There was also obtained 1.2 g. (26%) of recrystallized triphenylsilanol, m.p. 151–153°, and 0.75 g. (25%) of benzhydrol, m.p. 65–66.5°, both substances identified by mixed melting point, the latter products arising from alkaline cleavage of benzhydryloxytriphenylsilane.

Dilute Acid Hydrolysis of Triphenylsiloxydiphenylmethylpotassium.—The triphenylsiloxydiphenylmethylpotassium from 0.02 mole of triphenylsilylpotassium and 2.8 g. (0.015 mole) of benzophenone was mixed with 25 ml. of ether and poured, with stirring, into 200 ml. of water containing 5 ml. of concentrated HCl. After one additional extraction of the aqueous layer with ether the ether extracts were combined, dried over magnesium sulfate and the solvent was removed leaving a colorless, oily residue. This was dissolved in hot 95% ethanol and on cooling this solution there was obtained 4.6 g. (70%) of pure benzhydryloxytriphenylsilane, m.p. 82–84.5°, which was identified by mixed melting point. On concentration of the mother liquor there was obtained another 0.4 g. (5%) of less pure benzhydryloxytriphenylsilane, m.p. 77–83°.

Reaction of the Salt of 2-Triphenylsiloxytetraphenylethanol with Triphenylsilylpotassium.—To the triphenylsilylpotassium prepared from 3.75 g. (0.0072 mole) of hexaphenyldisilane in 80 ml. of ether was added in the special flask described above over 30 min., 1.82 g. (0.01 mole) of benzophenone in 25 ml. of ether. The red-brown precipitate of triphenylsiloxydiphenylmethylpotassium was filtered from the blue solution and the precipitate was washed twice with 50 ml. of ether. Then, after addition of 25 ml. of ether, 2.0 g. (0.011 mole) of benzophenone was added rapidly, forming a dense white precipitate and a pale blue solution. The precipitate again was filtered, and washed twice with ether. Part of the white solid was removed and dried by vacuum pump in a desiccator. To the remainder was added a suspension of triphenylsilylpotassium. After the first few ml. the medium suddenly became orange and further addition caused the separation of a dark red precipitate. This was filtered, washed twice with ether, and then treated with 1 ml. of benzyl chloride. The red precipitate rapidly disappeared to be replaced by a gray-white precipitate. The run was worked up as usual to give, after crystallization, 0.17 g. of 1-triphenylsiloxy-1,1,2-triphenylethane, m.p. 199–201°, as the insoluble residue, identified by mixed melting point with an authentic sample,[6] and from the ether layer 0.43 g. of the same material, m.p. 198–201°, identified by mixed melting point.

A weighed sample of the original dried precipitate was hydrolyzed in excess dilute standard acid. Back titration with standard base gave a neutralization equivalent of 739, calcd. for $C_{44}H_{35}O_2SiK$, 662, suggesting the presence of one molecule of ether (mol. wt. 74).

Treatment of an aliquot of the dry white precipitate, suspended in ether, with a few drops of sodium–potassium alloy, led to the formation of a deep blue color on the alloy surface. The precipitate seemed to dissolve slowly, and streamers of blue diffused into the colorless ether layer but slowly disappeared.

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

The Reaction of Triphenylsilylmetallics with Benzophenone. II. Triphenylsiloxydiphenylmethylpotassium

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The reactions of benzyl chloride, trimethylchlorosilane, carbon dioxide and formaldehyde with triphenylsiloxydiphenylmethylpotassium, isolated from the reaction of triphenylsilylpotassium with benzophenone, are reported, and certain anomalous reactions are interpreted.

During the course of a reinvestigation of the reaction between triphenylsilylpotassium and benzophenone[1] a precipitate was isolated from the reaction mixture which was believed to be the organometallic triphenylsiloxydiphenylmethylpotassium (I). This material is believed to be the precursor of benzhydryloxytriphenylsilane originally reported by Gilman and Wu[2] as the main product of the reaction and also of the compound, 2-triphenylsiloxytetraphenylethanol, which we have reported finding as a product of this reaction.[1] In order to characterize compound I a number of reactions have been carried out.

The preparation, isolation and subsequent reactions of I were carried out in a specially constructed flask which had a 1-inch sintered glass disk and stopcock sealed in the bottom. When the addition of benzophenone to triphenylsilylpotassium was completed in the flask, suction filtration of the mixture through the sintered glass disk left the dark red precipitate in the flask in an atmosphere of dry, oxygen-free nitrogen. After washing with dry ether to remove adhering mother liquor, the solid was ready for subsequent reactions in the flask.

It was found that the organometallic thus prepared reacted readily with benzyl chloride and trimethylchlorosilane to form the ethers 1-triphenylsiloxy-1,1,2-triphenylethane (II) and triphenylsiloxytrimethylsilyldiphenylmethane (III), respectively.

$$Ph_3SiOCPh_2K + PhCH_2Cl \longrightarrow$$

$$\underset{\text{II}}{Ph_3SiOCPh_2CH_2Ph} \longleftarrow Ph_3SiCl + NaOCPh_2CH_2Ph$$

$$Ph_3SiOCPhK + (CH_3)_3SiCl \longrightarrow \underset{\text{III}}{Ph_3SiOCPh_2Si(CH_3)_3}$$

Both compounds II and III were identified by analysis and by their infrared spectra and in addition II was prepared independently by the addition of triphenylchlorosilane to the sodium salt of 1,1,2-triphenylethanol. These reactions along with the previously reported[1] hydrolysis of I to yield benzhydryloxytriphenylsilane and the reaction of I with benzophenone to yield 2-triphenylsiloxytetraphenylethanol leave no doubt as to the structure of the compound I which was isolated.

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(1) A. G. Brook and N. V. Schwartz, THIS JOURNAL, **82**, 2435 (1960).

(2) H. Gilman and T. C. Wu, *ibid.*, **75**, 2935 (1953).

$$\begin{tikzcd}
\underset{\text{I}}{\text{Ph}_3\text{SiOCPh}_2\text{K}} \arrow[r, "\text{H}_2\text{O}", "\text{HCl}"'] \arrow[d, "\text{Ph}_2\text{CO}"] & \text{Ph}_3\text{SiOCPh}_2\text{H} \\
{} \arrow[d, "\text{H}_2\text{O}"] & \\
\text{Ph}_3\text{SiOCPh}_2\text{CPh}_2\text{OH} &
\end{tikzcd}$$

The carbonation of I did not yield the expected triphenylsiloxydiphenylacetic acid (IV), but rather small amounts of the triphenylsilyl ester of this acid (V), along with much benzilic acid and some triphenylsilanol. It appears, therefore, that the acid IV, or its potassium salt, is cleaved easily by water to yield benzilic acid and triphenylsilanol, and that the ester V probably was formed by attack of the anion VI on the Si–O bond of the salt of the acid with the formation of the ester V and benzilic acid.

$$\begin{tikzcd}
\text{Ph}_3\text{SiOH} + \text{HOCPh}_2\text{COOH} & \\
\underset{\text{VI}}{\text{Ph}_3\text{SiOCPh}_2\text{COO}^-} + \text{Ph}_3\text{SiOCPh}_2\text{COOK} \arrow[u, "\text{H}_2\text{O}"] \arrow[r] & \underset{\text{V}}{\text{Ph}_3\text{SiOCPh}_2\text{COOSiPh}_3} + {}^-\text{OCPh}_2\text{COOK} \arrow[d, "\text{K}^+"] \\
& \text{HOCPh}_2\text{COOH} \xleftarrow{\text{H}_2\text{O}} \text{KOCPh}_2\text{COOK}
\end{tikzcd}$$

The ester V was identified by analysis and by its infrared spectrum, which were consistent with the proposed structure. The lithium aluminum hydride reduction of V, however, yielded triphenylsilanol and 1,1-diphenylethanediol and not the expected 2-triphenylsiloxy-2,2-diphenylethanol (VII). However it also was found that the addition of formaldehyde to triphenylsiloxydiphenylmethylpotassium (I) yielded only small amounts of 2-triphenylsiloxy-2,2-diphenylethanol (VII) along with larger amounts of 1,1-diphenylethanediol and triphenylsilanol. It is evident that VII readily is cleaved, during hydrolysis, to give 1,1-diphenylethanediol and triphenylsilanol.

$$\underset{\text{V}}{\text{Ph}_3\text{SiOCPh}_2\text{COOSiPh}_3} \xrightarrow{\text{LiAlH}_4}$$

$$\underset{\text{VII}}{\text{Ph}_3\text{SiOCPh}_2\text{CH}_2\text{OLi}} + \text{Ph}_3\text{SiOLi} \xrightarrow{\text{H}_2\text{O}} 2\text{Ph}_3\text{SiOH} + \text{HOCPh}_2\text{CH}_2\text{OH}$$

$$\underset{\text{I}}{\text{Ph}_3\text{SiOCPh}_2\text{K}} + \text{CH}_2\text{O} \longrightarrow \text{Ph}_3\text{SiOCPh}_2\text{CH}_2\text{OK} \xrightarrow[\text{HCl}]{\text{H}_2\text{O}}$$

$$\underset{\text{VII}}{\text{Ph}_3\text{SiOCPh}_2\text{CH}_2\text{OH}} + \text{Ph}_3\text{SiOH} + \text{HOCPh}_2\text{CH}_2\text{OH}$$

The instability of the acid IV and the alcohol VII is not too surprising since similar but less extreme instability is exhibited by benzhydryloxytriphenylsilane which is cleaved easily at the Si–O bond by alkali.[1] Also triphenylsilylphenylacetic acid is reported[3] to be unstable and breaks down to phenylacetic acid and triphenylsilanol during hydrolysis of its salt.

Experimental[4]

The Preparation of Triphenylsiloxydiphenylmethylpotassium.—To the triphenylsilylpotassium from 6.5 g. (0.0125 mole) of hexaphenyldisilane in 100 ml. of ether was added with rapid stirring over a period of 30 min. 3.5 g. (0.019 mole) of benzophenone in 50 ml. of ether. The reaction was carried out in a special three-neck flask, complete with stirrer, dropping funnel and nitrogen inlet, which had a 1-inch sintered glass disk sealed in the bottom. In addition a stopcock was sealed below and around the sintered disk. A vacuum flask was attached to the stopcock outlet, the stopcock being closed during the reaction. At the end of the reaction the stopcock was opened and the reaction mixture was filtered by suction into the vacuum flask. There remained in the reaction flask a brick-red precipitate which was washed several times with ether. After evacuation of the flask to 0.6 mm. pressure until the flask and contents reached constant weight, the yield of I determined by the weight of the precipitate was 7.6 g. (64% based on the amount of hexaphenyldisilane started with). In similar runs yields of 51, 50 and 67% were obtained. It was found that the slow, dropwise addition of the benzophenone solution to triphenylsilylpotassium gave consistently better results than rapid addition of the benzophenone, presumably because the rapid addition allowed the formation of local excesses of benzophenone resulting in the reaction of I with the excess benzophenone.

Reactions of Triphenylsiloxydiphenylmethylpotassium. a. **With Benzyl Chloride.**—Triphenylsiloxydiphenylmethylpotassium was prepared as described above from 0.02 mole of triphenylsilylpotassium and 3.1 g. (0.017 mole) of benzophenone. After washing the organometallic with ether, another 25 ml. of ether was added to the solid and to the rapidly stirred suspension was added over a 2-min. period 2.15 g. (0.017 mole) of freshly distilled benzyl chloride dissolved in 25 ml. of ether. A vigorous reaction took place and the reaction mixture became gray in color. The mixture was stirred for 5 min. before being hydrolyzed in distilled water. A solid, insoluble in both the ether and aqueous layers, was filtered off. This solid weighed 3.2 g. (35%) and melted at 195–197°. Recrystallization of this substance from ethyl acetate raised the melting point to 201–203°. The ether layer was separated from the aqueous layer in the filtrate and the aqueous layer was extracted twice more with ether. The combined ether extracts after drying over anhydrous magnesium sulfate were concentrated to a partially solid residue. Some methanol was added to this residue and on filtering there was obtained 1.9 g. of white solid melting from 175–194°. This was recrystallized from ethyl acetate and yielded 1.45 g. (16%) of white solid identical with the first fraction, m.p. 202–203°. This solid was found to be identical with 1-triphenylsiloxy-1,1,2-triphenylethane formed from the reaction of the sodium salt of 1,1,2-triphenylethanol with triphenylchlorosilane described below. The infrared spectrum of this compound was consistent with the proposed structure including CH_2 absorption at 3.4 μ and Si–O absorption at 9.3 μ.

Anal. Calcd. for $\text{C}_{38}\text{H}_{32}\text{OSi}$: C, 85.72; H, 6.02; Si, 5.62. Found: C, 86.09; H, 6.10; Si, 5.48.

b. **With Trimethylchlorosilane.**—To a suspension of triphenylsiloxydiphenylmethylpotassium, from 0.04 mole of triphenylsilylpotassium and 6.5 g. (0.036 mole) of benzophenone, in 30 ml. of ether was added with stirring 4.25 g. (0.036 mole) of trimethylchlorosilane in 30 ml. of ether. The red color of the organometallic slowly faded and at the end of 20 min. the reaction mixture was completely gray. It then was hydrolyzed with dilute HCl, the ether layer was separated, and the aqueous layer was extracted twice more with ether. The combined extracts were dried over anhydrous magnesium sulfate and on removal of the solvent there remained a partially solid residue. Hot ethanol was added and after cooling there was obtained 7.3 g. of white solid, melting from 133–162°. Recrystallization from benzene–methanol yielded 5.2 g. (25%) of white crystalline solid, m.p. 170–172°. The infrared spectrum of this compound is consistent with the structure of triphenylsiloxytrimethylsilyldiphenylmethane (III) with Si–Ph absorption at 9.0, 9.7 and 10.0 μ, Si–CH_3 absorption at 6.9, 8.0 and 11.9 μ and Si–O absorption at 9.5 μ.

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(3) H. Gilman and H. Harzfeld, THIS JOURNAL, **73**, 5878 (1957).

(4) All reactions involving organometallics were carried out in a dry, oxygen-free nitrogen atmosphere in anhydrous solvents.

Anal. Calcd. for $C_{34}H_{34}Si_2O$: C, 79.38; H, 6.62; Si, 10.89. Found: C, 79.72, 79.60; H, 6.86, 6.75; Si, 11.01.

c. **With Carbon Dioxide.**—Triphenylsiloxydiphenylmethylpotassium from 0.02 mole of triphenylsilylpotassium and 3.1 g. (0.017 mole) of benzophenone was mixed with 25 ml. of dry ether and was poured into a Dry Ice–ether slurry. When the Dry Ice had all disappeared, but while the mixture was still cold, it was washed with dilute HCl. The aqueous washing was extracted once more with ether and the original ether layer and the extract were combined, dried over magnesium sulfate and were concentrated under reduced pressure. A partially solid residue remained to which was added some methanol and upon filtering this mixture there was obtained 1.35 g. (10.5%) of white solid melting from 190–202°. Recrystallization of this substance from ethyl acetate yielded 1.0 g. (8%) of white, crystalline triphenylsilyl triphenylsiloxydiphenylacetate (V), m.p. 212–216°. An analytical sample of this compound had a melting point of 215–216°. The infrared spectrum of this compound was also consistent with its proposed structure and included carbonyl absorption at 5.8 μ and Si–O absorption at 9.3 μ.

Anal. Calcd. for $C_{50}H_{40}O_3Si_2$: C, 80.65; H, 5.38; Si, 7.53. Found: C, 80.57, 80.80; H, 5.44, 5.52; Si, 7.51, 7.53.

The mother liquor from which the crude ester was obtained yielded 0.65 g. (6%) of crude triphenylsiloxytetraphenylethanol melting from 114–125°. Recrystallization of this material from chloroform–petroleum ether yielded 0.35 g. (3%) of triphenylsiloxytetraphenylethanol melting from 130–135°, which was identified by mixed melting point. The mother liquor was concentrated further and yielded 2.6 g. of solid melting from 127–142°. Recrystallization of this solid from benzene–petroleum ether (b.p. 90–100°) yielded 1.4 g. (36%) of benzilic acid, m.p. 148–150°, which was identified by mixed melting point.

A similar carbonation yielded 6% of the ester, melting from 214–217°; 20% of triphenylsiloxytetraphenylethanol melting from 125–130°; and 18% of benzilic acid, m.p. 146–150°. Another carbonation yielded 4% of the ester, m.p. 213–217°; 9% of triphenylsilanol, m.p. 150–152°; and 45% of benzilic acid, m.p. 147–151°. It is believed that the triphenylsiloxytetraphenylethanol that was isolated in two of the carbonations was formed during the preparation of the triphenylsiloxydiphenylmethylpotassium, since the salt of this compound forms a white precipitate in the reaction mixture and would remain with the organometallic.

d. **With Formaldehyde.**—The triphenylsiloxydiphenylmethylpotassium from 0.02 mole of triphenylsilylpotassium and 2.8 g. (0.015 mole) of benzophenone was mixed with 25 ml. of ether. Formaldehyde vapor, generated by heating 10 g. of paraformaldehyde to 130–140°, was passed over the rapidly stirring suspension of organometallic in a stream of dry nitrogen. The red suspension rapidly turned yellowish-green in color and after about 20 min. the mixture was hydrolyzed with dilute HCl. After separation of the organic layer, the aqueous layer was extracted once more with ether. The combined ether extracts were dried over magnesium sulfate and after removal of the solvent an oily residue was obtained. The residue was dissolved in benzene and was chromatographed on a silica gel column. There was obtained 1.1 g. (34%) of 1,1-diphenylethanediol, m.p. 120–122°, and 0.7 g. (17%) of triphenylsilanol, m.p. 151–153°. Both compounds were identified by mixed melting point with authentic samples. In addition, a total of 1.15 g. (16%) of 2-triphenylsiloxy-2,2-diphenylethanol, melting from 79–91°, was obtained which after two recrystallizations from petroleum ether (b.p. 90–100°) melted at 87–90°. An analytical sample had m.p. 91–92°. The infrared spectrum, with OH and Si–O absorption at 2.8 and 9.3 μ, respectively, was consistent with the proposed structure. The identity of the compound was confirmed by alkaline hydrolysis (see below).

Anal. Calcd. for $C_{32}H_{28}O_2Si$: C, 81.4; H, 5.93; Si, 5.93. Found: C, 81.7; H, 5.89; Si, 6.10.

Similar runs gave 23% of 1,1-diphenylethanediol and 9% of triphenylsilanol but no 2-triphenylsiloxy-2,2-diphenylethanol.

Alkaline Hydrolysis of 2-Triphenylsiloxy-2,2-diphenylethanol.—To a solution of 0.1 g. (0.00021 mole) of 2-triphenylsiloxy-2,2-diphenylethanol in 5 ml. of ethanol was added 2 ml. of 10% sodium hydroxide solution, and the solution was boiled for 2 min. The solution was drowned in water, acidified with acid and ether-extracted 4 times. On removal of the ether under reduced pressure the residue was refluxed with 5 ml. of water for 5 min. and then was filtered hot. On cooling, the filtrate yielded 0.04 g. (88%) of 1,1-diphenylethanediol, m.p. 119–122°, identified by mixed melting point. The residue from the aqueous extraction was recrystallized from petroleum ether (b.p. 90–100°) to yield 0.04 g. (68%) of triphenylsilanol, m.p. 149–152°, identified by mixed melting point.

Synthesis of 1-Triphenylsiloxy-1,1,2-triphenylethane.—The sodium salt of 1,1,2-triphenylethanol was prepared by refluxing a solution of 1.0 g. (0.0037 mole) of the alcohol in 15 ml. of dry benzene with excess sodium metal until the evolution of hydrogen ceased. The excess sodium was removed and 1.1 g. (0.0037 mole) of triphenylchlorosilane in 15 ml. of benzene was added to the solution of sodium salt. This solution was refluxed for 24 hr. and then the cloudy mixture was cooled and washed with water. The aqueous washing was extracted once with ether and then the ether extract and benzene layer were combined and an insoluble solid was filtered off. This solid, 0.25 g. (25%) of crude hexaphenyldisiloxane, melting from 211–222°, was recrystallized from ethyl acetate, m.p. 224–227°, identified by mixed melting point with an authentic sample. The original filtrate was dried over anhydrous magnesium sulfate and the solvent was removed leaving a partially solid residue. Some methanol was added to the residue and the mixture was filtered to yield 0.85 g. of white solid melting from 176–196°. Recrystallization of this material from ethyl acetate yielded 0.65 g. (33%) of 1-triphenylsiloxy-1,1,2-triphenylethane, m.p. 200–203°, which was identical with the material isolated from the addition of benzyl chloride to triphenylsiloxydiphenylmethylpotassium.

Lithium Aluminum Hydride Reduction of Triphenylsilyl Triphenylsiloxydiphenylacetate (V).—A solution of 0.5 g. (0.00067 mole) of the ester V dissolved in 30 ml. of dry ether–benzene was added with stirring to 0.05 g. (0.0013 mole) of lithium aluminum hydride in 10 ml. of ether. The mixture was stirred for 2.5 hr. at room temperature, the excess hydride was destroyed by the careful addition of ethyl acetate and then 95% ethanol, until effervescence ceased. The mixture finally was hydrolyzed in dilute HCl and after separation of the organic layer it was dried over magnesium sulfate and the solvent was removed under reduced pressure. A partially solid residue remained which was dissolved in petroleum ether (b.p. 60–70°) and there was obtained from this solution 0.1 g. of solid which began to melt at 118° but was not completely clear at 230°. A second fraction of solid weighing 0.15 g. and melting from 110–155° also was obtained. These two fractions were combined and recrystallized twice from petroleum ether (b.p. 90–100°), a small amount of insoluble material being filtered from the hot solution each time. There was finally obtained 0.1 g. (70%) of 1,1-diphenylethanediol, m.p. 119–121°, identified by mixed melting point. There was also obtained 0.1 g. (27%) of crude triphenylsilanol melting from 143–150°, identified by mixed melting point.

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