[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of Some Silicon Hydrides with Sulfur-containing Heterocycles and Related Compounds[1]

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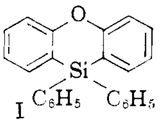
From the reaction of diphenylsilane with phenoxathiin, phenothiazine, 10-ethylphenothiazine and thianthrene, compounds were isolated in which the sulfur atom of the heterocycle is replaced by the diphenylsilylene group. Some derivatives of 10,10-diphenylphenazasiline were prepared. Diphenylsilane was found to reduce 10-ethylphenothiazine-5-oxide to the corresponding sulfide. Dibenzylsilane de-ethylated 10-ethylphenothiazine rather than replaced the sulfur atom. Triphenylsilane underwent disproportionation in the presence of hydrogen sulfide, whereas with *p*-thiocresol, hydrogen and triphenyl-(*p*-tolylthio)-silane were formed.

The carbon–sulfur bond has been cleaved by many different methods.[2] Thus benzyl phenyl sulfide was cleaved with aluminum bromide[3a] and with chlorine,[3b] and with sodium.[4] Phenyl alkyl sulfides react differently[5] with *n*-butyllithium, than does diphenyl sulfide with phenyllithium.[6] Allyl *p*-tolyl sulfide on heating rearranges to 2-allyl-4-methylthiophenol.[7]

The cleavage of the carbon–sulfur bond in some cyclic aromatic compounds has been accomplished by the use of reducing agents. It is possible to eliminate sulfur from phenothiazine by heating with copper to yield carbazole.[8] Treatment of phenothiazine with Raney nickel gave diphenylamine.[9] *m*-Carboxydiphenylamine was formed from 2-carboxyphenothiazine.[10] Whereas dibenzothiophene,[11] dibenzothiin[12] and 10-substituted phenothiazines[13] were not attacked by lithium aluminum hydride, diphenyl sulfoxide was reduced to diphenyl sulfide.[14] Dibenzothiophene has been cleaved by lithium in dioxane[15] and in tetrahydrofuran.[16] The carbon–sulfur bond in thianthrene was attacked by lithium in tetrahydrofuran.[16] Related reactions occur with phenoxathiin, phenothiazine and N-substituted phenothiazines.[17]

Though cleavages of sulfur-containing heterocycles have been recorded, there is to our knowledge no reported instance in which the sulfur atom has been replaced by an R_2Si, RSiH or SiH_2 grouping. We found that upon heating diphenylsilane with certain sulfur-containing heterocycles, hydrogen sulfide was evolved slowly and, from the crude reaction mixtures, compounds were isolated in which the sulfur atom is replaced by the diphenylsilylene group.

Refluxing an equimolar mixture of diphenylsilane and phenoxathiin for 6 days resulted in the formation of 10,10-diphenylphenoxasilin[18] (I) in a 2% yield. The compound was shown to be identical with an authentic sample obtained from the reaction of 2,2′-dilithiodiphenyl ether and dichlorodiphenylsilane.[19]



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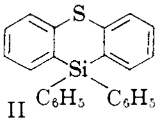

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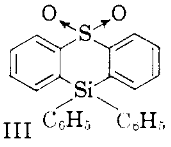

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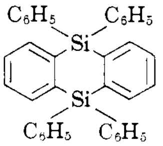

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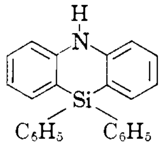

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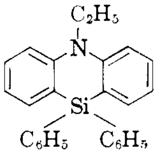

VI

From the reaction of diphenylsilane with thianthrene (1:1 ratio) after heating for 3.5 days at 250–260°, 10,10-diphenylphenothiasilin (II) was obtained in a 4.7% yield. The structure of the compound was confirmed by oxidation with hydrogen peroxide in acetic acid, which yielded 10,10-diphenylphenothiasilin-5-dioxide (III), a compound which had been prepared previously from the reaction of 2,2′-dilithiodiphenyl sulfone with dichlorodiphenylsilane.[20] An attempt to isolate 5,5,10,10-tetraphenylsilanthrene (IV) from the reaction of diphenylsilane and thianthrene in a 2:1 ratio has so far been unsuccessful; only compound II was isolated in 4% yield. Thianthrene-5-dioxide[21] also evolved hydrogen sulfide on heating with diphenylsilane, but attempts to isolate compound III from the reaction mixture were unsuccessful.

Only traces of hydrogen sulfide were evolved when a mixture of diphenylsilane and dibenzothio-

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[1] A preliminary account was reported in a communication to the editor, see H. Gilman and D. Wittenberg, THIS JOURNAL, **79**, 6339 (1957).

[2] For a detailed discussion see D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).

[3] (a) D. P. Harnish and D. S. Tarbell, THIS JOURNAL, **70**, 4123 (1948); (b) T. Zincke, *Ber.*, **44**, 769 (1911).

[4] P. Shorigin, *ibid.*, **58**, 2028 (1925).

[5] H. Gilman and F. J. Webb, THIS JOURNAL, **71**, 4062 (1949).

[6] A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker and G. Borth, *Ann.*, **557**, 62 (1945).

[7] G. D. Hurd and H. Greengard, THIS JOURNAL, **52**, 3356 (1930).

[8] A. Goke, *Ber.*, **20**, 232 (1887).

[9] K. A. Shah, B. D. Tilak and K. Venkataroma, *Proc. Indian Acad. Sci.*, **28A**, 142 (1948) [*C. A.*, **44**, 3958 (1950)].

[10] R. Baltzly, M. Harfenist and F. J. Bebb, THIS JOURNAL, **68**, 2673 (1946).

[11] F. G. Bordwell and W. H. McKellin, *ibid.*, **73**, 2251 (1951).

[12] Ahmed Mustafa and Mustafa Kama Hilmy, *J. Chem. Soc.*, 1343 (1952).

[13] F. Challenger, B. Fishwick and J. L. Holmes, *Chemistry & Industry*, 519 (1952).

[14] R. F. Nystrom, unpublished work, through W. G. Brown, in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 508.

[15] H. Gilman and D. L. Esmay, THIS JOURNAL, **75**, 2947 (1953).

[16] H. Gilman and J. J. Dietrich, *J. Org. Chem.*, **22**, 851 (1957).

[17] H. Gilman and J. J. Dietrich, THIS JOURNAL, **80**, 380 (1958).

[18] The names and numbering systems used herein were recommended by the editorial staff of "Chemical Abstracts."

[19] K. Oita and H. Gilman, THIS JOURNAL, **79**, 339 (1957); C. H. S. Hitchcock, F. G. Mann and A. Vanterpool, *J. Chem. Soc.*, 4537 (1957).

[20] K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957).

[21] H. Gilman and D. R. Swayampati, THIS JOURNAL, **77**, 5946 (1955).

phene was refluxed for 6 days. In the subsequent work-up, the heterocycle was recovered in 84% yield. None of the expected 5,5-diphenyldibenzosilole[22] was isolated.

A mixture of diphenylsilane and phenothiazine was refluxed for 3 days and 10,10-diphenylphenazasiline (V) was isolated in a 1.2% yield. Since it is possible to obtain carbazole from the reaction of phenothiazine with metallic copper,[8] we tried to catalyze the sulfur–silicon replacement reaction with copper powder. In addition, the copper was expected to capture some of the hydrogen sulfide and in this manner reduce secondary reactions. The yield of compound V, however, was not improved. The copper powder was recovered essentially unchanged, although the evolution of hydrogen sulfide was observed to be much slower than in experiments wherein no copper was present.

The preparation of 10-substituted phenothiazine derivatives by N-metalation with *n*-butyllithium followed by addition of the appropriate halide has been reported.[23] Excess *n*-butyllithium has been found to metalate phenothiazine also in the 1-position. When a reaction time of 40 hours was employed, carbonation gave 1-carboxyphenothiazine in 52% yield.[24] In order to avoid a similar metalation in the benzene nuclei of 10,10-diphenylphenazasiline, the preparation of N-substituted derivatives of the latter compound was carried out in such a manner that excess of the derivatizing agent was added immediately after the addition of *n*-butyllithium was complete. By this method, with benzoyl chloride, 5-benzoyl-10,10-diphenylphenazasiline was obtained in a 75% yield. Derivatization of the 5-lithio-10,10-diphenylphenazasiline intermediate with methyl sulfate and with ethyl sulfate gave good yields of 5-methyl- and 5-ethyl-10,10-diphenylphenazasiline (VI), respectively. The latter compound also was obtained in a 7.2% yield from the reaction of diphenylsilane with 10-ethylphenothiazine after 6 days at reflux temperature.

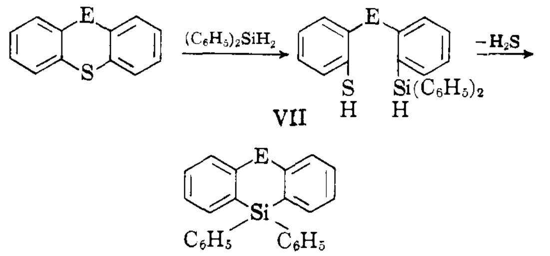
The sulfur- and nitrogen-containing heterocyclic silanes promised to be of value as built-in antioxidant functions, in high temperature lubricant studies. It seemed of interest to explore the formation of related types and derivatives.

Since highest yields of the silicon heterocycle had been obtained in the reaction of diphenylsilane with 10-ethylphenothiazine, the latter compound was allowed to react with dibenzylsilane at reflux temperature. However, attempts to isolate 5-ethyl-10,10-dibenzylphenazasiline from the reaction mixture were unsuccessful. In addition to small amounts of starting material and unidentified products, phenothiazine was obtained in a 10% yield. This indicated that de-ethylation of the heterocycle had taken place rather than a replacement of the sulfur atom. Subsequent experiments to de-methylate N-methyldiphenylamine by refluxing with dibenzylsilane, however, were unsuccessful. Neither the reaction mixture nor any of the fractions obtained in its distillation showed infrared absorption bands characteristic of the N–H group.

Whereas from the reactions of diphenylsilane with sulfur-containing heterocycles, the latter were recovered in yields ranging from 20–50%, the silicon hydride was consumed completely in most reactions. As by-products, triphenylsilane was obtained in 5–16% yields, together with small amounts of tetraphenylsilane. The formation of these compounds can be explained by a disproportionation reaction of diphenylsilane.[25]

Since hydrogen sulfide was evolved on exposure of the crude reaction mixtures to moisture and on chromatography of the distillation fractions on alumina, the formation of Si–S–H or Si–S–Si type by-products is postulated. Such products might have resulted as a consequence of a reaction between hydrogen sulfide and diphenylsilane or triphenylsilane. In order to investigate the action of hydrogen sulfide on silicon hydrides, triphenylsilane was allowed to react with hydrogen sulfide at 200–210°. Although not isolated in a pure state, the formation of compounds containing Si–S bonds was established. In addition, it was found that hydrogen sulfide catalyzes the disproportionation of triphenylsilane.[26] Diphenylsilane and tetraphenylsilane were isolated from the reaction mixture.

It seemed desirable to throw light on the possible course of the sulfur–silicon replacement reaction. It was assumed that in a first step, the carbon–sulfur bond of the heterocycle is cleaved by diphenylsilane with the formation of a triphenylsilane-thiophenol type intermediate VII, which subsequently loses hydrogen sulfide to form the silicon heterocycle.



The formation of a carbon–silicon bond by hydrogen sulfide elimination between a thiophenol and a silicon hydride had not been reported previously. As a simple model experiment, the reaction between triphenylsilane and *p*-thiocresol was investigated. After heating an equimolar mixture for 5 days at 220–230°, however, none of the expected triphenyl-*p*-tolylsilane was isolated, but triphenyl-(*p*-tolylthio)-silane (VIII) was obtained in a 69% yield. The structure of the compound was established by hydrolysis with alkali, which gave *p*-thiocresol, triphenylsilanol and hexaphenyldisiloxane. Additional confirmation of the structure

$$(C_6H_5)_3Si—S—C_6H_4CH_3—p$$
VIII

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

[23] H. Gilman and D. A. Shirley, *ibid.*, **66**, 888 (1944).

[24] H. Gilman, D. A. Shirley and P. R. Van Ess, *ibid.*, **66**, 625 (1944).

[25] H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958). This paper also gives references to a variety of related disproportionation reactions involving silanes.

[26] The catalyzed and non-catalyzed disproportionation of various silicon hydrides will be reported later.

was obtained from the reaction of VIII with triphenylsilyllithium in tetrahydrofuran,[27] which yielded hexaphenyldisilane in an 82% yield and *p*-thiocresol in a 57% yield. The formation of the thiosilane has its analog in the recently described preparation of certain alkoxysilanes from alcohols and appropriately substituted silicon hydrides.[28] The formation of a silicon–sulfur rather than a silicon–carbon bond in the example investigated, however, does not exclude the possible formation of an intermediate of type VII in the replacement reactions. It is also suggested that the reaction may actually involve addition of Si–H to one aryl group as a first step followed by elimination of H–S. If this process is repeated, the observed products would be obtained. The reaction of appropriately substituted thiophenols with silicon hydrides has to be investigated before final conclusions can be drawn.

Diphenylsilane also was allowed to react with 10-ethylphenothiazine-5-oxide. At temperatures of 200–250°, the sulfoxide was reduced in 76% yield to the corresponding sulfide, 10-ethylphenothiazine. Related reductions of organic compounds, not containing sulfur, by means of some Si–H types have been reported recently.[29]

Experimental[30]

10,10-Diphenylphenoxasilin.—A mixture of 30 g. (0.15 mole) of phenoxathiin and 27.6 g. (0.15 mole) of diphenylsilane was refluxed without added solvent for 6 days, at which time the evolution of hydrogen sulfide had essentially ceased. The reaction mixture was subsequently distilled at reduced pressure. No diphenylsilane was recovered. The first fraction (15.3 g., boiling over the range 98–125° (0.15 mm.)) contained mainly unchanged phenoxathiin, as indicated by its infrared spectrum. The spectrum of the next fraction (3.0 g., boiling over the range 135–175° (0.15 mm.)) indicated triphenylsilane as the main product. The fraction, 13.4 g., boiling over the range 175–240° (0.08 mm.) was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina, using petroleum ether as an eluent. A colorless oil was obtained, which solidified partially. The crystals melted to a turbid liquid at 145–160°, which became clear at 200°. Refluxing with a small amount of petroleum ether left a trace of crude tetraphenylsilane, m.p. 210–227°. The solution was concentrated and cooled to give 1.05 g. (2%) of impure 10,10-diphenylphenoxasilin, m.p. 160–168°. Eight recrystallizations from the same solvent raised the melting point to 178–179°. The compound gave no melting point depression with an authentic sample.[19] The infrared spectra were superimposable.

10,10-Diphenylphenothiasilin.—A mixture of 17.5 g. (0.081 mole) of thianthrene and 29.8 g. (0.162 mole) of diphenylsilane was refluxed without added solvent for 60 hours, at which time the evolution of hydrogen sulfide had essentially ceased. The reaction mixture was subsequently distilled at reduced pressure. The forerun, 0.5 g. of a colorless liquid boiling over the range 50–155° (3 mm.), crystallized partially. The crystals were washed with a few drops of petroleum ether and identified as biphenyl, m.p. 69–71°. The fraction distilling over the range 155–180° (3 mm.) was treated with petroleum ether (b.p. 60–70°) to separate 2.5 g. (14.3%) of thianthrene, m.p. 152–154°. Chromatography of the mother liquor on alumina, using the same solvent as an eluent, gave 7.0 g. (16.6%) of triphenylsilane. The fraction boiling over the range 185–235° (0.01 mm.) was dissolved in hot petroleum ether and chromatographed on alumina. Elution with the same solvent gave a colorless product. Treatment of this product with boiling ethanol left 0.5 g. of crude tetraphenylsilane. Concentration of the mother liquor gave 1.2 g. (4.05%) of crude *10,10*-diphenylphenothiasilin, m.p. 151–153°. Three recrystallizations from ethanol raised the melting point to 157–158°.

Anal. Calcd. for $C_{24}H_{18}SSi$: Si, 7.66. Found: Si, 7.72.

No crystalline product was isolated from the distillation residue.

When in a second experiment a mixture of 21.6 g. (0.1 mole) of thianthrene and 18.4 g. (0.1 mole) of diphenylsilane was heated for 3.5 days at 250–260° and worked up in the manner described above, 1.6% of diphenylsilane and 50% of thianthrene were recovered. Crude triphenylsilane was found in a 20% yield and 10,10-diphenylphenothiasilin in a 4.7% yield (1.7 g.). No other crystalline product was isolated.

10,10-Diphenylphenothiasilin has an interesting thermal stability, volatilizing at 460° with only slight decomposition.

10,10-Diphenylphenothiasilin-5-dioxide. A. By Oxidation of 10,10-Diphenylphenothiasilin.—A suspension of 0.3 g. of 10,10-diphenylphenothiasilin in a mixture of 5 ml. of acetic acid and 1 ml. of 30% hydrogen peroxide was heated for one hour on a steam-bath. Then a mixture of 2 ml. of acetic acid and 1 ml. of 30% hydrogen peroxide was added and the mixture heated for one additional hour. Removal of the solvents and recrystallization of the residue from ethanol gave 0.2 g. (64%) of 10,10-diphenylphenothiasilin-5-dioxide, m.p. 198–202°. Two recrystallizations from the same solvent raised the melting point to 208–209°. A mixed melting point with an authentic sample[20] was undepressed. The infrared spectra were superimposable.

B. From Diphenylsilane and Thianthrene-5-dioxide (**Attempted**).—Hydrogen sulfide was evolved when a mixture of 18.4 g. (0.1 mole) of diphenylsilane and 24.8 g. (0.1 mole) of thianthrene-5-dioxide[21] was heated at reflux temperature without added solvent. After refluxing for 18 hours, the mixture had turned to a black tar. Distillation at reduced pressure led to the recovery of 36% of the thianthrene-5-dioxide. A small amount of a higher boiling fraction was obtained, while the main part remained as a black distillation residue. Attempts to isolate any crystalline product *via* chromatography and crystallization were unsuccessful.

In a second reaction, the evolution of hydrogen sulfide ceased when the starting materials were heated for 24 hours at 240°. The work-up gave a similar result.

Reaction of Dibenzothiophene with Diphenylsilane.—A mixture of 9.2 g. (0.05 mole) of dibenzothiophene and 9.2 g. (0.05 mole) of diphenylsilane was refluxed for 6 days. During this time, only traces of hydrogen sulfide were evolved. The reaction mixture was worked up by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) gave a product, which after recrystallization from the same solvent yielded 7.7 g. (84%) of dibenzothiophene, m.p. 92–96°. Cyclohexane and benzene eluted 1.5 g. (16%) of impure tetraphenylsilane, m.p. 215–228°, identified by its infrared spectrum. No other crystalline compound was isolated.

10,10-Diphenylphenazasiline. First Experiment.—A mixture of 20.1 g. (0.1 mole) of phenothiazine and 18.4 g. (0.1 mole) of diphenylsilane was refluxed for 3 days, at which time the evolution of hydrogen sulfide had essentially ceased. The reaction mixture was worked up by distillation at reduced pressure. The spectrum of the first fraction (0.5 g., boiling over the range 140–165° (2.5 mm.)) indicated the presence of triphenylsilane as the main product. The next fraction (8.5 g., boiling over the range 165–210° (2.5 mm.)) was recrystallized from petroleum ether (b.p. 60–70°) and yielded 4.0 g. (20%) of phenothiazine, m.p. 180–182° (mixed m.p.). The highest boiling fraction

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(27) H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958).

(28) M. F. Shostakovskii, D. A. Kochkin, V. L. Vinogradov and V. A. Neterman, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1269 (1956) [*C. A.*, **51**, 4984 (1957)]. See also, W. S. Miller, J. S. Peake and W. H. Nebergall, THIS JOURNAL, **79**, 5604 (1957).

(29) R. Nitzsche and M. Wick, *Angew. Chem.*, **69**, 96 (1957).

(30) Melting points and boiling points are uncorrected. Silicon analyses were carried out according to the procedure of H. Gilman, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950). Diphenylsilane was prepared by reduction of dichlorodiphenylsilane with lithium aluminum hydride by a variation of the method of R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952). The yield was found, by E. A. Zuech (unpublished studies), to be increased when tetrahydrofuran instead of ether was used as a solvent.

(11.9 g., boiling over the range 175–260° (0.05 mm.)) was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent yielded an oil, from which 0.18 g. (2%) of tetraphenylsilane was obtained. Cyclohexane as an eluent gave a yellow oil, which solidified when treated with petroleum ether. The crystals were dissolved in hot ethanol, a few drops of water was added to the hot solution, giving 0.42 g. (1.2%) of 10,10-diphenylphenazasilane, m.p. 196–197°. Recrystallization from petroleum ether (b.p. 120–130°) raised the melting point to 197–198°. The compound contained no sulfur, and was soluble in cold concd. sulfuric acid. The addition of a small crystal of potassium nitrate to this solution caused a deep green color, whereas the addition of potassium nitrite to the sulfuric acid solution gave a purple color. In the thermal stability test, the compound turned pale yellow at 380°, and light brown at 410° with partial volatilization. At 480°, the dark oil boiled vigorously.

Anal. Calcd. for $C_{24}H_{19}NSi$: C, 82.49; H, 5.48; N, 4.01; Si, 8.03. Found: C, 82.08, 82.27; H, 5.28, 5.23; N, 4.04, 3.89; Si, 8.10.

Second Experiment.—A mixture of 92 g. (0.5 mole) of diphenylsilane and 69.5 g. (0.35 mole) of phenothiazine was heated for 12 days at 240° and thereafter for 6 days at 275°. On cooling, the pale yellow reaction mixture crystallized partially. Recrystallization from benzene resulted in a recovery of 25 g. of phenothiazine. The solvent of the filtrate was removed and the residue was distilled at reduced pressure to give 24 g. (34%) of unreacted diphenylsilane and 41 g. of impure unreacted phenothiazine. The distillation residue was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent yielded 0.22 g. of 10,10-diphenylphenazasilane, m.p. 194–198°. Recrystallization from the same solvent gave 0.2 g. (0.2%) of pure product, m.p. 198–199°.

Third Experiment. In the Presence of Copper Powder.—A mixture of 32 g. (0.5 mole) of copper powder, 92 g. (0.50 mole) of diphenylsilane and 69.5 g. (0.35 mole) of phenothiazine was heated at 240° for 12 days with constant stirring. Only traces of hydrogen sulfide were evolved during this period. The cooled reaction mixture was treated with boiling benzene and filtered hot to give a yellow filtrate and 33 g. of impure copper. The filtrate was cooled and 25.5 g. of impure phenothiazine removed by filtration. The solvent of the filtrate was removed and the residue distilled at reduced pressure to give 15.8 g. (17.2%) of unreacted diphenylsilane and 36.5 g. of slightly impure phenothiazine (the total recovery was 72.3%). The distillation residue was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent gave 1.6 g. of slightly impure 10,10-diphenylphenazasiline, m.p. 195–198°. Recrystallization from ethanol yielded 1.5 g. (1.23%) of pure product, m.p. 198–199°.

Fourth Experiment. In the Presence of Copper Powder and Isoquinoline (Attempted).—A mixture of 46 g. (0.25 mole) of diphenylsilane, 34.8 g. (0.175 mole) of phenothiazine, 16 g. (0.25 mole) of copper powder and 22.5 g. (0.175 mole) of isoquinoline was heated at 275° for 13 days with constant stirring. No hydrogen sulfide was detected during the reaction. The evolved gas was identified as hydrogen. The dark tar-like reaction mixture was dissolved in boiling benzene and filtered to give a quantitative recovery of the copper which now appeared in the form of shot and some large irregularly shaped pieces.

Distillation of the filtrate, after removal of the solvent, led to the recovery of 6 g. of isoquinoline and 12.5 g. of phenothiazine. No pure product was isolated from the distillation residue.

5-Ethyl-10,10-diphenylphenazasiline. A. From Diphenylsilane and 10-Ethylphenothiazine.—A mixture of 18.4 g. (0.1 mole) of diphenylsilane and 22.7 g. (0.1 mole) of 10-ethylphenothiazine was placed in a round flask, equipped with an air condenser, the upper end of which was connected with a gas wash bottle, partially filled with mineral oil. The mixture was kept at reflux temperature (approx. 240–255°) for seven days. During this time a slow evolution of hydrogen sulfide took place, which ceased at the end of the period. The pale yellow, viscous oil was transferred to a distillation flask and distilled at reduced pressure. The infrared spectrum of the first fraction (5.7 g., boiling over the range 60–115° (5 mm.)) indicated the presence of diphenylsilane as the main product (approx. 15% recovery). The second fraction (18.2 g., boiling over the range 185–195° (5 mm.)) was recrystallized from petroleum ether (b.p. 60–70°) to give 10.9 g. (59%) of 10-ethylphenothiazine, m.p. 102–103°. Its mother liquor was chromatographed on alumina. With petroleum ether, 5.2 g. of a colorless oil was eluted, the infrared spectrum of which was almost superimposable with that of triphenylsilane. Refluxing with sodium hydroxide in ethanol for 2 hours converted the silicon hydride to hexaphenyldisiloxane (4.0 g., m.p. 224–226°, 15%).

The highest boiling fraction, a pale yellow oil boiling over the range 200–270° (0.01 mm.), was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. The solution evolved hydrogen sulfide on contact with the alumina. Elution with the same solvent gave 3.8 g. of a colorless oil, which gradually crystallized. The crystals were washed with petroleum ether and melted at 120–122°. Recrystallization from the same solvent raised the melting point to 122–123°. The yield of pure 5-ethyl-10,10-diphenylphenazasiline was 2.5 g. (6.6%).

In a thermal stability test, the compound turned pale yellow at 400°, light brown at 450°, and dark brown at 480°. The compound volatilized partially at 410–450°.

Anal. Calcd. for $C_{26}H_{23}NSi$: C, 82.74; H, 6.14; N, 3.71; Si, 7.41. Found: C, 82.35; H, 6.03; N, 4.39, 4.12; Si, 7.48.

In a second experiment, a mixture of 50 g. (0.272 mole) of diphenylsilane and 61.6 g. (0.272 mole) of 10-ethylphenothiazine was heated for seven days at 240–255°. Subsequent distillation at reduced pressure gave 57 g. of material, boiling over the range 205–285° (0.01 mm.). The material was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with 2.5 liters of the same solvent gave a gummy substance, which gradually solidified. Recrystallization from petroleum ether gave 7.35 g. (7.2%) of 5-ethyl-10,10-diphenylphenazasiline, m.p. 123–124°.

No reaction took place when a mixture of diphenylsilane and 10-ethylphenothiazine was refluxed in xylene.

B. **From 5-Lithio-10,10-diphenylphenazasiline and Ethyl Sulfate.**—Twelve-hundredths of a gram (0.00034 mole) of 10,10-diphenylphenazasiline was dissolved under nitrogen in 5 ml. of anhydrous ether. With continuous stirring, approximately 0.001 mole of *n*-butyllithium in ether was added. A yellow color developed immediately. Two minutes later, with cooling, ethyl sulfate was added in excess. The yellow color was discharged immediately. After two hours of stirring at room temperature, the mixture was hydrolyzed, the organic layer extracted with base and water, dried with sodium sulfate and the solvent removed. The oily residue crystallized upon treatment with petroleum ether (b.p. 60–70°). The crystals (0.088 g., 68%) melted at 118–121° and gave no melting point depression when admixed with 5-ethyl-10,10-diphenylphenazasiline, obtained in the previous experiment. The infrared spectra were superimposable.

5-Methyl-10,10-diphenylphenazasiline.—Two-tenths of a gram (0.0005 mole) of 10,10-diphenylphenazasiline was dissolved in 8 ml. of dry ether under nitrogen. The addition of excess of *n*-butyllithium in ether gave a yellow solution and was accompanied by gas evolution. After shaking for 30 seconds, the mixture was chilled in a Dry Ice–acetone-bath and excess methyl sulfate was added with constant shaking. The solution was allowed to warm to room temperature and hydrolyzed. The dried organic layer yielded after evaporation of the solvent 0.21 g. of a white solid which, after washing with petroleum ether (b.p. 60–70°), melted at 152–170°. Recrystallization from the same solvent gave 0.10 g. (48%) of 5-methyl-10,10-diphenylphenazasiline, m.p. 186–188°.

Anal. Calcd. for $C_{25}H_{21}NSi$: C, 82.60; H, 5.82; N, 3.85. Found: C, 82.68; H, 5.70; N, 3.93.

5-Benzoyl-10,10-diphenylphenazasiline.—Two-tenths of a gram (0.0005 mole) of 10,10-diphenylphenazasiline was dissolved in dry ether under nitrogen and treated with excess of *n*-butyllithium to give a characteristic yellow solution and accompanying gas evolution. After being shaken for about 30 seconds, the solution was chilled in a Dry Ice–acetone-bath and excess of benzoyl chloride was added. The resulting green solution was warmed slowly to room temperature and hydrolyzed. The organic layer was dried and the solvent removed to leave a pasty residue. Thorough washing with petroleum ether (b.p. 60–70°) gave 0.20 g. of white crystals, m.p. 211–215°. Recrystallization from a mixture of benzene and petroleum ether yielded 0.18 g. (75%) of 5-benzoyl-10,10-diphenylphenazasiline, m.p. 214–216°.

Anal. Calcd. for $C_{31}H_{23}NOSi$: C, 82.49; H, 5.11; N, 3.09. Found: C, 82.49, 82.31; H, 5.03, 4.86; N, 3.11, 3.13.

Reaction of 10-Ethylphenothiazine with Dibenzylsilane.—A mixture of 13.7 g. (0.044 mole) of dibenzylsilane and 9.96 g. (0.044 mole) of 10-ethylphenothiazine was heated for 4 days at 290–300°, at which time the evolution of hydrogen sulfide had essentially ceased. The reaction mixture was worked up by distillation. The first fraction (1.95 g., boiling over the range 90–135° (0.07 mm.)) showed in its infrared spectrum no Si–H band, indicating the absence of dibenzylsilane. However, a strong absorption band at 2.95 μ indicated the presence of N–H compounds. No pure product was isolated from this fraction.

The second fraction (4.0 g., boiling over the range 135–180° (0.07 mm.)) was recrystallized from petroleum ether (b.p. 60–70°) and yielded 1.0 g. (10%) of phenothiazine, m.p. 176–178°, identified by its infrared spectrum and by a mixed melting point determination.

The highest boiling fraction (10.7 g., boiling over the range 220–300° (0.07 mm.)) was treated with hot petroleum ether (b.p. 60–70°), leaving a small amount of insoluble residue, m.p. 224–227°. The compound liberated hydrogen sulfide on exposure to moisture and is thought to be impure dibenzylsilanedithiol. The petroleum ether solution was chromatographed on alumina. Elution with the same solvent and with cyclohexane gave small amounts of colorless oils, which could not be crystallized. Elution with carbon tetrachloride yielded a pale yellow oil, from which on standing with ethanol 0.15 g. of colorless crystals was obtained, m.p. 136–137°. Recrystallization from the same solvent raised the melting point to 137–137.5°. The compound contained silicon, but no nitrogen. Its structure has not yet been determined.

Anal. C, 79.92, 80.14; H, 5.98, 5.81.

No crystalline product was isolated from the dark brown distillation residue.

Reaction of N-Methyldiphenylamine with Dibenzylsilane.—A mixture of 12.8 g. (0.070 mole) of N-methyldiphenylamine and 14.8 g. (0.070 mole) of dibenzylsilane was refluxed for 50 hours at 280–300°. Samples were withdrawn after 28 hours and after 50 hours of heating. Their infrared spectra were practically identical with that of the mixture of starting materials. Distillation at reduced pressure gave 24 g. (87%) of a colorless oil, boiling over the range 150–160° (10 mm.). The fraction was identified as a mixture of the starting materials by its infrared spectrum. No pure product was isolated from a small amount of higher boiling material (1.2 g., boiling over the range 160–175° (10 mm.)) or from the brown distillation residue (1.5 g.%). None of the fractions showed N–H absorption bands in the spectra.

Reaction of Triphenylsilane with Hydrogen Sulfide.—A slow stream of dry hydrogen sulfide was passed through 15 g. (0.058 mole) on rapidly stirred liquid triphenylsilane at 200–210°. After five hours the liquid had turned brown. Upon cooling, a precipitate was formed which was filtered off and washed with petroleum ether (b.p. 60–70°) to give 1.7 g. of a brown product, melting over the range 199–227°. Recrystallization from benzene yielded 1.3 g. (8.7%) of tetraphenylsilane, m.p. 230–232° (mixed m.p.). The filtered liquid was distilled at reduced pressure to give 0.25 g. (1.7%) of diphenylsilane, b.p. 75–80° (0.05 mm.), n^{20}_{D} 1.5815, and 11.55 g. (77%) of triphenylsilane, b.p. 128–135° (0.05 mm.). The distillation residue evolved hydrogen sulfide when exposed to moisture, indicating the possible presence of Si–S–H or Si–S–Si type products. Attempts to recrystallize the residue yielded no crystalline substances other than 0.7 g. of tetraphenylsilane, m.p. 230–232°.

Triphenyl-(*p*-tolylthio)-silane.—A mixture of 26 g. (0.1 mole) of triphenylsilane and 12.4 g. (0.1 mole) of *p*-thiocresol was refluxed for 5 days, during which time a slow gas evolution occurred. The mixture was subsequently distilled at reduced pressure. There was obtained 3.15 g. (25%) of *p*-thiocresol, m.p. 41–43°, b.p. 80–90° (3 mm.); 6.1 g. (23.5%) of triphenylsilane, b.p. 175–200° (3 mm.); and 20.2 g. (69%, based on non-recovered starting material) of triphenyl-(*p*-tolylthio)-silane, b.p. 250–265° (3 mm.), m.p. 79–80°. Recrystallization from petroleum ether (b.p. 60–70°) did not raise the melting point.

Anal. Calcd. for $C_{25}H_{22}SSi$: Si, 7.33. Found: Si, 7.27.

Cleavage of Triphenyl-(*p*-tolylthio)-silane with Alkali.—Three and eight-tenths grams (0.01 mole) of triphenyl-(*p*-tolylthio)-silane was refluxed with 20 ml. of ethanolic potassium hydroxide and 2 ml. of water for 15 min. On cooling, 0.7 g. (26%) of hexaphenyldisiloxane separated, m.p. 210–218°; the mother liquor was evaporated; and the residue was dissolved in ether and extracted with dilute aqueous alkali. The acidified aqueous layer was then extracted with ether. Distillation of the solvent left oily crystals, which were washed with a few drops of petroleum ether to give 0.68 g. (55%) of *p*-thiocresol, m.p. 43–44°. The first ether layer was evaporated and the residue recrystallized from petroleum ether (b.p. 60–70°) to give 1.4 g. (49%) of triphenylsilanol, m.p. 148–151°.

Cleavage of Triphenyl-(*p*-tolylthio)-silane with Triphenylsilyllithium.—A solution of 0.01 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 3.8 g. (0.01 mole) of triphenyl-(*p*-tolylthio)-silane. Subsequent to hydrolysis, a white precipitate was filtered off, which after washing with benzene gave 4.25 g. (82%) of hexaphenyldisilane, m.p. 357–360°. Ether was added to the filtrate and the organic layer extracted twice with aqueous alkali. Acidification of the aqueous layers yielded 0.625 g. (57%) of *p*-thiocresol, m.p. 40–42°.

Reaction of Diphenylsilane with 10-Ethylphenothiazine-5-oxide.—A mixture of 9.7 g. (0.052 mole) of diphenylsilane and 12.2 g. (0.05 mole) of 10-ethylphenothiazine-5-oxide was heated for 3 hours at 200°. A trace of water condensed in the cooler parts of the reaction flask. When, at the end of this period, the temperature was raised to 250° a small amount of hydrogen sulfide was evolved. The mixture solidified upon cooling. It was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent gave a solid material, which after recrystallization from petroleum ether yielded 8.6 g. (76%) of 10-ethylphenothiazine, m.p. 103–104°, identified by a mixed melting point. The use of cyclohexane as an eluent gave a small amount of pale yellow oil, from which upon standing with carbon tetrachloride 0.15 g. of crystals was obtained, m.p. 180–185°. This proved to be hexaphenylcyclotrisiloxane, as indicated by a mixed melting point and infrared spectra. The final elution with acetone and ethanol gave a resin-like substance, which was not further investigated.

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