In the present work the Grignard reagent of *p*-bromophenoxytrimethylsilane (VII) reacted with trimethylchlorosilane

$$\underset{\text{VII}}{(CH_3)_3SiOC_6H_4MgBr} + (CH_3)_3SiCl \longrightarrow \underset{\text{VIII}}{(CH_3)_3SiOC_6H_4Si(CH_3)_3}$$

The hydrolysis of (VIII) to the free phenol (IX) was accomplished by treatment with acidified dilute ethanol

$$\underset{\text{VIII}}{(CH_3)_3SiOC_6H_4Si(CH_3)_3} \longrightarrow \underset{\text{IX}}{HOC_6H_4Si(CH_3)_3}$$

Experimental

p-**Trimethylsilylbenzoic acid** (I) was prepared *via* the Grignard reaction using essentially the procedure of Roberts, McElhill and Armstrong.[1] The pure compound crystallized in colorless needles, m.p. 117–118° (uncor.).

p-**Trimethylsilylbenzoyl Chloride** (II).—In an erlenmeyer flask was placed 11.5 g. of *p*-trimethylsilylbenzoic acid, 4.7 g. of pyridine and 75 cc. of ether. A solution of 7.1 g. of thionyl chloride in 100 cc. of ether was gradually added with shaking. A white precipitate formed. After shaking for about ten minutes, pyridine hydrochloride was filtered off and the ethereal solution of the acid chloride was used directly for the preparation of the amide.

p-**Trimethylsilylbenzamide** (III).—The ethereal solution of the acid chloride (II) was added dropwise to an excess of concd. ammonium hydroxide solution, cooled by means of an ice-bath. Immediately a white precipitate formed. The solvent was removed and the precipitate filtered and washed repeatedly with cold water. The acid amide formed colorless plates, m.p. 153° (uncor.). The yields were between 70–80% based on the amount of acid used.

Anal. Calcd. for $C_{10}H_{15}ONSi$: Si, 14.5; N, 7.2. Found: Si, 14.8; N, 6.9.

p-**Trimethylsilylbenzaldehyde** (IV).—To the Grignard solution, made from 62.1 g. of *p*-bromophenyltrimethylsilane, was added a solution of 40.2 g. of ethyl orthoformate in 100 cc. of ether. The mixture was refluxed for 14 hours. It was then ether extracted and the solvent afterwards removed. The residual, brown solid mass was ground up into a fine powder and was slowly added to 750 cc. of a 6% hydrochloric acid solution which was maintained at about 5° by means of an ice-bath. After all the powder had been dissolved it was stirred for four hours and the temperature rose to room temperature. The mixture was ether extracted and the solvent removed. The residual material, representing the acetal (V), was added to 700 cc. of an aqueous solution, containing 100 g. of concd. sulfuric acid. The mixture was refluxed for 15 minutes. Low-boiling material was first removed by distillation. The residual liquid was steam-distilled. The distillate was ether extracted and the solvent afterwards removed. The residual oil crystallized on seeding with a crystal of the aldehyde. The crude yield was 96%. The aldehyde can be purified by recrystallization from ligroin, forming colorless needles, m.p. 109–110° (uncor.). It can also be purified by vacuum distillation, b.p. 119° at 15 mm.

Anal. Calcd. for $C_{10}H_{14}OSi$: Si, 15.73. Found: Si, 15.9.

Infrared analysis showed the presence of carbonyl, phenyl, $Si–CH_3$ and Si–C.

The 2,4-dinitrophenylhydrazone of *p*-trimethylsilylbenzaldehyde formed reddish-orange crystals and recrystallized from alcohol and ethyl acetate melted at 209° (uncor.). The infrared analysis indicated the presence of N–H, $Si–CH_3$, Si–C, $-NO_2$ and phenyl, accounting well for the structure of the 2,4-dinitrophenylhydrazone.

p-**Bromophenoxytrimethylsilane**.—This compound, previously described by Speier,[2] was prepared from *p*-bromophenol and trimethylchlorosilane using pyridine as hydrohalogen acceptor. The yield was 76–85%.

Anal. Calcd. for $C_9H_{13}OBrSi$: Si, 11.4. Found: Si, 11.3.

p-**Trimethylsiloxyphenylmagnesium Bromide** (VII).—In a three-necked flask were placed 19 g. of magnesium turnings and 200 cc. of anhyd. ether. A solution of 185 g. of *p*-bromophenoxytrimethylsilane in 200 cc. of ether was gradually added through the dropping funnel. The mixture was then refluxed for 18 hours; 3.8 g. of magnesium was recovered, indicating a 83% yield of the Grignard reagent.

p-**Trimethylsilylphenoxytrimethylsilane** (VIII).—Half of the above Grignard solution (VII) was slowly added to a solution of 42.7 g. of trimethylchlorosilane in 150 cc. of ether. The mixture was then refluxed for three hours. The inorganic precipitate was filtered off and washed with ether. The ether was removed from the filtrate and the residual liquid fractionated. The product distilled at 114–115° at 20 mm. as a colorless liquid.

Anal. Calcd. for $C_{12}H_{22}OSi_2$: Si, 23.5. Found: Si, 22.0.

The product was slightly impure probably due to contamination by some *p*-bromophenoxytrimethylsilane.

p-**Trimethylsilylphenol** (IX).—The hydrolysis of the trimethylsiloxy group could not be brought about by mere treatment in dilute acid at room temperature probably due to the insolubility of the compound. Ether extraction of the product, followed by fractionation, resulted in an almost complete recovery of the starting product. The hydrolysis was effected as follows:

10.2 g. of *p*-trimethylsilylphenoxytrimethylsilane (VIII) was added to a solution of 100 cc. of ethanol and 60 cc. of water. The solution was slightly acidified with hydrochloric acid. The mixture was refluxed for one hour, leaving a solid which was recrystallized several times from water, yielding colorless needles, m.p. 74–75° (uncor.). This is in good agreement with the melting point reported by Speier,[2] m.p. 74–74.2°.

Anal. Calcd. for $C_9H_{14}OSi$: Si, 16.9. Found: Si, 16.6.

NEW PRODUCTS DEVELOPMENT LABORATORY
GENERAL ELECTRIC COMPANY, CHEMICAL DIVISION
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Some Reactions of Pentaphenylchlorodisilane

BY HENRY GILMAN AND JACK J. GOODMAN

RECEIVED OCTOBER 6, 1952

The reactions of pentaphenylchlorodisilane have been studied to determine their relationship to those of analogous monosilane compounds, and to test the stability of the Si–Si bond in this hexasubstituted unsymmetrical disilane series.

The reaction of pentaphenylchlorodisilane with primary alcohols proceeds smoothly to give the corresponding pentaphenylalkoxydisilanes. Analogous reactions in the monosilane series have given

$$(C_6H_5)_3SiSi(C_6H_5)_2Cl + RCH_2OH \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2OCH_2R + HCl$$

similar results.[1] Attempts to make the corresponding derivatives of secondary or tertiary alcohols, under conditions used for the preparation of primary alkoxides from pentaphenylchlorodisilane, failed. The preparation of secondary and tertiary alkoxymonosilanes, however, has been reported.[2,3] These results may indicate a characteristic difference between the di- and monosilanes of this type. It is believed that the factor of steric hindrance might be in large part responsible for the anomalous results obtained.

The preparation of pentaphenylhydroxydisilane by the hydrolysis of pentaphenylchlorodisilane

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(1) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

(2) R. H. Krieble and C. A. Burkhard, *ibid.*, **69**, 2689 (1947); M. N. Kalinin, *Compt. rend. acad. Sci.* (*U.S.S.R.*), **26**, 365 (1940) [*C. A.*, **35**, 2470 (1941)]; C. S. Miner, Jr., L. A. Bryan and R. P. Holysz, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

(3) Privately communicated studies by Dr. G. N. R. Smart, who has observed some interesting results in reactions between the sterically hindered o-Tol_3SiCl and ROH and RONa compounds.

in aqueous basic media, as previously reported,[4] was unsuccessful. With both 5% and 1% ethanolic potassium hydroxide, cleavage of the Si–Si bond results. The only products so far isolated were triphenylsilanol and hexaphenyldisiloxane. The hydroxydisilane was prepared in good yield by

$$(C_6H_5)_3SiSi(C_6H_5)_2Cl + KOH \xrightarrow[H_2O]{C_2H_5OH} (C_6H_5)_3SiOH + (C_6H_5)_3SiOSi(C_6H_5)_3$$

the hydrolysis of pentaphenylchlorodisilane with water in dioxane. In this connection it is interesting to note that whereas the reaction of triphenylsilanol with formic acid gave hexaphenyldisiloxane,[5] the corresponding *sym*-bis-(triphenylsilyl)-tetraphenyldisiloxane, $(C_6H_5)_3SiSi(C_6H_5)_2$-O-$(C_6H_5)_2SiSi(C_6H_5)_3$, could not be made by the analogous reaction with pentaphenylhydroxydisilane.

When treated with phenyllithium, pentaphenylchlorodisilane was converted in good yield into hexaphenyldisilane.[6] A similar reaction of pentaphenylethoxydisilane with phenyllithium also gave an excellent yield of this compound. In this respect the unsymmetrical disilanes gave results identical with those obtained for the monosilane series.[7]

Experimental conditions[8] in essential accordance with those for the preparation of triphenylsilane were employed to make pentaphenyldisilane. Reaction of this compound with phenyllithium gave a quantitative yield of hexaphenyldisilane.[9]

Experimental

Pentaphenylethoxydisilane.—To 20.0 g. (0.435 mole) of absolute ethanol[10] was added slowly and with stirring 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane.[11] The mixture was refluxed with stirring on a water-bath for one hour. At no time did complete solution take place. After cooling the reaction mixture, which was acid to litmus, a solid material was filtered off. There was obtained 1.84 g. of a white powder melting at 207–211°. On standing there was separated from the mother liquors 0.15 g. of material melting at 207–210°. Two recrystallizations of total solids from petroleum ether (b.p. 60–70°) gave 1.70 g. (83.3%) of product melting at 210.5–212°.

Anal.[12] Calcd. for $C_{32}H_{30}OSi_2$: Si, 11.50. Found: Si, 11.35, 11.58.

Pentaphenylbenzyloxydisilane.—To 20.0 g. (0.185 mole) of benzyl alcohol[10] was added slowly and with stirring 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane. The mixture was heated and complete solution resulted at 85–90°. The solution was then heated to 135° and allowed to cool slowly. There was filtered off 1.40 g. of crystals melting at 164–167°. An additional 0.25 g. of crystals melting at 168–171° was separated from the mother liquors. Two recrystallizations of all solids from petroleum ether (b.p. 60–70°) yielded 1.35 g. (58.7%) of crystals melting at 170–171.5°.

Anal. Calcd. for $C_{37}H_{32}OSi_2$: Si, 10.20. Found: Si, 10.20, 10.31.

Reaction of secondary or *t*-butyl alcohol[3] with pentaphenylchlorodisilane gave no alkoxydisilane derivative. Since the molar quantity of organosilicon compound is so small, a minute amount of moisture in the reagents could be responsible for the product isolated, pentaphenylhydroxydisilane. Special drying techniques[13] applied to the reagents produced no desired derivative.

Attempted Preparation of Pentaphenylhydroxydisilane.—To 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane was added 95 ml. of 5% ethanolic (95%) potassium hydroxide. The mixture was refluxed over a water-bath for 4 hours. More of the alcoholic hydroxide was added until the total volume was 120 ml., and complete solution resulted. After cooling, the solution was evaporated to dryness. A white solid residue was extracted several times with hot petroleum ether (b.p. 60–70°). The remaining material was water and ether extracted. The ether layer was dried, evaporated to dryness, and the residue recrystallized from petroleum ether (b.p. 60–70°). From the first petroleum ether extract there was finally isolated 0.80 g. (69%) of material melting at 142.5–144°. This solid was identified as triphenylsilanol by a mixed melting point. From the ether extract there was finally obtained 0.20 g. (8.9%) of shiny crystals melting at 220–222°. This product was identified as hexaphenyldisiloxane by a mixed melting point.

The reaction using 1% ethanolic (95%) potassium hydroxide was carried out in the same manner. The same products were isolated and in similar yields.

Pentaphenylhydroxydisilane.—To 20.0 ml. of dioxane was added 2.0 g. (0.0042 mole) of pentaphenylchlorodisilane. On gentle warming the solid dissolved. Then 10.0 g. (0.56 mole) of distilled water was added. The solution was refluxed for 5 hours and allowed to cool. There was filtered off 1.81 g. of solids melting at 111.5–115°. The material was recrystallized three times from petroleum ether (b.p. 60–70°). The first yield of product was 1.62 g. (84.4%) melting at 134–134.5°. An infrared spectrogram showed a strong absorption band for the hydroxyl group.

Anal. Calcd. for $C_{30}H_{26}OSi_2$: Si, 12.17; active H, 1.00. Found: Si, 12.15, 12.30; active H, 1.06, 1.08 (Zerewitinoff).

Attempts to prepare the *sym*-bis-(triphenylsilyl)-tetraphenyldisiloxane proved unsuccessful. Using pentaphenylhydroxydisilane and formic acid[5] (98–100%), there was obtained a 50% recovery of the starting material. From the reaction of the sodium salt of pentaphenylhydroxydisilane and pentaphenylchlorodisilane, a glass-like substance which has so far resisted crystallization was the only product isolated.

Pentaphenyldisilane.—In a dry, three-necked flask fitted with Trubore glass stirrer, gas inlet tube, and a glass stopper were placed 5.0 g. (0.011 mole) of pentaphenylchlorodisilane and 100 ml. of anhydrous ether. After the silicon compound had dissolved, there was added 4.0 g. (0.11 mole) of lithium aluminum hydride. The mixture was brought to reflux and kept there with constant stirring and under dry nitrogen for 18 hours. The excess lithium aluminum hydride was slowly destroyed with water and the reaction mixture acidified with hydrochloric acid. The ether and water layers were separated. After the water layer had been extracted with ether several times, the combined ether fractions were dried and the solvent distilled. The white residue weighed 2.01 g. Several recrystallizations from an ethanol–benzene solution gave 1.22 g. of shiny, flaky crystals with a melting point of 128–129°. The mother liquors gave an additional 0.25 g. of this material. The total yield of pentaphenyldisilane was 1.50 g. (32.3%). A Si–H bond was present in the infrared spectrogram for this compound.

Anal. Calcd. for $C_{30}H_{26}Si_2$: Si, 12.67. Found: Si, 12.50, 12.60.

Pentaphenyldisilane and Phenyllithium.—To 0.27 g. (0.00061 mole) of pentaphenyldisilane in 20 ml. of anhy-

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[4] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, THIS JOURNAL, **74**, 561 (1952).

[5] Unpublished studies of H. W. Melvin, Jr.

[6] Unpublished studies of S. H. Eidt.

[7] R. F. Fleming, Jr. (to Corning Glass Works), U. S. Patent 2,386,452 (October 9, 1945) [*C. A.*, **40**, 603 (1946)]; H. Gilman and R. N. Clark, THIS JOURNAL, **68**, 1675 (1946).

[8] H. Gilman and C. G. Brannen, *ibid.*, **73**, 4640 (1951).

[9] H. Gilman and S. P. Massie, *ibid.*, **68**, 1128 (1946); R. N. Meals, *ibid.*, **68**, 1880 (1946); H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947); H. Gilman and H. W. Melvin, Jr., *ibid.*, **71**, 4050 (1949); W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

[10] Excess of alcohol was used as solvent in all cases. A product of high purity was obtained by this procedure.

[11] The preparation of pentaphenylchlorodisilane was carried out in essential accordance with the directions given in reference 4. Our yield was 66.8%.

[12] The analysis was carried out in essential accordance with the directions of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

[13] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath Co., Boston, Mass., 1941, pp. 358–359.

drous ether was added 2.5 ml. (0.0021 mole) of phenyllithium.[14] The mixture was stirred under dry nitrogen with a magnetic stirrer. Within 5 minutes, a milky solution resulted. After the solution was stirred and refluxed under dry nitrogen for 4 hours, a white precipitate settled out. As the reaction mixture was hydrolyzed with distilled water, a gas was evolved. The solid was now suspended between the ether and water layers. The material was filtered off and dried. There was obtained 0.306 g. (97.8%) of white powder melting at 361–363°. This was identified by a mixed melting point as hexaphenyldisilane.

Pentaphenylethoxydisilane and Phenyllithium.—To 0.50 g. (0.0010 mole) of pentaphenylethoxydisilane in a benzene-ether solution was quickly added 2 ml. (0.0017 mole) of phenyllithium. The solution was magnetically stirred. The reaction mixture took on a milky-white appearance in 15 minutes. After 1 hour, the suspended solids were filtered off, washed with petroleum ether (b.p. 60–70°), and dried. There was obtained 0.44 g. (83%) of material melting at 361–363°. This product was identified as hexaphenyldisilane by a mixed melting point.

Acknowledgment.—The authors are grateful to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared data.

[14] R. G. Jones and H. Gilman, in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 353–354.

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The Alkylation of Gramine and of Indole-N-methylgramine

BY ALLAN P. GRAY

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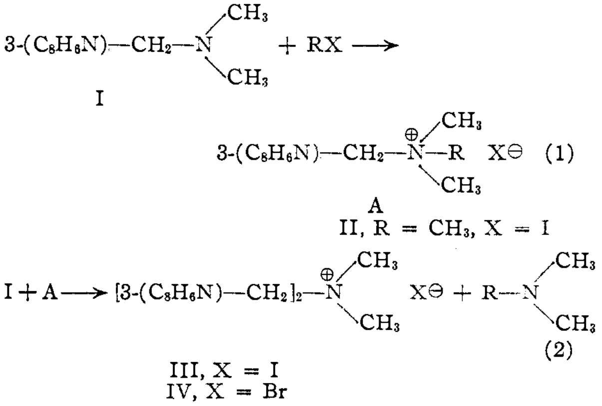
As a result of recent investigations[1] the reaction of gramine (I) with alkyl halides has been clarified. It has been shown that the product of reaction of gramine with methyl iodide (in ethanol) is not gramine methiodide (II), as reported in the literature,[2] but is actually a mixture containing tetramethylammonium iodide, bis-(3-indolemethyl)-dimethylammonium iodide (III) together with small amounts of II. The reaction may be generalized as



$$3\text{-}(C_8H_6N)\text{—}CH_2\text{—}N\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix} + RX \longrightarrow$$

I

$$3\text{-}(C_8H_6N)\text{—}CH_2\text{—}\overset{\oplus}{N}\begin{smallmatrix}\diagup CH_3\\ \text{—}R\\ \diagdown CH_3\end{smallmatrix}\; X^{\ominus} \quad (1)$$

A

II, $R = CH_3$, $X = I$

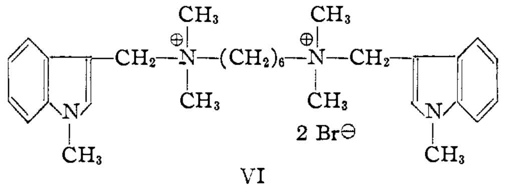
$$I + A \longrightarrow [3\text{-}(C_8H_6N)\text{—}CH_2]_2\text{—}\overset{\oplus}{N}\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}\; X^{\ominus} + R\text{—}N\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix} \quad (2)$$

III, $X = I$
IV, $X = Br$

The relative proportions of quaternary products are naturally dependent on the proportions of reactants used, on the relative rates of reactions 1 and 2 and on solubility of the products.

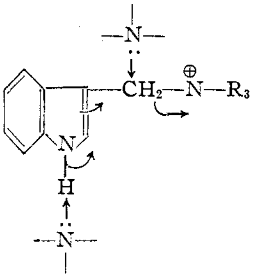
Similar results have been independently obtained in this Laboratory. In attempting to prepare a variety of quaternary derivatives, I was allowed to react with molar proportions of 1,6-dibromohexane, 1,10-dibromodecane and 1-bromohexane at room temperature in either methanol or acetonitrile. The product, which precipitated in large colorless prisms, was in each case bis-(3-indolemethyl)-dimethylammonium bromide (IV). When methanol was the solvent, IV crystallized directly from the reaction in analytically pure form.

It was of some interest to determine if indole-N-methylgramine (V) behaved in similar fashion. The possibility that it might not was supported by the fact that although prior to the recent reports[1] no complete analytical data had ever been reported for gramine methiodide,[2] a satisfactory analysis had been obtained for a sample of N-methylgramine methiodide prepared in alcohol in the ordinary way.[3] It was found that when V was allowed to react at room temperature with 1,6-dibromohexane in methanol, the main product, although somewhat difficult to separate from small amounts of impurities, was the normal 1,6-bisquaternary derivative (VI).



VI

This does not mean that products similar to III and IV might not be obtained from N-methylgramine, but only that the displacement reaction, 2, does not take place as readily with the N-methyl base. Explanation may lie in possible lowering of the activation energy for the displacement by base-catalyzed formation of an intermediate, *viz.*



Available evidence does not permit a decision as to whether the postulated base-catalyzed elimination precedes or coincides with formation of the new C to N bond. This picture of the reaction is supported by the fact that Schöpf and Thesing[1] were able to obtain pure gramine methosulfate in good yield by neutralizing the gramine with acetic acid prior to the addition of methyl sulfate.

Acknowledgment.—Many helpful and stimulating discussions with Dr. C. J. Cavallito were deeply appreciated.

Experimental[4]

Bis-(3-indolemethyl)-dimethylammonium Bromide (IV).—The following are representative experiments in which IV was the only isolated product.

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[1] T. A. Geissman and A. Armen, THIS JOURNAL, **74**, 3916 (1952); C. Schöpf and J. Thesing, *Angew. Chem.*, **63**, 377 (1951).

[2] See for example: A. Orechoff and S. Norkima, *Ber.*, **68**, 436 (1935); H. R. Snyder, C. W. Smith and J. M. Stewart, THIS JOURNAL, **66**, 200 (1944).

[3] H. R. Snyder and E. L. Eliel, *ibid.*, **70**, 1703 (1948).

[4] Microanalyses were performed by the Clark Microanalytical Laboratories, Urbana, Illinois.