[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Triphenylsilylpotassium with Benzophenone and with 4,4'-Dimethylbenzophenone

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Triphenylsilylpotassium adds to the carbonyl groups of benzophenone and 4,4'-dimethylbenzophenone. Upon hydrolysis, however, the addition products are not the products to be expected from normal addition of an organometallic compound to the carbonyl group, but instead suggest that reversed addition has occurred, since the triphenylsilyl group is attached to the oxygen atom. Possible mechanisms for this "abnormal" addition are presented.

In extending the studies of the addition of triphenylsilylpotassium to unsaturated linkages such as *trans*-stilbene[1] we found that when triphenylsilylpotassium is treated with benzophenone or 4,4'-dimethylbenzophenone the products obtained on hydrolysis are the diarylmethoxytriphenylsilanes instead of the carbinols one might have expected.

$$(C_6H_5)_3SiK + (C_6H_5)_2CO \xrightarrow{H_2O} \underset{\text{I}}{(C_6H_5)_3SiOCH(C_6H_5)_2}$$

$$(C_6H_5)_3SiK + (p\text{-}CH_3C_6H_4)_2CO \xrightarrow{H_2O} (C_6H_5)_3SiOCH(C_6H_4CH_3\text{-}p)_2$$

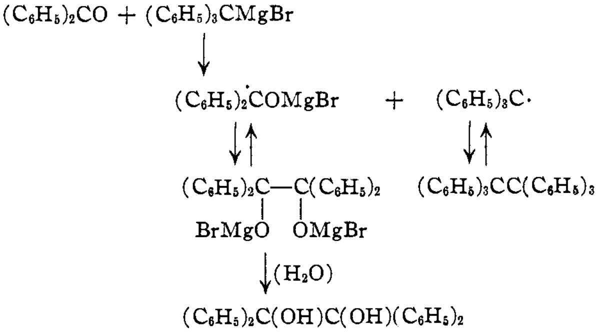
Supporting evidence for the formation of the diarylmethoxytriphenylsilanes is revealed by the fact that neither product shows absorption characteristic of a hydroxyl group in their infrared spectra. Instead, there is a characteristic band due to the silicon–oxygen bond present in the spectra. Furthermore, an authentic specimen of benzohydryloxytriphenylsilane prepared by the reaction between triphenylchlorosilane and sodium benzohydryloxide was found to be identical with the product obtained by the reaction of triphenylsilylpotassium with benzophenone. This latter reaction product was hydrolyzed by alcoholic potassium hydroxide to give hexaphenyldisiloxane and benzohydrol.

$$(C_6H_5)_3SiCl + NaOCH(C_6H_5)_2 \longrightarrow \underset{\text{I}}{(C_6H_5)_3SiOCH(C_6H_5)_2}$$

$$(C_6H_5)_3SiOCH(C_6H_5)_2 + H_2O \xrightarrow[95\%\ C_2H_5OH]{KOH\ in} (C_6H_5)_3SiOSi(C_6H_5)_3 + (C_6H_5)_2CHOH$$

It is generally true that an organometallic compound like phenylmagnesium bromide adds to the carbonyl linkage of benzophenone in such a way that the organic radical is attached to the carbon atom and with the metal attached to the oxygen atom. However, there are exceptional cases in which the normal addition does not take place. It has been reported that both triphenylmethylsodium[2] and triphenylmethylmagnesium bromide[3] react with benzophenone to give the ketyls which can be converted to the benzopinacol by hydrolysis. The radicals formed from these reactions preferentially form the symmetrical dimers, rather than associating to form the "normal" addition product, pentaphenylethanol.[3]

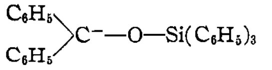
There seems to be no good reason for associating the "abnormal" addition of triphenylsilylpotassium with the above phenomena. In the first place, the stoichiometry of the reaction is quite different in that the silicon species is not oxidized and pinacols are not produced. Furthermore, one would not anticipate such behavior under any circumstances since resonance stabilization of the triphenylsilyl radical is probably much less important than is the case with the carbon analog.[4]



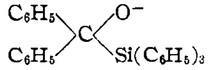
The apparently "abnormal" addition of triphenylsilylpotassium to the carbonyl group is quite interesting since the "normal" reaction between benzophenone and triphenylsilylpotassium would be predicted to occur in the following way.

$$(C_6H_5)_3SiK + (C_6H_5)_2CO \xrightarrow{H_2O} \underset{\text{II}}{(C_6H_5)_3SiC(OH)(C_6H_5)_2}$$

An examination of the anions of compounds I and II shows that in compound I the anion III is stabilized by the resonance energy of the diphenylmethylene grouping, while this is absent in anion IV of compound II. In addition, the energy of the silicon–oxygen bond (89.3 kcal./mole[5]) of anion III is higher than that of the silicon–carbon bond (57.6 kcal./mole[5]) of anion IV. If the structures of anions III and IV contribute substantially in the transition state of the reaction between triphenylsilylpotassium and benzophenone, one would obtain product I instead of product II. The reaction between triphenylsilylpotassium and 4,4'-dimethylbenzophenone may be explained similarly.



III



IV

Another possible mechanism leading to the formation of compound I is that the triphenylsilyl anion first adds to the carbonyl group of benzophenone in the "normal" manner to give anion IV, followed by a rearrangement of structure IV to the more stable

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(1) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 234 (1953).

(2) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916).

(3) W. E. Bachmann, THIS JOURNAL, **53**, 2758 (1931).

(4) H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951).

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

structure III. In either mechanism the end-product has the structure I.

Experimental[6]

Reaction of Triphenylsilylpotassium with Benzophenone.—A suspension of triphenylsilylpotassium in ether was prepared by cleaving 5.2 g. (0.01 mole) of hexaphenyldisilane with sodium–potassium alloy according to the improved procedure recently described.[7] Three and six-tenths grams (0.02 mole) of benzophenone dissolved in 30 ml. of ether was added in a period of about 3 minutes to the triphenylsilylpotassium suspension containing the excess alloy. During the course of addition the reaction mixture became orange, and then brown. It was observed that the addition of a temporary excess of benzophenone solution to the reaction mixture gave a deep blue color which, on stirring with interruption in the addition of benzophenone solution, faded away with the resumption of a brown color. At the end of the addition a dark blue suspension was formed. Some heat was evolved during the period of addition. There was no further change in appearance after 2 hours of stirring at room temperature. The reaction mixture was carefully hydrolyzed with water. During the hydrolysis the color of the mixture changed to green, then yellow, and finally white. The hydrolysis mixture was filtered by suction to remove a trace of solid. Following evaporation of the sodium sulfate-dried ethereal solution there was obtained 9.0 g. of oily solid residue. This was dissolved in a hot solution containing 50 ml. of benzene and 50 ml. of chloroform. The solution was then concentrated to about 80 ml. and allowed to cool to room temperature. There was obtained 4.0 g. of colorless crystals melting at 216–222°. One recrystallization from petroleum ether (b.p. 77–110°) yielded 2.9 g. (54%) of lustrous plates melting at 227–229°; a mixed melting point with an authentic specimen of hexaphenyldisiloxane showed no depression. The mother liquor after the removal of the crude hexaphenyldisiloxane was concentrated to give an oily residue. On standing some crystals slowly separated, and these were recrystallized from 50 ml. of petroleum ether (b.p. 60–70°) to give 0.8 g. (22%) of benzohydrol (mixed m.p.) melting at 68–69°. The oily residue after the removal of the crude benzohydrol was allowed to stand. Gradually some colorless crystals separated. These were collected by filtration and were recrystallized from ethanol. There was obtained 2.2 g. (25%) of benzohydryloxytriphenylsilane melting at 83–84°.

Anal.[8] Calcd. for $C_{31}H_{26}OSi$: Si, 6.34. Found: Si, 6.40, 6.35.

A second reaction was carried out using the same amounts of reagents except that the excess sodium–potassium alloy was removed from the triphenylsilylpotassium suspension by amalgamation[7] prior to the addition of benzophenone solution, and the reaction mixture was stirred at room temperature for 2 hours. At the end of this period, Color Test I[9] was negative. Following hydrolysis the mixture was filtered by suction to remove a very small amount of grey solids. From the ethereal solution there was obtained 8.5 g. of oily residue. This was dissolved in 50 ml. of petroleum ether (b.p. 60–70°) and allowed to cool. One gram of colorless crystals melting at 120–140° separated from the solution. A recrystallization of this product from petroleum ether (b.p. 60–70°) gave 0.7 g. (13%) of triphenylsilanol (mixed m.p.) melting at 150–151°. The mother liquor from which the crude triphenylsilanol separated was evaporated and redissolved in 50 ml. of ethanol. On standing some oily material separated. The ethanolic solution was decanted from the oil and was concentrated to yield 3.5 g. (40%) of benzohydryloxytriphenylsilane melting at 83–84°.

Preparation of Benzohydryloxytriphenylsilane from Triphenylchlorosilane and Sodium Benzohydryloxide.—Thirteen grams (0.044 mole) of triphenylchlorosilane dissolved in 50 ml. of benzene was added to a benzene solution of sodium benzohydryloxide prepared by treating 8.0 g. (0.044 mole) of benzohydrol with 1.0 g. (0.044 g. atom) of sodium in benzene. The reaction mixture became somewhat cloudy after the addition. After 22 hours of reflux there was no appreciable change in the reaction mixture. The gummy residue obtained by evaporation of the solvent was boiled with petroleum ether (b.p. 60–70°) and filtered hot. The solid residue was stirred in a mixture of water and ether. From the ethereal solution there was obtained 1.6 g. of solid melting at 224–228°. One recrystallization from petroleum ether (b.p. 60–70°) yielded 1.4 g. (12%) of hexaphenyldisiloxane (mixed m.p.) melting at 226–228°. The hexaphenyldisiloxane probably came from the hydrolysis of unreacted triphenylchlorosilane.

The petroleum ether solution from the extraction of the original reaction mixture was distilled. The residue was recrystallized twice from ethanol to give 5.2 g. (27%) of colorless crystals melting at 83–84°. A mixed melting point determination with the product obtained by the reaction of triphenylsilylpotassium and benzophenone showed no depression, and the infrared spectra of these two products were identical.

Basic Cleavage of Benzohydryloxytriphenylsilane.—A mixture of 1 g. of benzohydryloxytriphenylsilane, 0.3 g. of potassium hydroxide and 25 ml. of 95% ethanol was refluxed for 1 hour. The solvent was distilled off and the residue was extracted with hot petroleum ether (b.p. 60–70°) from which 0.44 g. of solid melting at 210° separated. This was recrystallized to give shining crystals melting at 227–228°; a mixed m.p. determination with hexaphenyldisiloxane was not depressed. The mother liquor, after removal of the crude hexaphenyldisiloxane, was concentrated to give a trace of solid melting from 150–200°. Further evaporation of the mother liquor deposited 0.35 g. of solid melting at 60–65°. One recrystallization from a small amount of petroleum ether (b.p. 60–70°) raised the melting point to 68–69°; a mixed m.p. determination with benzohydrol showed no depression.

Reaction of Triphenylsilylpotassium with 4,4′-Dimethylbenzophenone.—A solution of 4.2 g. (0.02 mole) of 4,4′-dimethylbenzophenone in 50 ml. of ether was added in a period of about 3 minutes to an amalgamated triphenylsilylpotassium suspension prepared by cleaving 5.2 g. (0.01 mole) of hexaphenyldisilane with sodium–potassium alloy in ether.[7] A deep blue color developed locally where the ketone solution came in contact with the triphenylsilylpotassium suspension. After the addition was complete the dark brown mixture was stirred at room temperature for 24 hours. At the end of this period Color Test I[9] was still positive. Water was added to the reaction mixture and the resulting light gray suspension was filtered to remove traces of light gray powder melting at 360°. The ethereal solution was separated, dried over sodium sulfate, and distilled. The oily residue (9 g.) solidified on standing. This solid was recrystallized from petroleum ether (b.p. 60–70°). The first fraction (1.5 g., 27%) of fine granular crystals melting at 149–151° was identified as triphenylsilanol by a mixed m.p. determination with an authentic sample. Evaporation of the mother liquor gave a second fraction (4.4 g.) of solid melting at 100° to a turbid mass. Further concentration of the mother liquor resulted in a molasses-like residue. The solid obtained from the second fraction was recrystallized three times from ethanol to give 2.4 g. (26%) of colorless, fluffy crystals melting at 111–112°.

Anal.[8] Calcd. for $C_{33}H_{30}OSi$: Si, 5.96. Found: Si, 5.85, 5.90.

An infrared spectrum of this compound showed absorption characteristic of a silicon–oxygen bond but no absorption characteristic of a hydroxyl group.

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[6] All melting points are uncorrected.

[7] H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, in press (1953).

[8] H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950). For micro analysis see H. Gilman and L. S. Miller, *ibid.*, **73**, 968 (1951).

[9] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).