α-Silyl-Substituted Ylides. Tetraphenylallene *via* the Wittig Reaction

HENRY GILMAN AND RICHARD A. TOMASI

Chemical Laboratory of Iowa State University, Ames, Iowa

Received May 28, 1962

Attempts to obtain vinyl silicon compounds from the treatment of organosilylmethylides with benzophenone or Michler's ketone were not successful. From a reaction involving benzophenone, tetraphenylallene was isolated, indicative of the presence of a diphenylvinylide. Tetraphenylallene was also obtained from the reaction of benzophenone with (2,2-diphenylvinylidene)triphenylphosphorane. Octaphenylcyclotetrasilane was found to react with methylenetriphenylphosphorane.

Some preliminary reactions were carried out on the possibility of utilizing organosilyl-substituted ylides[1] for the preparation of vinyl silicon compounds. Trimethylsilylmethyl- and triphenylsilylmethylphosphonium salts were synthesized by the method of Seyferth and Grim.[2] The difficulty experienced by them in isolating trimethylsilylmethyltriphenylphosphonium bromide[2] led to the treatment of the salts, *in situ*, with phenyllithium. The reaction scheme is shown in the following equation.

$$R_3SiCl + C^-H_2P^+(C_6H_5)_3 \longrightarrow R_3SiCH_2P^+(C_6H_5)_3 + Cl^- \xrightarrow{C_6H_5Li} R_3SiC^-HP^+(C_6H_5)_3 + C_6H_6$$

(R is phenyl or methyl)

Chlorotrimethylsilane was carried through the sequence of reactions, followed by the addition of benzophenone. Among the materials obtained there was isolated a rather unexpected product, tetraphenylallene, in yields of 20 and 35% in two runs. This compound would be the normal product from the reaction of diphenylvinylide with benzophenone, a reaction which was established in a separate experiment, as illustrated in the following equation. The crude yield of tetraphenylallene from this reaction was 54% in a small-scale run. Using this method, it may be possible to synthesize allenes with any degree of substitution from vinylides and carbonyl compounds, as shown in the following equation. This technique should compliment allene syntheses from methylides

$$(C_6H_5)_2C{=}CHP^+(C_6H_5)_3,\ Br^- \xrightarrow{C_6H_5Li} \underset{\text{I}}{(C_6H_5)_2C{=}C^-{-}P^+(C_6H_5)_3} \xrightarrow{(C_6H_5)_2C=O} (C_6H_5)_2C{=}C{=}C(C_6H_5)_2 + (C_6H_5)_3P{=}O$$

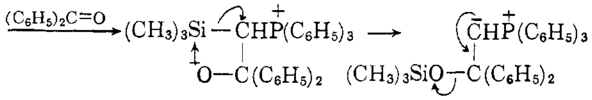
$$R^1R^2C{=}C{=}P(C_6H_5)_3 + R^3R^4C{=}O \longrightarrow R^1R^2C{=}C{=}CR^3R^4 + (C_6H_5)_3P{=}O$$

and ketenes, as reported from the reaction of diphenylketene with triphenyl(diphenylmethylidene)phosphorane,[3] and more recently developed by Wittig and Haag,[4] as illustrated in the following equation.

$$R^1R^2C{=}P(C_6H_5)_3 + (C_6H_5)_2C{=}C{=}O \longrightarrow R^1R^2C{=}C{=}C(C_6H_5)_2 + (C_6H_5)_3P{=}O$$

The formation of (2,2-diphenylvinylidene)triphenylphosphorane (I) in the reaction involving the trimethylsilylmethylide may be illustrated by the following mechanism. The reaction of II with benzophenone is apparently slow enough that appreciable amounts of the ketone are available to react with I.

$$(CH_3)_3SiCH_2P^+(C_6H_5)_3,\ X^- \xrightarrow{C_6H_5Li} \underset{\text{II}}{(CH_3)_3SiC^-HP^+(C_6H_5)_3}$$



$$\xrightarrow{(C_6H_5)_2C=O} \begin{array}{l}(CH_3)_3Si{-}\overset{}{C}H\overset{+}{P}(C_6H_5)_3 \\ \quad\ \ O{-}C(C_6H_5)_2\end{array} \longrightarrow \begin{array}{r}\bar{C}H\overset{+}{P}(C_6H_5)_3 \\ (CH_3)_3SiO{-}C(C_6H_5)_2\end{array}$$

$$\longrightarrow (CH_3)_3SiO^- + (C_6H_5)_2C{=}CHP^+(C_6H_5)_3 \longrightarrow (CH_3)_3SiOH + \text{I}$$

In addition to tetraphenylallene and triphenylphosphine oxide, there was also obtained a low yield of material which was apparently impure 1,1-diphenylethylene containing a small amount of (2,2-diphenylvinyl)trimethylsilane as indicated by analysis, but this was not confirmed. The formation of 1,1-diphenylethylene is indicative of a reaction of phenyllithium at the silicon in the intermediate salt, but only traces of phenyltrimethylsilane were obtained.

It seems that the solvent has an effect on the reaction, as no tetraphenylallene was isolated when the reaction was refluxed in xylene instead of tetrahydrofuran.

An attempt to effect a similar reaction with Michler's ketone in tetrahydrofuran did not provide any allene, and the ketone was recovered in good yield.

A similar sequence of reactions was carried out with chlorotriphenylsilane. Only a 6% yield of tetraphenylsilane was obtained, showing that the

---

[1] (a) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954). (b) See also the review by U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1961).

[2] D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1610 (1961).

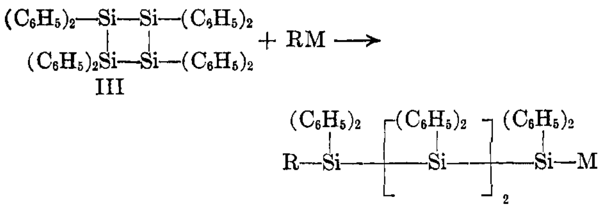
[3] G. Lüscher, *Dissertation*, Eidg. Tech. Hochschule, Zürich (1922) [cited in J. Meyer, *Ber.*, **89**, 842 (1956)].

[4] G. Wittig, private communication, 1962.

primary reaction of phenyllithium with the salt did not take place at the silicon. However, attempts to form a derivative of the proposed triphenylsilylmethylide with benzophenone in refluxing tetrahydrofuran or xylene did not afford (2,2-diphenylvinyl)triphenylsilane in isolable amounts. The principal products were triphenylsilanol and hexaphenyldisiloxane, evidently formed by hydrolysis of the ylide and the resulting salt. Methyltriphenylphosphonium salts were also obtained. About 15% of triphenylphosphine oxide was isolated (as a 1:1 mole-ratio complex with part of the triphenylsilanol). This is usually indicative that a Wittig reaction had occurred. A portion of the triphenylphosphine oxide would arise from a reaction of benzophenone with methylenetriphenylphosphorane formed simultaneously with the tetraphenylsilane. The remainder of the phosphine oxide (about 10%) may have resulted from a reaction of triphenylsilylmethylide with benzophenone, although no (2,2-diphenylvinyl)triphenylsilane or tetraphenylallene was isolated. Similar results were obtained with Michler's ketone, except that no triphenylphosphine oxide was isolated.

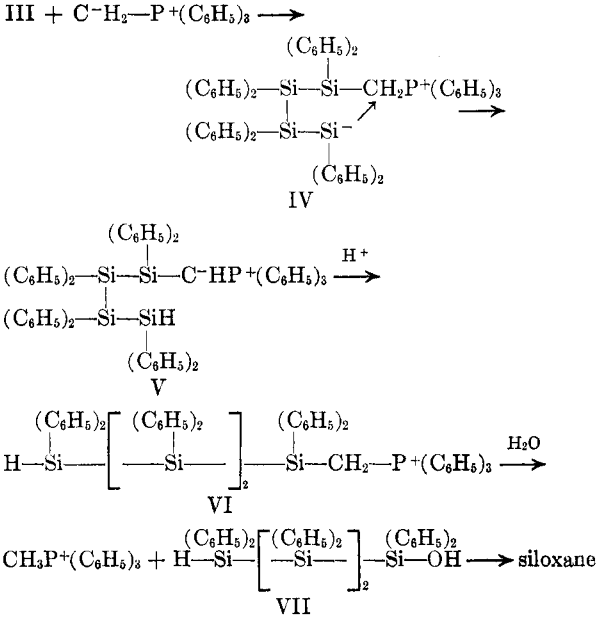
Apparently, the triphenylsilylmethylide was unable to react appreciably with the diaryl ketones under the conditions employed.

Octaphenylcyclotetrasilane (III)[5] has recently been observed to undergo ready cleavage by organometallic compounds,[6,7] including silylmetallics,[6] as shown in the following equation.



These reactions suggested that Wittig reagents might effect a similar cleavage.

Octaphenylcyclotetrasilane was treated with methylenetriphenylphosphorane in refluxing tetrahydrofuran and, subsequent to hydrolysis, products containing the silicon–hydrogen group were isolated in low yields. These materials also contained silanol or siloxane groups. Apparently, the reaction took the course illustrated in the following equation. The hydrolysis of the proposed phosphonium salt VI is analogous to that recently observed for trimethylsilylmethyltriphenylphosphonium bromide.[2] Hydrolysis of either IV or V would lead initially to VI. However, there is no reason to suspect that a silyl anion[8] would not react with the active hydrogen on the methylene group. Furthermore, the reaction mixture gave a negative Color Test I.[9] In addition, VII was also isolated in a second experiment in which benzophenone had been added, indicating that the silicon–hydrogen group had been formed prior to hydrolysis. No diphenylvinyl-substituted organosilicon compound could be isolated from this reaction, as would have resulted from a normal Wittig reaction of V with benzophenone. However, the results obtained in the other reactions are compatible with the nonreactivity of the intermediate ylide V toward benzophenone.



Experimental

All reactions were carried out in oven-dried glassware under atmospheres of oxygen-free, dry nitrogen. The temperatures reported are uncorrected. Ether and xylene were dried by storage over sodium wire. The tetrahydrofuran (THF) was purified by refluxing over sodium for at least 24 hr., distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. Methylenetriphenylphosphorane (VIII) was prepared in ether from treatment of methyltriphenylphosphonium bromide[1a] with phenyllithium. The method is essentially that of a published procedure,[1a] except that phenyllithium was prepared from bromobenzene and lithium instead of from diphenylmercury and lithium.

VIII and Chlorotrimethylsilane, Followed Successively by Phenyllithium and Benzophenone. Run 1.—To an ether suspension of methylenetriphenylphosphorane (VIII), prepared from 7.1 g. (0.02 mole) of methyltriphenylphosphonium bromide and 0.02 mole of phenyllithium in a total of *ca.* 50 ml. of ether, there was added 2.2 g. (0.02 mole) of chlorotrimethylsilane in 50 ml. of ether solution. There was an immediate formation of a light yellow precipitate. The reaction mixture was allowed to stir for 2 hr. at room

---

(5) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 1921 (1961); *ibid.*, **82**, 2076 (1960).

(6) A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, **26**, 1999 (1961).

(7) H. Gilman, K. Y. Chang, G. L. Schwebke, and A. W. P. Jarvie, unpublished studies.

(8) For reviews on silylmetallic chemistry, see D. Wittenberg and H. Gilman, *Quart. Rev.*, **13**, 116 (1959); H. Gilman and H. J. S. Winkler, "Organosilylmetallic Chemistry," in H. Zeiss, ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, 1960, pp. 270–345.

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

temperature, followed by the addition of 0.02 mole of phenyllithium. Color Test I was weakly positive after 2 hr. of stirring. Benzophenone, 3.6 g. (0.02 mole), was added directly to the dark suspension along with 50 ml. of THF. The ether was removed by distillation and the remaining suspension refluxed for 24 hr. The reaction mixture was hydrolyzed in dilute acid and worked up in the usual manner. Subsequent to the removal of solvents, petroleum ether (b.p. 60–70°) was added to give 3.6 g. (64.9%) of triphenylphosphine oxide, m.p. 155–156° (mixed m.p.). The petroleum ether was removed from the mother liquor and the addition of ethanol gave 0.7 g. (19.4%) of impure tetraphenylallene, m.p. 155–160°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 164–165° (mixed m.p. with an authentic sample prepared by the pyrolysis of barium diphenylacetate according to published directions[10]). The solvent was removed from the mother liquor and the residue distilled under reduced pressure to give several fractions: 0.1 g. (3%), b.p. 50–55° (60 mm.), the infrared spectrum of which indicated it to be impure trimethylphenylsilane; 0.1 g., b.p. 100–105° (1.7 mm.); 1.0 g., b.p. 105–110° (1.7 mm.), $n^{20}D$ 1.5921. The infrared spectra of the last two fractions were similar to that of 1,1-diphenylethylene except for weak absorption bands usually associated with the trimethylsilyl group. These materials were combined and redistilled to give several small fractions boiling in the range 88–102° (1.5 mm.). An analysis on one of the fractions, b.p. 100–102° (1.5 mm.), gave the combined carbon and hydrogen content as 97.5%, a value too high for (2,2-diphenylvinyl)-trimethylsilane, which requires 88.7%.

Run 2.—The reaction was carried out as described in Run 1, except that twice the quantities of reagents were used, and, prior to the addition of the benzophenone, the reaction mixture was refluxed for 30 min., 50 ml. of THF was added, and most of the ether removed by distillation. Color Test I[9] was negative. After addition of the benzophenone, the reaction mixture was refluxed for 24 hr., during which most of the solvent escaped. Ether was added and the mixture was hydrolyzed and worked up as described in Run 1. Subsequent to the removal of the solvents acetone was added to the residue and the insoluble material filtered to give 2.4 g. (35.5%) of impure tetraphenylallene, m.p. 157–163°. Recrystallization from acetone gave 1.9 g. (27.6%) of pure product, m.p. 164–166° (mixed m.p.). A reduced pressure distillation of the materials remaining in the mother liquor gave several small fractions of materials boiling over a wide range. From the distillation residue, there was isolated 1.0 g. (9.1%) of triphenylphosphine oxide, m.p. 156–157° (mixed m.p.).

Run 3.—The reaction was carried out as described in Run 1, except that xylene was added instead of THF and two molar equivalents of benzophenone was used. The final mixture was refluxed for 70 hr., hydrolyzed, and worked up as previously described. No tetraphenylallene could be isolated. The yield of impure triphenylphosphine oxide was 2.3 g. (41.5%), m.p. 140–150°. The melting point was raised to 155–157° (mixed m.p.) upon recrystallization. Distillation of the material remaining in the mother liquor gave four fractions boiling between 90–112° (1.6 mm.), the infrared spectra of which indicated them to be mixtures of 1,1-diphenylethylene and benzophenone.

VIII and Chlorotrimethylsilane, Followed Successively by Phenyllithium and Michler's Ketone (Attempted).—The reaction was carried out in an analogous manner to that described in the preceding experiment, Run 1, except that Michler's ketone, 5.4 g. (0.02 mole) was used. After removal of the ether, the THF suspension was refluxed for 18 hr. Subsequent to hydrolysis and work-up, 4.4 g. (81.5%) of recovered, impure Michler's ketone was isolated, m.p. 158–164°. Recrystallization raised the melting point to 174–176° (mixed m.p.). There was also obtained 1.0 g. (18%) of triphenylphosphine oxide, m.p. 154–155° (mixed m.p.). Attempts to isolate other products were unsuccessful.

VIII and Chlorotriphenylsilane, Followed Successively by Phenyllithium and Benzophenone.—Methylenetriphenylphosphorane was prepared from 7.2 g. (0.02 mole) of methyltriphenylphosphonium bromide and 0.02 mole of phenyllithium in a total of 75 ml. of ether. Addition of 6.0 g. (0.02 mole) of chlorotriphenylsilane resulted in an immediate formation of a heavy, pale yellow precipitate. The reaction mixture was allowed to stir at room temperature for 2 hr. A second equivalent of phenyllithium was added and, after stirring for 2 hr., Color Test I[9] was negative; 3.6 g. (0.02 mole) of benzophenone and 50 ml. of THF were added. The ether was removed by distillation and the THF suspension refluxed for 3 hr. The brown, homogeneous mixture was hydrolyzed in dilute hydrochloric acid. An oily interphase formed which was separated with the aqueous layer. The oily material solidified on standing. It was filtered, treated with hot benzene, and refiltered. The material was boiled with hot water, filtered, and dried to give 1.6 g. (30%) of impure hexaphenyldisiloxane, m.p. 212–220°. Recrystallization raised the melting point to 224–226° (mixed m.p.). An additional 1.5 g. (28.2%) of hexaphenyldisiloxane, m.p. 224–226° (mixed m.p.), was obtained upon cooling the benzene filtrate. The wash water and the aqueous layer were combined and evaporated under a jet of air, leaving a gummy residue. The material was taken up in chloroform, dried over sodium sulfate, and precipitated by the addition of benzene to give 3.8 g. (51.6%) of impure methyltriphenylphosphonium salts, m.p. 220–230°. Its infrared spectrum was superimposable upon that of the pure bromide. The organic layer was worked up in the usual manner and, subsequent to the removal of solvent, a light brown oil was obtained. Treatment with cold methanol left 0.4 g. (6%) of impure tetraphenylsilane, m.p. 200–220°. Recrystallization from ethyl acetate raised the melting point to 230–232° (mixed m.p.). The methanol filtrate was evaporated and yielded a brown oil which was dissolved in benzene. The solution was treated with decolorizing charcoal, filtered, and concentrated. The addition of hot petroleum ether (b.p. 60–70°) and cooling gave 1.5 g. (16%) of solid material, m.p. 120–130°. Recrystallization, after treatment with decolorizing charcoal, gave 1.1 g. of crystals, m.p. 122–123°. The melting point remained constant on subsequent recrystallization. This material was identified as a 1:1 mole-ratio complex of triphenylsilanol and triphenylphosphine oxide by infrared, n.m.r., and elemental analysis.[11]

Anal. Calcd. for $C_{36}H_{31}O_2PSi$: C, 77.97; H, 5.65; Si, 5.06. Found: C, 77.94, 78.01; H, 5.66, 5.80; Si, 5.06, 4.70.

This complex was also obtained simply by crystallization of a prepared mixture of 1.0 g. (0.003 mole) of triphenylphosphine oxide (m.p. 156–157°), and 1.0 g. (0.003 mole) of triphenylsilanol (m.p. 154–155°), from a mixture of benzene and petroleum ether (b.p. 60–70°); 1.8 g. (90%) of crystals were obtained, which melted at 123–124° and did not depress the melting point of the material isolated from the reaction mixture. The infrared spectra were superimposable.

The solvents were removed from the original mother liquor and the residue chromatographed on alumina. The petroleum ether (b.p. 60–70°), cyclohexane, and benzene eluates, upon removal of the solvents, gave oils, the infrared spectra of which indicated that they were mainly benzophenone. Attempts to crystallize these oils were unsuccessful. From the methanol eluate, there was obtained 0.7 g. (12.5%) of impure triphenylsilanol, m.p. 140–150°. Recrystallization raised the melting point to 152–155° (mixed m.p.).

---

(10) D. Vorländer and C. Siebert, *Ber.*, **39**, 1024 (1906).

(11) A molecular weight determination in camphor by the Rast method gave inconsistent values ranging from 300–430. Silicon analyses were carried out in the usual manner; the residues were fused with sodium carbonate, and the silica reprecipitated after dehydration from hydrochloric acid. The filtrate was concentrated and gave a positive qualitative test for phosphorus with ammonium molybdate.

Similar results were obtained from two other runs. In one case, the final THF suspension was refluxed for 24 hr. prior to hydrolysis. The other run was carried out using xylene in the place of THF; the mixture was refluxed for 64 hr. after removal of the ether.

VIII and Chlorotriphenylsilane, Followed Successively with Phenyllithium and Michler's Ketone (Attempted).—The reaction was carried out as described in the preceding experiment, with the exception that 5.4 g. (0.02 mole) of Michler's ketone was added instead of benzophenone and the reaction mixture, subsequent to removal of the ether, was refluxed for 18 hr. Hydrolysis in excess dilute acid afforded an oil which solidified and was filtered off. Recrystallization from ethyl acetate gave 5.0 g. (69.5%) of impure methyltriphenylphosphonium salt, m.p. 200–230° (identified by its infrared spectrum). The aqueous layer was neutralized by the addition of sodium carbonate and yielded 4.1 g. (76%) of recovered ketone, m.p. 173–175° (mixed m.p.). Work-up of the organic layer afforded 4.4 g. (78%) of impure triphenylsilanol, m.p. 135–144°. Recrystallization raised the melting point to 152–154° (mixed m.p.).

Preparation of (2,2-Diphenylvinyl)triphenylphosphonium Bromide.—The method used was similar to that described for the preparation of tetraphenylphosphonium bromide.[12] 2,2-Diphenylvinylmagnesium bromide was prepared from 30 g. (0.12 mole) of 2,2-diphenylvinyl bromide[13] and 4.9 g. (0.2 g.-atom) of magnesium in a total of 150 ml. of ether. The solution was filtered through a glass-wool plug into an addition funnel, where the Grignard reagent precipitated with the evolution of considerable heat. Upon cooling, the material was dissolved by the addition of 25 ml. of THF. The yield, based on acid titration, was 77%. To 19.0 g. (0.072 mole) of triphenylphosphine in 100 ml. of ether 0.072 mole of the Grignard reagent was added. The mixture was allowed to stir overnight and was refluxed for 1 hr. Dry oxygen was bubbled through the solution for 3 hr., during which the reaction vessel was cooled by a water bath. A sticky, semisolid material formed and gathered in one lump. The mixture was poured upon crushed ice containing excess hydrobromic acid. The mixture was filtered to give 1.1 g. of a solid, m.p. 186–190°. The infrared spectrum indicated that it did not contain the triphenylphosphorus group, so this material was not further investigated. The filtrate was composed of an oil suspended in the aqueous phase. The oil was separated and washed with ether. The oil, when heated for 15 min. in boiling toluene, solidified to give 5.7 g. (15.2%) of a brown solid, m.p. 190–200°. This material was placed in hot THF and dissolved upon the addition of a few drops of water. The hot solution was treated with decolorizing charcoal, filtered, and cooled to give 3.4 g. (9.1%) of light brown crystals. Recrystallization gave 2.7 g. (7.2%) of solid, m.p. 248–250°. The melting point was unchanged after another recrystallization. The phosphonium salt was thoroughly dried at 100° under 0.5 mm. pressure without loss in weight.

Anal. Calcd. for $C_{32}H_{26}BrP$: C, 73.71; H, 5.03; Br, 15.33. Found: C, 73.81, 73.89; H, 4.72, 4.93; Br, 15.76, 16.06.

Preparation of (2,2-Diphenylvinylidene)triphenylphosphorane and Reaction with Benzophenone.—Two grams (0.004 mole) of (2,2-diphenylvinyl)triphenylphosphonium bromide, suspended in 25 ml. of ether, was treated with 0.004 mole of phenyllithium. The mixture turned a dark red immediately upon the addition. After 1 hr. of stirring at room temperature, only a small amount of solids remained, which dissolved upon the addition of 75 ml. of THF. To the dark, purplish brown solution, 0.9 g. (0.005 mole) of benzophenone was added. Subsequent to the removal of the ether by distillation, the mixture was refluxed for 12 hr. and hydrolyzed in dilute acid. The mixture was worked up in the usual fashion and the solvents removed by distillation, yielding a brown, semisolid material. Treatment with cold ethanol and filtration gave 0.7 g. (53.5%) of impure tetraphenylallene, m.p. 160–165°. Recrystallization from acetone gave 0.6 g. (45.7%) of pure product, m.p. 164–165° (mixed m.p.). The solvent was removed from the mother liquor and the residue crystallized from cyclohexane to give 0.4 g. (40%) of triphenylphosphine oxide, m.p. 154–157° (mixed m.p.).

VIII and Octaphenylcyclotetrasilane. Run 1.—Methylenetriphenylphosphorane, prepared from 2.5 g. (0.007 mole) of methyltriphenylphosphonium bromide and 0.007 mole of phenyllithium in a total of 40 ml. of ether, and 5.0 g. (0.007 mole) of octaphenylcyclotetrasilane were refluxed for 3 hr., in a THF suspension after removal of the ether. The light yellow suspension, which gave a negative Color Test I,[9] was hydrolyzed in dilute acetic acid. The sticky solid obtained was washed with methanol and dried to give 3.0 g. (60%) of recovered octaphenylcyclotetrasilane, m.p. 317–320° (mixed m.p.). The methanol used to wash the solids was evaporated to give a brown oil. Treatment with ethyl acetate gave 0.5 g. (25%) of methyltriphenylphosphonium bromide, m.p. 225–230° (mixed m.p.). The aqueous layer, on standing, turned cloudy. It was extracted with ether and filtered to give 0.3 g. of unidentified material, m.p. 110–140°. Recrystallizations failed to give any pure products. The infrared spectrum showed the presence of bands characteristic of phenyl–silicon, silicon–hydrogen, silanol, and siloxane groups. The ether extracts were worked up in the usual manner. Subsequent to the removal of the solvents, a sticky solid was obtained. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 0.5 g. (9.5%) of impure 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, m.p. 156–162°. Recrystallization raised the melting point to 180–182° (mixed m.p.).

Run 2. Addition of Benzophenone.—A second run was carried out using the same quantities of starting materials. After refluxing the THF suspension for 2 hr., 1.3 g. (0.007 mole) of benzophenone was added and the mixture refluxed an additional 2 hr. Work-up in a manner similar to that described in the preceding paragraph gave 1.0 g. (20%) of recovered octaphenylcyclotetrasilane, m.p. 316–320° (mixed m.p.); 1.4 g. (57%) of methyltriphenylphosphonium bromide, m.p. 227–229° (mixed m.p.); 0.5 g. (10%) of impure, m.p. 145–164°, and 0.3 g. (6%) of pure 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, m.p. 182–184° (mixed m.p.); and 1.4 g. (28%) of material, m.p. 110–125°, from which there was obtained, after four recrystallizations from ethyl acetate, 0.3 g. (6%) of the same siloxane obtained upon hydrolysis of 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 140–142° (mixed m.p.).[14]

Acknowledgment.—This research was supported in part by the United States Air Force under contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

---

[12] J. Dodanov and H. Medox, *Ber.*, **61**, 907 (1928); H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, **67**, 824 (1945); and H. H. Willard, L. R. Perkins, and F. F. Blicke, *ibid.*, **70**, 737 (1948).

[13] Prepared by the method of G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

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