyllithium. The reaction was carried out and worked up in the same manner as described for the reaction of 10-phenylphenoxasilin with phenyllithium. There was obtained 0.70 g. (35.3%) of crude 10,10-diphenylphenoxasilin melting over the range 149°– to a turbid liquid. Two recrystallizations from petroleum ether (b.p. 80–110°) raised the melting point to 177–179° (mixture melting point). 10-Hydroxy-10-phenylphenoxasilin, 0.55 g. (33.5%), was also isolated.

10,10'-Diphenyl-10,10'-bi-(phenoxasilin) (XIV). To a solution of 5.00 g. (0.014 mole) of 10-bromo-10-phenylphenoxasilin and 75 ml. of xylene was added 0.35 g. (0.015 g.-atom) of sodium cut into several small pieces. The mixture was heated at reflux for 24 hr. After the brown solution had cooled, it was poured into ethanol and the ethanol was diluted with an equal volume of water. A small amount of insoluble material was filtered off, but, since it partially dissolved upon washing with benzene, it was added to the organic layer. The layers were separated and the aqueous layer was extracted several times with benzene. Evaporation of the solvent left a yellow solid which was slurried with ethanol to give 3.55 g. (91.2%) of crude 10,10'-diphenyl-

(14) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **60**, 1847 (1940).

(15) H. Gilman, H. A. McNinch, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

10,10'-bi(phenoxasilin), melting range 206–225°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) and from petroleum ether (b.p. 80–110°) gave 2.20 g. (56.5%) of pure product, m.p. 231–233°.

Anal. Calcd. for $C_{38}H_{26}O_2Si_2$: Si, 10.28. Found: Si, 10.15, 10.22. The infrared spectrum as a carbon disulfide solution was superimposable with that of 10,10-diphenylphenoxasilin except for the band at 14.45 μ , which is smaller and not split into a doublet.

2-Trimethylsilyl-10,10-diphenylphenoxasilin (XVI). To 10.0 g. (0.041 mole) of 4-trimethylsilylphenyl phenyl ether dissolved in 60 ml. of tetrahydrofuran and cooled to ice-bath temperature was added slowly an ether solution containing 0.092 mole of *n*-butyllithium. The light yellow solution gave a positive Color Test II. The ice-bath was removed, and, after the solution had stirred at room temperature for 1 hr., mild warming was applied for 15 hr. Color Test II was then negative, but Color Test I was positive. The reaction mixture after it had been poured jet-wise through a glass wool plug into a dried, nitrogen swept addition funnel, was added dropwise to a flask with the simultaneous addition of 10.4 g. (0.041 mole) of dichlorodiphenylsilane dissolved in 50 ml. of tetrahydrofuran. Spontaneous refluxing occurred, and Color Test I was negative upon completion of addition. Following hydrolysis with dilute aqueous ammonium chlo-

ride solution, the usual work-up was carried out to yield a brown oil. This was distilled at reduced pressure to give 8.05 g. of oil boiling over the range 185–198° (0.05 mm.). Treatment of the oil with methanol gave 3.15 g. (18.2%) of a white solid, melting range 114–120°. After several recrystallizations from methanol, the melting point of the 2-trimethylsilyl-10,10-diphenylphenoxasilin was raised to 123–124°, 2.95 g. (16.9%).

Anal. Calcd. for $C_{27}H_{26}OSi_2$: C, 76.70; H, 6.20. Found: C, 76.85, 77.00; H, 5.75, 5.83.

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

Studies in Organosilicon Chemistry. XLIV. Synthesis and Infrared Studies of Analogous Heterocyclic Compounds of Periodic Column IV-B

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The synthesis of five compounds, 1,1-diphenylcyclohexane and its 1,1-analogs of silicon, germanium, tin, and lead, has been completed. Their infrared patterns are presented, together with a critique. Bromination of cyclopentamethylene-diphenylstannane yields cyclopentamethylenedibromostannane. Iodination removes only one phenyl group. Similar action by anhydrous hydrogen bromide gas yields cyclopentamethylenedibromostannane.

In a paper published by Oshesky and Bentley,¹ the use of infrared absorption data for the identification of a series of silacyclohexane compounds was based on a group of absorption bands appearing characteristically in both the rock salt and cesium bromide regions of the infrared. Tentatively these were assigned as being attributable to the heterocyclic system. A cursory investigation was undertaken to test the hypothesis that a similar set of correlations would hold for the identification of a hetero-ring system involving the remaining Group IVB elements, germanium, tin, and lead.

Our investigation, limited only to the rock salt region (4000–650 cm^{-1}) was carried out on the six-membered, heterocyclic system shown in Fig. 1.

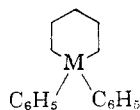


Fig. 1. M = C, Si, Ge, Sn, Pb

In addition to the characteristic metal-phenyl absorptions² between 1125 and 1050 cm^{-1} , there occurred a series of three absorption bands at 2650, 990–965, and 910 cm^{-1} which very favorably agreed with those observed for the silacyclohexane system (Table I). It is interesting to note that 1,1-diphenylcyclohexane, with the exception of the weak absorption band at 2650 cm^{-1} , showed no

TABLE I
ABSORPTION DATA

| Compound | Frequency, Absorption, cm^{-1} | | |
|------------------------|----------------------------------|---------|---------|
| $(CH_2)_5C(C_6H_5)_2$ | 2640 (w) ^a | — | 905 (m) |
| $(CH_2)_5Si(C_6H_5)_2$ | 2640 (w) | 987 (s) | 908 (s) |
| $(CH_2)_5Ge(C_6H_5)_2$ | 2640 (w) | 987 (s) | 913 (s) |
| $(CH_2)_5Sn(C_6H_5)_2$ | 2640 (w) | 970 (s) | 907 (s) |
| $(CH_2)_5Pb(C_6H_5)_2$ | 2650 (w) | 965 (s) | 909 (s) |
| $(CH_2)_5SnBr_2$ | 2650 (w) | 970 (s) | 910 (s) |
| $(CH_2)_5Sn(I)C_6H_5$ | 2650 (w) | 970 (s) | 910 (s) |
| $(CH_2)_5SnCl_2$ | 2650 (w) | 990 (s) | 910 (s) |

^a w = weak, m = medium, s = strong.

(1) G. D. Oshesky and F. F. Bentley, *J. Am. Chem. Soc.*, 79, 2057 (1957).

(2) J. G. Noltes, M. C. Henry, and M. J. Janssen, *Chem. & Ind.*, 298 (1959).