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AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Diphenyl Sulfone and Diphenyl Sulfide by Triphenylsilyllithium

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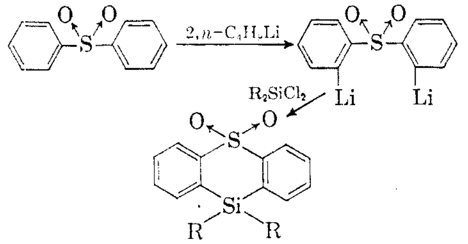
Triphenylsilyllithium (I) has been found to cleave diphenyl sulfone with the formation of phenyllithium and triphenyl(phenylsulfonyl)silane, which in a second step interact to give tetraphenylsilane and lithium benzenesulfinate. In addition, a variety of other products was obtained, when an excess of I was used. The reaction of I with diphenyl sulfide gave, in addition to hexaphenyldisilane, phenyllithium and lithium thiophenolate as the cleavage products.

The metalation of diphenylsulfone with *n*-butyllithium has been reported[1] to give mono- and dimetalated products, depending on the molar ratio of the organolithium reagent. The reaction of the thus formed 2,2′-dilithiodiphenyl sulfone with dichlorodimethylsilane and dichlorodiphenylsilane gave 10,10-dimethyl- and 10,10-diphenylphenothiasilin-5,5-dioxide,[2] respectively.



Triphenylsilylpotassium has been shown to metalate triarylmethanes rapidly and almost quantitatively.[3] Similarly triphenylsilyllithium in tetrahydrofuran was found to metalate fluorene.[4] The present investigation was carried out in order to further test the metalating properties of these highly reactive silylmetallic compounds.

If triphenylsilyllithium (I) or triphenylsilylpotassium (II) metalates diphenyl sulfone (III) in a manner similar to *n*-butyllithium, one might expect a coupling reaction of the initially formed mono- or dimetalated diphenyl sulfone and triphenylsilane[5] to give metal hydride and a silyl-substituted sulfone.

Triphenylsilylpotassium has been allowed to react with III, and tetraphenylsilane was isolated in a 36% yield. Tetraphenylsilane, however, was found to be the main product from the reaction of II with triphenylsilane[3,6] as well as with organic compounds which are metalated by the reagent with the formation of triphenylsilane.[3,6] These results appeared to support the assumption that II metalated III, and that in a secondary step tetraphenylsilane had resulted from the triphenylsilane formed in this manner and excess of triphenylsilylpotassium. In order to exclude the secondary reaction of the silylmetallic compound with the silicon hydride, triphenylsilyllithium (I) was chosen as a reagent in the further study of the reaction. The silyllithium compound I has the advantage over II in that it is fairly stable at room temperature toward triphenylsilane,[7] and furthermore I has been made readily available by lithium cleavage of hexaphenyldisilane in tetrahydrofuran.[8]

When a solution of I in tetrahydrofuran was added at room temperature to diphenyl sulfone (III), a deep red solution resulted. Color Test I[9] was negative after the addition of one equivalent. Subsequent hydrolysis gave tetraphenylsilane in a 50% yield, together with benzenesulfinic acid and 18% of triphenylsilanol. These products suggested as the course of reaction a cleavage of the carbon-sulfur bond of III according to equation A.

$$\text{(A)}\quad \underset{\text{I}}{(C_6H_5)_3SiLi} + \underset{\text{III}}{C_6H_5{-}SO_2{-}C_6H_5} \longrightarrow (C_6H_5)_4Si + C_6H_5SO_2Li$$

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[1] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951); H. Gilman and D. L. Esmay, *J. Am. Chem Soc.*, **75**, 278 (1953).

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

[3] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 2333, 2338 (1954).

[4] D. Wittenberg, unpublished studies.

[5] For general references on the reaction of silicon hydrides with organometallic reagents see, H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **79**, 4560 (1957).

[6] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 2509 (1953).

[7] R. D. Gorsich, unpublished studies.

[8] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

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

TABLE I

REACTIONS OF DIPHENYL SULFONE WITH TRIPHENYLSILYLLITHIUM

	(1)	(2)	(3)	(4)	(5)
		Conditions			
Ratio Sulfone:R_3SiLi	1:1	1:2	1:2	1:2	1:3
Temperature	25°	25°	25°	−35°	25°
Reaction time	1 hr.	72 hr.	1 hr.	5 hr.	48 hr.
Work-up by	hydrol.	hydrol.	carbon.	carbon.	hydrol.
		Products			
$(C_6H_5)_6Si_2$	−	traces	2%	−	traces
$(C_6H_5)_4Si$	50%	27.4%	5.6%	1.8%	36.4%
m-$[(C_6H_5)_3Si]_2C_6H_4$	1%	21.5%	10.2%	−	25.4%
$(C_6H_5)_3SiH$	−	−	+	1.9%	−
$(C_6H_5)_3SiOH$	18%	6.5%	29.8%	56%	−
$[(C_6H_5)_3Si]_2O$	traces	5.4%	3.1%	−	15%
p-$(C_6H_5)_3Si{-}C_6H_4COOH$	−	−	4%	−	−
C_6H_5COOH	−	−	9.8%	43.5%	−
$C_6H_5SO_2H^a$	+	+	+	+	+
$C_6H_5SH^a$	−	−	−	+	+
H_2S^a	−	−	−	−	+

[a] The presence of these compounds was determined only qualitatively. For details, see the experimental part.

When I, however, was allowed to react with III at −35°, Color Test I remained positive. Subsequent carbonation and hydrolysis gave benzoic acid in a 43.5% yield, together with benzenesulfinic acid and triphenylsilanol (56%) as the main products. Tetraphenylsilane was found only in a trace amount. In light of these results, the course of reaction may be interpreted by equations B and C.

$$\text{(B)}\ \underset{\text{I}}{(C_6H_5)_3SiLi} + \underset{\text{III}}{C_6H_5{-}SO_2{-}C_6H_5} \xrightarrow{-35^\circ} \underset{\text{IV}}{(C_6H_5)_3Si{-}SO_2{-}C_6H_5} + C_6H_5Li$$

$$\xrightarrow[\text{2. } H_2O]{\text{1. } CO_2} (C_6H_5)_3SiOH + C_6H_5SO_2H + C_6H_5COOH$$

$$\text{(C)}\ \text{IV} + C_6H_5Li \xrightarrow{20^\circ} (C_6H_5)_4Si + C_6H_5SO_2Li$$

The reaction intermediate IV, triphenyl(phenylsulfonyl)silane, was apparently hydrolyzed under the conditions of the work-up to give triphenylsilanol and benzenesulfinic acid; while at room temperature it had reacted further with phenyllithium to form tetraphenylsilane and lithium benzenesulfinate.

Compound IV has not been reported previously. Its carbon analog, phenyl triphenylmethyl sulfone, was obtained from the reaction of triphenylmethyl chloride and sodium benzenesulfinate.[10] Corresponding attempts to synthesize IV from chlorotriphenylsilane and sodium benzenesulfinate were unsuccessful.[11] A second possible route to the synthesis seemed to be the reaction of triphenylsilyllithium with benzenesulfonyl chloride. Although an excess of the acid chloride was applied and the reaction carried out at −50°, IV could not be isolated from the reaction mixture. The products were hexaphenyldisilane and lithium benzenesulfinate.

$$2\text{I} + C_6H_5{-}SO_2Cl \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + C_6H_5{-}SO_2Li + LiCl$$

The course of the latter reaction might be interpreted as a halogen-metal interconversion reaction[12] with lithium benzenesulfinate and chlorotriphenylsilane as the primary products, the latter then coupling with I with the formation of hexaphenyldisilane. However, no such interconversion reaction has been reported to occur with acid chlorides. Since acetyl chloride reacts with I to give acetyltriphenylsilane,[13] it seems more likely, that IV is formed as an intermediate, but is further cleaved by I to yield the reaction products isolated.

$$\begin{tikzcd} \text{I} + C_6H_5SO_2Cl \arrow[r] & \underset{\text{IV}}{(C_6H_5)_3Si{-}SO_2{-}C_6H_5} + LiCl \arrow[d, "+\text{I}"] \\ & (C_6H_5)_3SiSi(C_6H_5)_3 + C_6H_5SO_2Li \end{tikzcd}$$

When, in further experiments, diphenyl sulfone was treated with two or three equivalents of triphenylsilyllithium, the course of reaction seemed to be much more complex than in the first runs. A variety of products was isolated (see Table I). The isolation of small amounts of hexaphenyldisilane seems to be significant. Its formation might be due to a competition reaction of phenyllithium and I with IV, which gives as the main product tetraphenylsilane, and hexaphenyldisilane as a by-product, in accordance with the above reaction scheme. From the analogous reaction of III with

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(10) A. Baeyer and V. Villiger, *Ber.*, **36**, 2789 (1903).

(11) H. Gilman and H. W. Melvin, Jr., unpublished studies.

(12) For halogen-metal interconversion with silylmetallic compounds see, A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953) and A. G. Brook and S. Wolfe, *J. Am. Chem. Soc.*, **79**, 1431 (1957).

(13) D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 4529 (1958).

triphenylsilylpotassium, hexaphenyldisilane has been isolated in a 25% yield.

Surprising, however, was the isolation of *m*-phenylenebis(triphenylsilane) in yields ranging from 10 to 25%. The identity of this compound with an authentic sample, obtained from the reaction of *m*-phenylenebis(trichlorosilane) and phenyllithium,[14] was shown by mixed melting point and infrared spectra. Carbonation of the reaction mixture in experiment 4 gave, in addition to other products (see Table I), a 4% yield of 4-(triphenylsilyl)benzoic acid. Infrared spectra and a mixed melting point determination showed the identity with an authentic sample, obtained by oxidation of triphenyl-*p*-tolylsilane.[15]

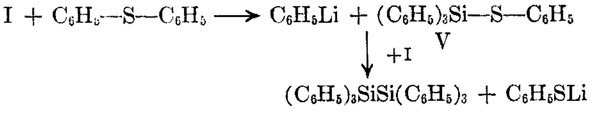
In order to exclude the possible formation of the latter two compounds from the interaction of I with the reaction products tetraphenylsilane or phenyllithium, in independent experiments I was allowed to react with tetraphenylsilane and with phenyllithium in tetrahydrofuran.[16] The products isolated indicated that apparently no reaction had taken place.

When I had been allowed to react with III in a 3:1 ratio over a 72 hour period, thiophenol and hydrogen sulfide were detected in the work-up.

In order to throw some light on the course of the reaction, it seemed of interest to treat I with dibenzothiophene-5,5-dioxide, which has a diphenyl sulfone skeleton, combined in the *o*-positions. The reaction, however, did not seem to proceed at room temperature.[17] At the reflux temperature of tetrahydrofuran, the only product isolated[17] was, in addition to the starting materials, 4-(triphenylsilyl)butan-1-ol,[18] the cleavage product from tetrahydrofuran and I.

From the reaction of I with di-*p*-tolyl sulfone at room temperature, followed by carbonation and hydrolysis, *p*-toluic acid was isolated in a 17% yield. The presence of *p*-toluenesulfinic acid was determined qualitatively.

Diphenyl sulfide did not react with I at −30°. At room temperature, the reaction mixture gave, subsequent to carbonation, benzoic acid and thiophenol, in addition to hexaphenyldisilane. The formation of these products can be explained by a cleavage of the phenyl-sulfur bond to give phenyllithium and triphenyl(phenylthio)silane (V).



$$\begin{array}{l} I + C_6H_5{-}S{-}C_6H_5 \longrightarrow C_6H_5Li + \underset{V}{(C_6H_5)_3Si{-}S{-}C_6H_5} \\ \qquad\qquad\qquad\qquad\quad \downarrow +I \\ \qquad\qquad\qquad\quad (C_6H_5)_3SiSi(C_6H_5)_3 + C_6H_5SLi \end{array}$$

The latter compound then reacts with I to form hexaphenyldisilane and lithium thiophenolate.

The reaction is analogous to the reported cleavage of triphenyl(*p*-tolylthio)silane[19] by I to give hexaphenyldisilane and lithium *p*-thiocresolate.

Dibenzothiophene under the same conditions was not attacked by I.[17]

The reaction of triphenylsilylpotassium with diphenyl sulfide in ether gave after 24 hours of stirring at room temperature a 6% yield of tetraphenylsilane, in addition to triphenylsilanol (65%), the latter compound apparently formed by hydrolysis of the unreacted starting material. Hexaphenyldisilane was not isolated. From the reaction of triphenylsilylpotassium with diphenyl sulfoxide, the products obtained were hexaphenyldisilane (12%), hexaphenyldisiloxane (21%), and tetraphenylsilane (27%).

EXPERIMENTAL[20]

Reaction of triphenylsilyllithium with diphenyl sulfone. First experiment. A solution of 0.058 mole of triphenylsilyllithium[8] in tetrahydrofuran was added slowly to 8.25 g. (0.058 mole) of diphenyl sulfone. During the addition, the reaction flask was cooled with ice. A deep red color developed, although Color Test I was found to be positive immediately after the addition was complete. Subsequent stirring for one hour at room temperatue gave a negative Color Test I. After hydrolysis with water and addition of some ether, 4.4 g. (34%) of a colorless precipitate was filtered off, m.p. 232–234°. A mixed m.p. with tetraphenylsilane showed no depression, although the compound, on attempts to dissolve it in benzene, left 0.13 g. of insoluble residue, m.p. 345–349°. The residue was later shown to be slightly impure *m*-phenylenebis(triphenylsilane) (1% yield).

The layers of the filtrate were separated, the organic layer washed several times with water, dried with sodium sulfate, and the solvents removed by distillation. The oily residue was washed with petroleum ether (b.p. 60–70°) and with ethanol, and yielded 2.0 g. of pale yellow crystals, m.p. 210–227°. Recrystallization from benzene raised the melting point to 230–234°. The product was shown to be tetraphenylsilane (16%) by mixed melting point.

When benzene was added to the concentrated mother liquor, 0.18 g. of a precipitate was formed, melting at 280–320° with decomposition. The product was not identified. The addition of petroleum ether (b.p. 60–70°) to the concentrated filtrate gave 2.9 g. of triphenylsilanol, m.p. 151–153° (mixed m.p.). In addition, a small amount of hexaphenyldisiloxane, m.p. 225–228° was isolated.

The combined aqueous layers gave, after acidification, an orange voluminous precipitate with ferric chloride solution, which was shown to be insoluble in dilute hydrochloric acid. This indicated the presence of benzenesulfinic

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[14] H. Gilman and H. G. Brooks, unpublished studies.

[15] H. Gilman, C. G. Brannen, and R. K. Ingham, *J. Am. Chem. Soc.*, **78**, 1689 (1956).

[16] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

[17] H. Gilman and H. McNinch, unpublished studies.

[18] D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

[19] H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957).

[20] All melting points and boiling points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran used was dried and purified by successively shaking with sodium hydroxide pellets, refluxing over sodium metal for at least 24 hr., and finally distilling immediately before use from lithium aluminum hydride. Silicon analyses were carried out according to the directions of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

acid.[21] A sample of the aqueous solution was refluxed for 30 min. with an equal volume of an ethanolic mercuric chloride solution. The precipitate formed was filtered off and extracted with benzene. Concentration of the eluate gave a small amount of phenylmercuric chloride,[22] m.p. 151–152° (mixed m.p.).

Second experiment. A solution of 0.076 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 8.25 g. (0.038 mole) of diphenyl sulfone. Color Test I[9] was positive immediately after the addition, and also 12 hr. later. After 72 hr. of stirring at room temperature, the solution showed a negative Color Test. Subsequent to hydrolysis with water, the mixture was filtered to give 10.6 g. of a colorless powder, melting over the range 235–320°. Extraction with boiling benzene left 4.85 g. (21.5%) of undissolved *m*-phenylenebis(triphenylsilane), m.p. 343–345°. Recrystallization of a sample from tetrahydronaphthalene raised the melting point to 348.5–349.5°. A mixed melting point with an authentic sample, obtained from the reaction of *m*-phenylenebis(trichlorosilane) and phenyllithium,[14] was undepressed. Also the infrared spectra were identical.

Anal. Calcd. for $C_{42}H_{34}Si_2$: Si, 9.45. Found: Si, 9.42, 9.45.

The benzene solution gave on concentration a small amount of impure hexaphenyldisilane, m.p. 355–363° (mixed m.p.). Further concentration and addition of petroleum ether (b.p. 60–70°) yielded 3.5 g. (27.4%) of tetraphenylsilane, m.p. 230–234° (after recrystallization).

The layers of the first filtrate were separated. After the addition of some ether, the organic layer was washed several times with water, dried with sodium sulfate, and the solvents removed by distillation. The oily residue, on treatment with a small amount of benzene, gave 1.1 g. (5.4%) of colorless crystals, m.p. 225–228°. A mixed melting point with an authentic sample of hexaphenyldisiloxane was not depressed. From the concentrated filtrate, by fractional crystallization and recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°), 1.4 g. (6.5%) of triphenylsilanol, m.p. 151–153° (mixed m.p.) was isolated.

The aqueous layer of the run showed the same properties as in the first experiment. The presence of benzenesulfinic acid was established by the reactions with ferric chloride[21] and mercuric chloride.[22]

Third experiment. A solution of 0.048 mole of triphenylsilyllithium in tetrahydrofuran was added at room temperature within a period of 15 min. to 5.2 g. (0.024 mole) of diphenyl sulfone. After one hour of stirring, the deep red reaction mixture, which showed a positive Color Test I,[9] was poured on a slurry of Dry Ice and anhydrous ether. In the work-up, water was added and the mixture filtered to give 2.1 g. of an insoluble residue, melting over the range 290–328°. The product was extracted with boiling benzene and yielded 1.4 g. (10.2%) of *m*-phenylenebis(triphenylsilane), m.p. 342–343° (mixed m.p.). Concentration of the benzene filtrate gave 0.25 g. (2%) of hexaphenyldisilane, m.p. 352–357° (mixed m.p.).

The two layers of the first filtrate were separated, the organic layer extracted twice with dilute sodium hydroxide and twice washed with water. After drying with sodium sulfate and removal of the solvents by distillation, an oily residue was obtained, which partially crystallized on the addition of petroleum ether (b.p. 60–70°). The product was washed with the same solvent and with cold ethanol to give 0.95 g. of crystals, melting over the range 185–205°. Since recrystallization did not improve the melting point, the product was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.45 g. (5.6%) of tetraphenylsilane, m.p. 230–234° (after recrystallization from benzene). Elution with benzene gave a product, which after recrystallization from cyclohexane yielded 3.1% of hexaphenyldisiloxane, m.p. 220–225°.

The petroleum ether–ethanol filtrate described in the previous paragraph was concentrated and treated with petroleum ether. The precipitate which formed (3.95 g.), was identified as triphenylsilanol, m.p. 148–152°. The yield was 29.8%. No crystalline product was obtained from the mother liquor. The infrared spectrum of the latter, after removal of the solvent, indicated the presence of triphenylsilane. Further evidence for the presence of this silicon hydride was the evolution of hydrogen gas on treatment with potassium hydroxide in ethanol.

The alkaline aqueous layer was refluxed for a few minutes in order to remove traces of organic solvents. On cooling, a precipitate was formed. The product was filtered off, suspended in dilute sulfuric acid and ether-extracted. Removal of the solvent gave 2.1 g. of a compound, m.p. 178–190°. Recrystallization from acetic acid and from cyclohexane raised the melting point to 213–214°. A mixed melting point with an authentic sample of 4-(triphenylsilyl)benzoic acid[15] was not depressed. Also the infrared spectra were identical. The yield of pure acid was 4%.

The alkaline aqueous filtrate was acidified with dilute hydrochloric acid. The solution turned turbid, and the odor of thiophenol was noticed. Subsequent to ether extraction, drying of the organic layer and concentration to a smaller volume, a sample showed on treatment with sodium nitrite and dilute sulfuric acid the intermediate formation of a green color, indicative of thiophenol.[23] Evaporation of the ether left 1.93 g. of crude acid melting over the range 75–98°. A sample of it gave with ferric chloride solution an orange precipitate, which was insoluble in dilute acid, indicating the presence of benzenesulfinic acid.[21] The crude acidic material was extracted with boiling petroleum ether (b.p. 60–70°). After evaporation of the solvent, the residue was recrystallized from water to give 0.5 g. (9.8%) of benzoic acid, m.p. 121–122°, identified by a mixed melting point.

Fourth experiment. A solution of 0.0396 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 4.31 g. (0.0198 mole) of diphenyl sulfone. During the addition a temperature of −30 to −40° was maintained. The deep red solution was stirred at this temperature for 5 hr., kept overnight at −70° and subsequently carbonated. Ether was added to the colorless reaction product, and the solution extracted twice with dilute sodium hydroxide. After washing with water, the organic layer was dried with sodium sulfate and the solvents removed by distillation. The oily residue was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as an eluent, 0.2 g. (1.9%) of triphenylsilane was obtained, identified by its infrared spectrum. Further extraction with the same solvent yielded 0.25 g. (1.8%) of tetraphenylsilane, m.p. 232–235°. Final elution with acetone gave 6.1 g. (56%) of triphenylsilanol, m.p. 150–154°, identified by mixed melting point and infrared spectra.

The alkaline aqueous layer was acidified and extracted with ether. Drying of the organic layer and removal of the solvent left an oil. The reaction of the latter with ferric chloride solution to give an orange precipitate indicated the presence of benzenesulfinic acid.[21] The oil was extracted with three 50-ml. portions of boiling petroleum ether (b.p. 60–70°). Evaporation of the solvent gave 2.1 g. (43.5%) of crude benzoic acid, m.p. 98–110°. Recrystallization from water raised the melting point to 120–121°. The yield of pure product was 1.4 g. (29%).

Fifth experiment. A solution of 0.069 mole of triphenylsilyllithium in tetrahydrofuran was added to 5.0 g. (0.023 mole) of diphenyl sulfone. The dark red reaction mixture was stirred for 48 hr. at room temperature. Color Test I[9] was still positive. The mixture was hydrolyzed and, after the addition of some ether, filtered to give 7.1 g. of insoluble

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(21) F. Feigl, *Spot Tests*, Fourth Edition, Elsevier, Amsterdam, 1954, Vol. II, 181. See also, S. Krishna and H. Singh, *J. Am. Chem. Soc.*, **50**, 792 (1928).

(22) W. Peters, *Ber.*, **38**, 2570 (1905).

(23) For the qualitative determination of thiophenol by this method, see, H. Rheinholdt, *Ber.*, **60**, 184 (1927).

residue, melting over the range 230–335°. On extraction with boiling benzene, 3.5 g. (25.6%) of *m*-phenylenebis-(triphenylsilane), m.p. 342–345° (mixed m.p.), was left undissolved. Recrystallization of a sample from tetrahydronaphthalene raised the melting point to 348–349°. From the benzene filtrate 1.5 g. (19.5%) of tetraphenylsilane, m.p. 230–233°, was isolated.

The layers of the filtrate were separated, the organic layer washed with water, dried with sodium sulfate and the solvents removed. The residue was washed with petroleum ether (b.p. 60–70°) and with cold ethanol to give 4.2 g. of colorless crystals, melting over the range 193–208°. This product was chromatographed on alumina. With benzene as an eluent, 1.3 g. (16.9%) of tetraphenylsilane was obtained, m.p. 228–234°. Elution with acetone gave 2.75 g. (15%) of hexaphenyldisiloxane, m.p. 228–229°, identified by a mixed melting point. No pure crystalline compound was isolated from the first petroleum ether–ethanol filtrate.

Acidification of the alkaline aqueous layer caused evolution of hydrogen sulfide, as indicated by odor and by a positive lead acetate test. The solution gave an orange precipitate with ferric chloride solution, indicative of benzenesulfinic acid.[21] When the solution was refluxed for a few minutes, in order to remove the hydrogen sulfide, the characteristic odor of thiophenol was noticed.

Reaction of triphenylsilyllithium with di-p-tolyl sulfone. A solution of 0.0244 mole of triphenylsilyllithium in tetrahydrofuran was added to 6.0 g. (0.0244 mole) of di-*p*-tolyl sulfone. The dark red solution was stirred for 2 hr. at room temperature, at which time Color Test I[9] was still positive. The mixture was carbonated in the usual manner. Subsequent to the addition of water and ether, the mixture was filtered to give 0.2 g. (3.2%) of hexaphenyldisilane, m.p. 350–355° (mixed m.p.).

The layers of the filtrate were separated, the organic layer was extracted with dilute sodium hydroxide and water and dried with sodium sulfate. After removal of the solvents, the oily residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 3.25 g. (38%) of triphenylsilane, m.p. 41–43° (after recrystallization from methanol). The use of benzene as an eluent gave a yellow oil, from which 0.3 g. (5%) of di-*p*-tolyl sulfone, m.p. 156–158° was isolated. Elution with acetone yielded 1.55 g. (24%) of triphenylsilanol, m.p. 150–152°. The final extraction with methanol gave 0.8 g. of an unidentified compound, which decomposed without melting at temperatures above 370° and was not further purified.

The alkaline aqueous layer was acidified. The solution gave a precipitate with ferric chloride solution, indicating the presence of a sulfinic acid.[21] The solution was ether-extracted, the organic layer dried, and the solvent removed. Part of the oily residue could be crystallized by extraction with boiling petroleum ether (b.p. 60–70°) and with aqueous ethanol. There was obtained 0.55 g. (17%) of crude *p*-toluic acid, m.p. 168–174°, which after recrystallization from water melted at 178–180°. A mixed melting point with an authentic sample was not depressed.

Reaction of triphenylsilylpotassium with diphenyl sulfone.[24] A triphenylsilylpotassium suspension was prepared by cleaving 0.01 mole of hexaphenyldisilane with excess sodium-potassium alloy in ether according to a published procedure.[25] An ethereal solution containing 4.4 g. (0.02 mole) of diphenyl sulfone in 70 ml. of benzene was added rapidly to the suspension. The reaction mixture became brownish-red with evolution of heat. After 24 hr. of stirring at room temperature, the mixture was hydrolyzed and filtered to separate some insoluble residue. One recrystallization of this solid from dioxane yielded 1.3 g. (25%) of hexaphenyldisilane[26] (identified by mixed melting point). The organic solution was dried over sodium sulfate and the solvent removed. The residue was recrystallized twice from benzene to give 1.2 g. (36%) of tetraphenylsilane, m.p. 233–234° (mixed m.p.).

Reaction of triphenylsilyllithium with tetraphenylsilane. A solution of 0.015 mole of triphenylsilyllithium in 20 ml. of tetrahydrofuran was added to 5.0 g. (0.015 mole) of tetraphenylsilane. The mixture was stirred for 5 hr. at room temperature and subsequently carbonated in the usual manner. After the addition of some water and ether, the mixture was filtered to give 4.7 g. (94%) of tetraphenylsilane, m.p. 231–233°. The organic layer was washed with dilute sodium hydroxide. Acidification of the aqueous layer gave no acidic material. Evaporation of the organic layer to dryness gave 4.0 g. (97%) of crude triphenylsilanol, m.p. 147–151°.

Reaction of triphenylsilyllithium with phenyllithium. A solution of phenyllithium in tetrahydrofuran was prepared from bromobenzene according to the reported procedure.[16] The yield, based on titration, was 96%.

A mixture of 0.0246 mole of phenyllithium and 0.0246 mole of triphenylsilyllithium in tetrahydrofuran was stirred for 6 hr. at −30 to −40°, kept at −70° overnight, and carbonated thereafter. The mixture was worked up by addition of water and ether, and extraction of the organic layer with aqueous alkali. The combined water layer was acidified and ether extracted. Evaporation of the solvent yielded 2.3 g. (77%) of crude benzoic acid, m.p. 113–115°. Recrystallization from water raised the melting point to 121–122°. No water-insoluble acidic fraction was found.

The organic layer was filtered to give 0.2 g. (2.4%) of tetraphenylsilane, m.p. 232–234°. The filtrate was dried with sodium sulfate and the solvents removed. The residue, on treatment with 15 ml. of ethanol, yielded 0.31 g. of a white solid, melting over the range 185–220°, which was shown to be a mixture of hexaphenyldisiloxane and tetraphenylsilane by its infrared spectrum. The ethanolic filtrate gave on concentration 3.8 g. (53%) of triphenylsilanol, m.p. 150–153°.

In a second run, using the same amounts of reagents, the mixture was stirred for 1.5 hr. at room temperature and subsequently carbonated. The work-up in the manner described in the previous experiment gave 1.6 g. (53%) of crude benzoic acid, m.p. 100–106°, which after recrystallization from water melted at 120–121° (40% of pure material). From the organic layer 0.9 g. (11%) of tetraphenylsilane, m.p. 234–235°, was obtained, together with 0.55 g. of a mixture of tetraphenylsilane and hexaphenyldisiloxane, melting over the range 182–228°, and 3.4 g. (50%) of triphenylsilanol, m.p. 148–151°.

Reaction of triphenylsilyllithium with benzenesulfonyl chloride. A solution of 0.036 mole of triphenylsilyllithium in tetrahydrofuran was added at −50° to a stirred solution of 6.2 g. (0.036 mole) of benzenesulfonyl chloride in 10 ml. of tetrahydrofuran. Color Test I[9] was negative immediately after the addition. The mixture was allowed to warm to room temperature. Filtration yielded 6.2 g. (67%) of a white powder, m.p. 366–368°, which was shown by mixed melting point to be hexaphenyldisilane. The filtrate was concentrated and 30 ml. of petroleum ether (b.p. 60–70°) was added. The white precipitate formed was filtered off (2.65 g.). It was completely soluble in water and was thought to be a mixture of lithium chloride and lithium benzenesulfinate. The aqueous solution gave an orange precipitate with ferric chloride, which was insoluble in dilute hydrochloric acid, indicating the presence of benzenesulfinic acid.[21] The petroleum ether filtrate deposited after concentration and cooling 0.21 g. (2.2%) of hexaphenyldisiloxane, m.p. 226–227°. No other crystalline compound was isolated from the mother liquor.

Reaction of triphenylsilyllithium with diphenyl sulfide. A solution of 0.018 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 3.72 g. (0.018 mole) of diphenyl sulfide. Heat was evolved in the reaction, and the color

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(24) Experiments of T. C. Wu.

(25) H. Gilman and T. C. Wu, *J. Org. Chem.*, 18, 753 (1953).

(26) The possibility can not be excluded that part of the hexaphenyldisilane might be uncleaved starting material from the preparation of the triphenylsilylpotassium.

changed to brown. After 10 min. of stirring, Color Test I[9] was still strongly positive. The mixture was poured on a Dry Ice–ether slurry. Subsequent to the addition of water and ether, the mixture was filtered to give 2.95 g. (64%) of hexaphenyldisilane, m.p. 350–356° (mixed m.p.).

The layers of the filtrate were separated, the organic layer washed with dilute sodium hydroxide and water, dried with sodium sulfate, and the solvents removed. The addition of petroleum ether to the oily residue gave 0.35 g. (7%) of colorless crystals of triphenylsilanol, m.p. 152–154°. By distillation of the filtrate, 1.2 g. (32%) of diphenyl sulfide was recovered.

The aqueous layer had after acidification the pungent, characteristic odor of thiophenol. Ether extraction gave a yellow oil, from which by recrystallization from petroleum ether (b.p. 60–70°) 0.32 g. (29.5%) of benzoic acid, m.p. 120–121°, was isolated.

When in a second experiment, triphenylsilyllithium was allowed to react with diphenyl sulfide at −30° for 5 hr., the work-up by carbonation gave only traces of acidic material and traces of hexaphenyldisilane. Diphenylsulfide and triphenylsilanol were recovered in high yields.

Reaction of triphenylsilylpotassium with diphenyl sulfide.[24] A suspension of triphenylsilylpotassium in ether was prepared by cleaving 0.01 mole of hexaphenyldisilane with excess of sodium-potassium alloy.[25] A solution of 0.02 mole of diphenyl sulfide in 50 ml. of ether was added and the mixture stirred for 24 hr. The deep-brown reaction mixture was hydrolyzed. There was no insoluble solid formed. The ethereal solution was dried and the solvent removed by distillation. The yellow residue had the pungent odor of thiophenol. The crude product was dissolved in a mixture of benzene and petroleum ether (b.p. 60–70°) and cooled to give 3.5 g. (63%) of triphenylsilanol, m.p. 150–151°. Evaporation of the mother liquor gave a solid, melting at 225–229°. Three recrystallizations from a mixture of benzene and petroleum ether (b.p. 60–70°) yielded 0.2 g. (6%) of tetraphenylsilane, m.p. 233–235° (mixed m.p.).

Reaction of triphenylsilylpotassium with diphenyl sulfoxide.[24] A solution of 4.0 g. (0.02 mole) of diphenyl sulfoxide in 50 ml. of ether was added to a triphenylsilylpotassium suspension,[25] prepared from 0.01 mole of hexaphenyldisilane and excess sodium-potassium alloy in ether, containing the excess alloy. Heat was evolved and a white precipitate was formed. The reaction mixture was stirred for 45 min. at room temperature and subsequently hydrolyzed. A white ether-insoluble powder was filtered off (1.0 g.). This was recrystallized from dioxane to give 0.6 g. (12%) of hexaphenyldisilane,[26] m.p. 364–367°. The ethereal solution was evaporated to give a gummy residue, which was dissolved in benzene. On standing there was obtained 1.1 g. (21%) of hexaphenyldisiloxane, m.p. 227–229° (mixed m.p.). Evaporation of the mother liquor gave 1.3 g. of a solid, m.p. 225–232°. Recrystallization from benzene yielded 0.9 g. (27%) of tetraphenylsilane, m.p. 232–234° (mixed m.p.).

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Some New *N*-Substituted Phenothiazine Derivatives and Their 5-Oxides and 5,5-Dioxides

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Several new *N*-substituted phenothiazine derivatives were prepared by heating a mixture of phenothiazine and an aryl or heterocyclic halide in the presence of sodium carbonate and copper powder. Many of these derivatives were oxidized to sulfoxides and sulfones using hydrogen peroxide in ethanol and hydrogen peroxide in glacial acetic acid, respectively. In the preparation of the sulfoxides, the use of a high concentration of reactants was found to be advantageous. Complexes of phenothiazine and 10-(2-pyridyl)phenothiazine with boron trifluoride were investigated.

10-Phenylphenothiazine,[1] 10-(*n*-octadecyl)phenothiazine,[1] and several others have been prepared successfully by heating a mixture of phenothiazine and the appropriate organic halogen compound (usually the bromide or iodide) in the presence of sodium carbonate and copper powder. To denote such a process, the term "no-solvent" is used in this paper.

The no-solvent method has certain advantages over the other general techniques employed for *N*-alkylation of *N*-arylation (sealed tube reactions,[2] reactions employing a solvent such as benzene or xylene,[3] and reactions in anhydrous liquid ammonia[4]) in that temperatures can be reached which effect condensations that are not successful with milder conditions.

The preparation of 10-(2-pyridyl)phenothiazine by treating 10-sodiophenothiazine with 2-chloropyridine in liquid ammonia was unsuccessful.

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