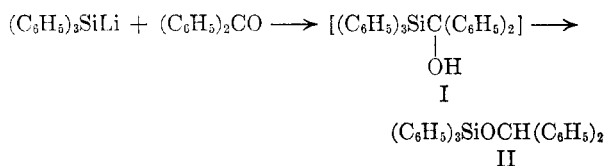


Addition of Triphenylsilane, Diphenylsilane, and Phenylsilane to Benzophenone

HENRY GILMAN AND DIETMAR WITTENBERG

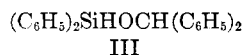
Received October 2, 1957

It has been reported that triphenylsilylpotassium¹ and triphenylsilyllithium² add to the carbonyl group of benzophenone. Upon hydrolysis, however, the "abnormal" addition product benzohydroxytriphenylsilane (II) was obtained, in which the silicon atom is bonded to the oxygen. It has been shown recently,³ that the "normal" addition product (I) might have been formed as an intermediate, since I rearranges in the presence of a catalytic amount of base to form II.



We wish to report some results on the addition of triphenylsilane, diphenylsilane and phenylsilane to benzophenone at high temperatures, in the absence of any added catalyst or an activating agent, as a new approach to similar compounds containing an Si—O—C group. Among the analogous carbon compounds triphenylmethane, diphenylmethane, and toluene, the two latter were reported⁴ to add to benzophenone after prolonged radiation in sunlight to form the "normal" addition products 1,1,2,2-tetraphenylethanol and 1,1,2-triphenylethanol. In the reaction of silicon hydrides with benzophenone, however, only "abnormal" addition products were obtained, and there is no evidence for the formation of any Si—C—OH type by-products. However, a rearrangement of the carbonyl by catalytic influences is not excluded.

When an equimolecular mixture of triphenylsilane and benzophenone was heated for 3 hr. at 250–270°, II was obtained in a 62% yield. Diphenylsilane on heating for 2 hr. at 220–230° with benzophenone gave benzohydroxydiphenylsilane (III) in a 68.5% yield.



On heating phenylsilane with benzophenone (1:1 ratio) in a sealed tube for 5 hr. at 200°, starting material was recovered. However, when the

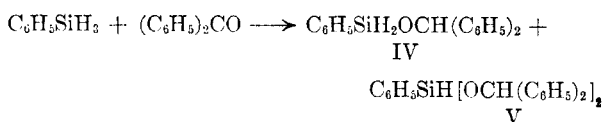
(1) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 2935 (1953).

(2) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 607 (1958).

(3) A. G. Brook, private communication.

(4) E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **39**, II, 415 (1909); G. Ciamician and P. Silber, *Ber. deut. chem. Ges.*, **43**, 1536 (1910).

same reaction was carried out at 250°, distillation of the reaction mixture gave benzohydroxyphenylsilane (IV) in a 20% yield and bis(benzohydroxy)phenylsilane (V) in a 64.5% yield.



In other reactions, attempts to isolate the addition products of two molecules of benzophenone to one of diphenylsilane or three molecules of benzophenone to one of phenylsilane have not yet been successful. Using higher reaction temperatures or longer reaction periods gave mixtures from which only decomposition products such as benzohydrol, benzohydryl ether, and 1,1,2,2-tetraphenylethane were isolated. Benzalacetophenone did not react with triphenylsilane at 150°. At higher temperatures only decomposition products (stilbene,⁵ benzylacetophenone, triphenylsilanol, and hexaphenyldisiloxane) were obtained.

In a publication,⁶ which just appeared, the reaction of trichlorosilane and triphenylsilane with aliphatic ketones in the presence of ultraviolet radiation was investigated and similar compounds containing an Si—O—C group were obtained. Under their conditions, however, acetophenone and benzophenone failed to react.

EXPERIMENTAL⁷

Materials. Triphenylsilane was prepared as reported previously.⁸ Diphenylsilane and phenylsilane were prepared by reduction of the corresponding chlorosilanes with lithium aluminum hydride by a variation of the method of R. A. Benkeser,⁹ using tetrahydrofuran as a solvent instead of ether. Eastman White Label benzophenone was used in all reactions.

Triphenylsilane and benzophenone. Thirteen grams (0.05 mole) of triphenylsilane and 9.1 g. (0.05 mole) of benzophenone were heated in a distillation flask for 3 hr. at 250–270°. After removal of 4.7 g. (21%) of starting material by distillation, boiling over the range 135–175°/3 mm., the residue was dissolved in petroleum ether (b.p. 60–70°) and allowed to stand overnight in the refrigerator. There was obtained 13.7 g. (62%) of benzohydroxytriphenylsilane (II), m.p. 82.5–84°. Recrystallization of a sample from petroleum ether (b.p. 60–70°) raised the melting point to 83–84°. A mixed melting point with an authentic sample obtained from the reaction of triphenylsilyllithium and benzophenone² was not depressed. Also the infrared spectra were identical.

(5) Stilbene is one of the reported pyrolysis products of benzalacetophenone; H. Stobbe and K. Bremer, *J. prakt. Chem.*, [2] **123**, 36 (1929).

(6) R. Calas and N. Duffaut, *Compt. rend.*, **245**, 906 (1957).

(7) Melting points and boiling points are uncorrected.

(8) H. Gilman and H. W. Melvin, Jr., *J. Am. Chem. Soc.*, **71**, 4050 (1949). See also H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, *J. Am. Chem. Soc.*, **51**, 3070 (1929).

(9) R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 648 (1952).

Diphenylsilane and benzophenone. Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.1 g. (0.05 mole) of benzophenone were heated in a distillation flask for 2 hr. at 220–230°. Distillation gave 0.3 g. (3%) of crude diphenylsilane, b.p. 113–125°/3 mm., and 1.05 g. (11%) of crude benzophenone, b.p. 130–135°/3 mm. The colorless, solid distillation residue was recrystallized from petroleum ether (b.p. 60–70°) to give 12.5 g. (68.5%) of benzohydroxydiphenylsilane (III), m.p. 79–81°. Recrystallization of a sample from ethanol raised the melting point to 81.5–82.5°.

Anal. Calcd. for $C_{25}H_{22}OSi$: Si, 7.65. Found: Si, 7.59, 7.59.

Supporting evidence for the structure was obtained by the infrared spectrum, which was almost identical with the spectrum of compound II except for a band at 4.7 μ attributable to the Si—H group.

Additional evidence conforming the structure of this compound was obtained by acid hydrolysis, which yielded an oil, from which some benzohydril ether, m.p. 108–109° was isolated. This benzohydril ether was shown to be identical with an authentic sample by mixed melting point and infrared spectra.

Phenylsilane and benzophenone. Five and four-tenths grams (0.05 mole) of phenylsilane and 9.1 g. (0.05 mole) of benzophenone were placed under nitrogen in a Schlenk tube. The sealed tube was immersed in an oil bath, which was heated slowly up to 250° and maintained at this temperature for 4 hr.¹⁰ The run was worked up by distillation. There were recovered 0.35 g. (6.5%) of phenylsilane, b.p. 115–120°/750 mm., and 0.55 g. (6%) of crude benzophenone, boiling over the range 130–145°/3 mm. In addition, 2.9 g. (20%) of benzohydroxyphenylsilane (IV), b.p. 145–148°/0.07 mm., n_D^{20} 1.5863, d_4^{20} 1.076, and 7.6 g. (64.6%) of bis(benzohydroxy)phenylsilane (V), b.p. 238–243°/0.07 mm., n_D^{20} 1.6032, were obtained. After standing for 5 days in the refrigerator, V crystallized, melting over the range 53–60°. Recrystallization from methanol raised the melting point to 63–63.5°.

Anal. Calcd. for $C_{19}H_{15}OSi$ (IV): Si, 9.66; MR, 90.44. Found: Si, 9.49, 9.56; MR, 90.62. Calcd. for $C_{22}H_{20}O_2Si$ (V): Si, 5.94. Found: Si, 5.98, 6.07.

Supporting evidence for the structure of both compounds IV and V was obtained by the infrared spectra, which were almost identical with that of compound III except some difference in the absorption intensity at 4.6–4.7 μ where the Si—H band is located.

Triphenylsilane and benzalacetophenone. Thirteen grams (0.05 mole) of triphenylsilane and 10.4 g. (0.05 mole) of benzalacetophenone were heated in a distillation flask for 16 hr. at 150°. Distillation under reduced pressure thereafter gave back 85% of the starting materials. No crystalline material was isolated from the dark brown distillation residue.

In a second run 13 g. (0.05 mole) of triphenylsilane and 10.4 g. (0.05 mole) of benzalacetophenone were heated for 2 hr. at 250°. The dark brown reaction mixture was worked up by distillation. Fraction 1, 1.7 g., boiling at 145–160°/3 mm., gave after crystallization from petroleum ether (b.p. 60–70°) 0.70 g. (15.5%) of stilbene, m.p. 120–122°. Fraction 2, 3.1 g., boiling at 175–200°/3 mm., gave after crystallization from petroleum ether (b.p. 60–70°) 0.80 g. (5.8%) of triphenylsilanol. The dark brown distillation residue was dissolved in petroleum ether and chromatographed on alumina. Besides yellow oils, which could not be crystallized or further purified, there were obtained 0.60 g. (5.5%) of benzylacetophenone, m.p. 71–72°, and 1.25 g. (9.4%) of hexaphenyldisiloxane, m.p. 223–226°.

Acknowledgment. This research was supported by the United States Air Force under Contract

AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to E. Miller Layton and Miss M. Powers for the spectra.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

Preparation of 3,4-Dichlorotetrahydrothiophene-1,1-dioxide-Cl³⁶

F. H. FIRSCHING AND IRVING ROSEN

Received October 3, 1957

After the discovery of the nematocidal activity of 3,4-dichlorotetrahydrothiophene-1,1-dioxide,¹ it became necessary to prepare this compound in a radioactive form for tracer studies. The incorporation of carbon-14, sulfur-35, and chlorine-36 in the compound was considered. Chlorine-36 was selected because it involved the minimum handling of radioactive material and would provide desired information on the fate of the chlorine in the molecule.

Although the steps in the synthesis are not new, modification was necessary for the use of radioactive chlorine. The need for preparing the compound with an adequate specific activity made it necessary to avoid an excessive dilution of the chlorine-36 with stable chlorine, and to perform the reaction at elevated temperatures to ensure the maximum yield of product. (The reaction of chlorine with 2,5-dihydrothiophene-1,1-dioxide does not proceed readily at room temperatures.) The availability of chlorine-36 labeled hydrochloric acid² fixed the starting point, and the known chloride-chlorine exchange reaction³ was selected to provide the labeled chlorine gas. The reaction between equivalent quantities of the labeled chlorine and 2,5-dihydrothiophene-1,1-dioxide at 60–70°C for four hours gave an 80% yield (crude) of the 3,4-dichlorotetrahydrothiophene-1,1-dioxide -C1³⁶, consisting predominantly of the *trans* isomer.

EXPERIMENTAL

The radiochlorination method of Craig, Tryon, and Brown⁴ was used with some modifications. A gas train was arranged in the following sequence: a cylinder of chlorine gas, a concentrated sulfuric acid bubbler, a bleed-off valve, a fritted

(1) Diamond Alkali Company, trade name, "PRD."

(2) Oak Ridge National Laboratory, Oak Ridge, Tenn.

(3) R. S. Halford, *J. Am. Chem. Soc.*, **62**, 3233 (1940).

(4) J. T. Craig, P. F. Tryon, and W. G. Brown, *Anal. Chem.*, **25**, 1661 (1953).

(10) As a precautionary measure, this sealed tube reaction was carried out behind appropriate shields.