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[Contribution from the Department of Chemistry, University of Toronto]

The Reaction of Triphenylsilylmetallics with Benzophenone, A Reinvestigation. I[1]

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Reinvestigation of the reaction of triphenylsilylmetallics with benzophenone has led to the isolation of two new species, triphenylsiloxydiphenylmethylpotassium and 2-triphenylsiloxytetraphenylethanol. The role of the new products in the over-all reaction, and some of their reactions are described.

It has been reported by Gilman and Wu[2] that the reaction of triphenylsilylpotassium with benzophenone gave not the expected triphenylsilyldiphenylcarbinol (I) but instead the isomeric silyl ether, benzhydryloxytriphenylsilane (II). More recently Gilman and Lichtenwalter[3] reported similar results from the reaction of triphenyl-, methyldiphenyl- and dimethylphenylsilyllithium with benzophenone where in each case the silyl ether was the product obtained.

Gilman and Wu attempted to explain these unusual results by suggesting the possibility of either "abnormal" addition to the carbonyl group, or of normal addition followed by rearrangement. We recently have reported that triphenylsilyldiphenylcarbinol[4a] and α-silylcarbinols in general[4b] are isomerized to the isomeric silyl ethers such as benzhydryloxytriphenylsilane by a variety of reagents including alkali, pyridine or traces of sodium or sodium–potassium alloy.

$$\underset{\text{I}}{\mathrm{Ph_3SiCPh_2OH}} \longrightarrow \underset{\text{II}}{\mathrm{Ph_3SiOCHPh_2}}$$

Since the salt of the carbinol may be an intermediate in the rearrangement of the carbinol to the ether,[4a,b] it follows that the salt of I, which would be formed by normal addition of triphenylsilylpotassium to benzophenone, should form the ether II actually isolated. In an attempt to establish with certainty the mode of addition of silylmetallics to benzophenone we have completely reinvestigated the reaction.

We have found, in agreement with the original authors, that the addition of benzophenone to triphenylsilylpotassium does under their conditions give rise to benzhydryloxytriphenylsilane accompanied by triphenylsilanol, triphenylsilane and recovered benzophenone. However, in many cases with slight changes in the conditions good yields of a new compound, 2-triphenylsiloxytetraphenylethanol (III), were obtained with little or no II being isolated. The yields and products isolated from a number of runs are summarized in Table I.

When benzophenone was added to one mole-equivalent of triphenylsilylpotassium the medium acquired intense color, dark brown or red-brown or blue. The mixture usually increased markedly in viscosity shortly after the reagents were mixed and a precipitate appeared to be present. Stirring for some time caused part of the precipitate to disappear. The viscosity decreased, and the medium usually became a very deep blue. However, when the reaction mixture was filtered at the time of maximum viscosity a dark red precipitate and a blue filtrate were obtained. The precipitate behaved as if it were triphenylsiloxydiphenylmethylpotassium (IV). Thus hydrolysis with dilute acid

$$\underset{\text{III}}{\mathrm{Ph_3SiOCPh_2CPh_2OH}} \qquad \underset{\text{IV}}{\mathrm{Ph_3SiOCPh_2K}}$$

gave benzhydryloxytriphenylsilane (II) in 70% yield, but hydrolysis with water, resulting in an alkaline aqueous phase, gave a lower yield of II as well as benzhydrol and triphenylsilanol.[5] Treatment of the red precipitate with one equivalent of benzophenone gave good yields of III, and its reactions with other reagents,[6] together with rough equivalent weight determinations described in the Experimental section, seem to confirm its identity as IV.

Evidently when benzophenone is added to triphenylsilylpotassium the first isolable material formed is the metallic IV. The metallic and triphenylsilylpotassium then compete for the remaining benzophenone, the latter reaction evidently being the faster since the metallic has been isolated in yields as high as 65–70%. However if more than one equivalent of benzophenone was added, or if a local excess of benzophenone was present resulting from very rapid addition of the benzophenone, the yield of IV was decreased and 2-triphenylsiloxytetraphenylethanol (III) was the chief product.[7] It should be noted, however, that III was not stable in the presence of triphenylsilylpotassium but was converted back to the metallic IV.

It was found that III was thermally unstable and could be recovered on recrystallization only in low yield, together with benzophenone and benzhydryloxytriphenylsilane (II) not present in the original crude III. For this reason crude yields of III are reported in Table I as being a more significant measure of the course of the reaction.

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[1] Presented in part at the 41st Annual Conference of the Chemical Institute of Canada at Toronto, Canada, May, 1958.

[2] H. Gilman and T. C. Wu, This Journal, **75**, 2935 (1953).

[3] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 607 (1958).

[4] (a) A. G. Brook, *ibid.*, **80**, 1886 (1958); (b) A. G. Brook, C. M. Warner and M. E. McGriskin, *ibid.*, **81**, 781 (1959).

[5] Gilman and Wu[2] used distilled water to hydrolyze their reaction mixtures. Benzhydryloxytriphenylsilane is cleaved readily at room temperature to yield benzhydrol and triphenylsilanol.

[6] Paper II, N. V. Schwartz and A. G. Brook, This Journal, **82**, 2439 (1960).

[7] The yields of III shown in Table I, where the molar ratio of silylmetallic to benzophenone is 1:1, were calculated on the basis of moles of silylmetallic, and thus appear low. If based on benzophenone the yields would be doubled, and thus high. In this connection, the moles of benzophenone employed was calculated on the basis that triphenylsilylmetallic was formed quantitatively from hexaphenyldisilane. Experience has indicated that a quantitative cleavage is rarely achieved, and in most cases a yield of 90–95% is obtained. Hence an excess of benzophenone beyond the 1:1 mole ratio was actually present.

TABLE I

REACTIONS OF TRIPHENYLSILYLMETALLICS WITH BENZOPHENONE

Mole of metallic^a	Mole of Ph_2CO	Time of addn., min.	Time of reacn., min.	Work-up^b	Products,	% yield^c
(1) 0.038 Na/K	0.038	20^d	80	HCl	Ph_6Si_2	10^p
					III	34
					Ph_3SiOH	15
					Ph_2CHOH	2
(2) .038 Na/K	.038	20^d	80	HCl	III	12.5^p
					Ph_3SiOH	12
					$Ph_3SiOCHPh_2$	13
(3) .038 Na/K	.038	10^d	60^e	HCl	Ph_3SiOH	27
					$Ph_3SiOCHPh_2$	38
(4) .04 Na/K	.04	10^d	10^g	HCl	III	52.5
					Ph_3SiOH	18
			265^h	H_2O	III	47
					Ph_3SiOH	23
(5) .02 Na/K	.04	20^f	20^i	HCl	III	48
					Ph_3SiOH	4
					Ph_2CO	26
					Ph_3SiH test	
			240^j	HCl	$Ph_3SiOCHPh_2$	5
					Ph_3SiOH	50
					Ph_2CO	45
(6) .02 Na/K	.04	15^f	15^k	HCl	III	60
			420^l	HCl	III	9
					Ph_3SiOH	11
					$Ph_3SiOCHPh_2$	3
					Ph_2CO	50
(7) .02 Li	.02	7^f	7	HCl	III	42.5
					Ph_3SiOH	8
(8) .02 Li	.02	15^{f,m}	15	HCl	III	39.5
					Ph_3SiOH	13
(9) .02 Na/K	.02	15^d	210	CO_2	Benzilic acid	12
					III	42.5
					Ph_6Si_2	4
				H_2O	III	30
					Ph_6Si_2	4
(10) .02 Na/K	.02	15^d	105	CO_2	Benzilic acid	19
					III	38.5
					Ph_3SiOH	11
(11) .01 Na/K	.008	2^d	75	CO_2	Benzilic acid	49
					Ph_3SiOH	58
(12) .02 Na/K	.016	5^d	90	CO_2	Benzilic acid	30
					Ph_3SiOH	54.5
(13) .04 Na/K	.04	70^d	80^n	CO_2	Ph_3SiOH	15
					Ph_2COH-COOH	25
			150	H_2O	Ph_3SiOH	25
					$Ph_3SiOCHPh_2$	49
					Ph_6Si_2	2
					Ph_3SiH	21
			145	HCl	Ph_3SiOH	24
					$Ph_3SiOCHPh_2$	25
					Ph_6Si_2	2
					Ph_3SiH	14

[a] Actually 2 × moles of Ph_6Si_2 cleaved by Na/K, *i.e.*, assuming 100% yield of metallic. [b] Reagent with which reaction mixture was treated in work-up. Note that in some runs (*e.g.*, 4) aliquots of the reaction mixture were treated with several reagents after different times. [c] Yields of III are crude, and are based on moles of metallic used. [d] Reaction carried out at room temperature. [e] Red-brown after a few min., became blue after 55 min. stirring. [f] Reaction carried out at −70°. [g] No significant color change during addition. [h] 50% of above mixture stirred for 145 min. at −70°, then warmed to 10° over 60 min. and hydrolyzed. [i] Deep blue after 25% of benzophenone added; excess alloy had not been removed completely from Ph_3SiK. [j] 50% of above warmed to 20° over 60 min. and hydrolyzed after total of 270 min. by which time blue color had disappeared and mixture was yellow-brown. [k] Slight blue color after 50% of benzophenone added. [l] 50% of above warmed to 20°. [m] Metallic added to benzophenone. [n] Started to turn blue after 80 min.; this was not generally characteristic of the runs which usually turned blue earlier. [p] The apparent lack of reproducibility of these runs is characteristic of the longer reaction periods. It is probably attributable to the presence in run 2 of traces of sodium–potassium alloy.

We believe that the deep blue color formed in the reaction mixture of triphenylsilylpotassium and benzophenone is attributable to the presence of benzophenone ketyl (V) $\cdot CPh_2OK$. Although carbonation of the red metallic IV yields large amounts of benzilic acid and triphenylsilanol, rather than the expected triphenylsiloxydiphenylacetic acid (VI),[6] it was found that carbonation of the deep blue filtrate from the isolation of the metallic IV also yielded small amounts of benzilic acid which we believe arose from carbonation of the ketyl.[8]

$$\underset{\text{IV}}{Ph_3SiOCPh_2K} + CO_2 \longrightarrow \underset{\text{VI}}{[Ph_3SiOCPh_2COOH]} \longrightarrow$$
$$HOCPh_2COOH + Ph_3SiOH$$

The large yields of benzilic acid obtained from the carbonation of the entire reaction mixture, however, arose chiefly from the carbonation of IV.

Benzophenone ketyl probably arises in the reaction mixture in several ways. It is quite probable in some cases, though not all, that traces of sodium–potassium alloy, not removed by amalgamation during the preparation of the triphenylsilylpotassium,[9] would react with benzophenone to form the ketyl. In addition it seems possible that benzophenone may in part abstract the metal from triphenylsilylpotassium to form the ketyl and by-products such as the triphenylsilane and triphenylsilanol frequently encountered.[10] In addition, benzophenone ketyl undoubtedly was formed in some runs by decomposition of III. In some cases where the mixture was stirred for some hours prior to hydrolysis the amount of III was much less than the amount isolated from a portion of the mixture worked up immediately (runs 5 and 6). In other runs no appreciable change in the yield of III occurred with several hours stirring (runs 4, 9). This reduction in the yield of III is again associated with the presence of traces of sodium–potassium alloy, the initial products of the decomposition probably being benzhydryloxytriphenylsilane and benzophenone ketyl, but on further reaction the benzhydryloxytriphenylsilane is further cleaved yielding tripheny silanol and benzophenone (runs 5b, 6b).

Thus III, or its salt in ether, when treated with alloy, rapidly gave a deep blue solution, which on carbonation yielded 10% of benzilic acid, 90% of benzhydryloxytriphenylsilane and 68% of benzophenone. The decomposition of III can be described by the sequence

$$\begin{tikzcd}
\underset{\text{VII}}{Ph_3SiOPh_2CPh_2ONa} \arrow[r] & \underset{\text{IV}}{Ph_3SiOCPh_2Na} \text{ or } Ph_3SiOCPh_2\cdot + \cdot CPh_2ONa \arrow[d, "Ph_3SiOCPh_2CPh_2OH"] \\
\underset{\text{III}}{Ph_3SiOCPh_2CPh_2OH} \arrow[u, "Na"'] & \underset{\text{VII}}{Ph_3SiOCPh_2CPh_2ONa} + Ph_3SiOCPh_2H \text{ or } Ph_2CO
\end{tikzcd}$$

On treatment with metal, III undoubtedly forms the salt VII. This compound in the presence of

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(8) E. Beckmann and T. Paul, *Ann.*, **266**, 1 (1891).

(9) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(10) It will be observed that in those cases where equimolar quantities of benzophenone and silylmetallic were used, only half the silylmetallic is consumed in the formation of III. The rest appears in the form of triphenylsilane or its hydrolysis product, triphenylsilanol.

metal dissociates or reacts to form benzophenone ketyl and either the radical triphenylsiloxydiphenylmethyl or the organometallic IV. These species do not accumulate in the system initially but instead react with additional III to form benzhydryloxytriphenylsilane, benzophenone and more of the salt VII which thus continues the cycle. It is significant that only a catalytic amount of metal is necessary to convert large quantities of III to these products and that no detectable hydrogen is liberated in the reaction. It has thus far proved impossible to demonstrate the presence of IV in this system, regardless of the conditions, which suggests that if formed, it subsequently reacts very rapidly with other species present in the reaction mixture.

Wittenberg, Wu and Gilman[11] recently have described rather similar reactions, based on this work, for the reaction of triphenylsilylithium with benzaldehyde, although the identity of some of their products, especially the analog of IV, has not been uniquely established. They account very satisfactorily for the isolation of hexaphenyldisilane, which also was isolated occasionally in this research, probably from similar reactions.

Although the formation of 2-triphenylsiloxytetraphenylethanol from the system benzophenone and triphenylsilylpotassium is accounted for by the isolation and reactions of the metallic triphenylsiloxydiphenylmethylpotassium (IV), the mode of formation of the metallic is still open to speculation. Triphenylsilylmetallics are known to add normally to the carbonyl group of aliphatic aldehydes[4,12] and aliphatic ketones[13] and the closely related triphenylgermylmetallics add normally even to benzophenone[14] and benzaldehyde.[15] While the rearrangement of these carbinols to the isomeric ether is relatively slow, and the salts of the carbinols probably do not rearrange at all,[16] the rearrangement of the diphenylcarbinols to their isomeric ethers is exceedingly rapid. Furthermore the rearrangement is catalyzed by traces of triphenylsilylpotassium, the metallic IV or sodium–potassium alloy, all of which may be present in the reaction mixture. Hence there is considerable justification for proposing that triphenylsilylpotassium reacts with benzophenone by normal addition, followed by a rapid rearrangement.

However, it has never been possible to isolate the salt of triphenylsilyldiphenylcarbinol or to demonstrate that the metallic IV is an intermediate in the rearrangement to its isomeric ether since the reaction cannot be stopped at an intermediate stage; the ether is isolated when the carbinol is treated with catalyst even without hydrolysis of the reaction mixture. Hence the isolation of the metallic IV in good yield from the reaction mixture suggests that triphenylsilylmetallic may have added to benzophenone by "abnormal" addition. In the absence of additional evidence it is therefore impossible to specify definitely the mode of addition of triphenylsilylmetallics to benzophenone.

Experimental[17]

Addition of Benzophenone to Triphenylsilylpotassium.—To 0.038 mole of triphenylsilylpotassium, from which excess sodium–potassium alloy had been removed by amalgamation, in 175 ml. of anhydrous ether was added with rapid stirring over 20 min. a solution of 6.9 g. (0.038 mole) of benzophenone in 70 ml. of ether. The system turned brown at first, but at the end of the addition turned intense blue in color and became quite viscous. It appeared that a precipitate had formed. A few minutes of additional stirring resulted in the viscous medium becoming more fluid. After 1 hr. of stirring the intensely blue reaction mixture was poured into 500 ml. of ice and dilute hydrochloric acid. An insoluble precipitate weighing 1.05 g. (10%) was filtered off and shown to be hexaphenyldisilane, m.p. 354–356°, since its mixed melting point with an authentic sample was not depressed. The ether layer and ether extracts of the aqueous layer were dried over anhydrous sodium sulfate, the ether was removed under reduced pressure, and the residue was recrystallized from petroleum ether (b.p. 90–100°). Three main fractions were obtained: (1) 1.53 g. (14%) of triphenylsilanol, m.p. 150–152° after recrystallization; (2) 7.55 g. (36.5% based on triphenylsilylpotassium) of white crystalline solid melting at 124–136°; and (3) 1.94 g. (11%) of benzhydryloxytriphenylsilane, m.p. 80–82°, identified by mixed melting point. The oily mother liquors evidently contained benzophenone since they gave a 2,4-dinitrophenylhydrazone, m.p. 237–238°, which was not depressed when admixed with authentic benzophenone 2,4-dinitrophenylhydrazone. The mother liquors also gave a positive test for the Si–H group[18] indicating the presence of triphenylsilane.

Several recrystallizations of the large fraction above from hot petroleum ether (b.p. 90–100°) or, better, by dissolving the compound in a minimum of warm chloroform followed by the addition of several volumes of hot petroleum ether, raised the melting point of this 2-triphenylsiloxytetraphenylethanol (III) to 132–133.5°, obtained in poor yield (15%).

Anal. Calcd. for $C_{44}H_{36}O_2Si$: C, 84.6; H, 5.82; Si, 4.49. Found: C, 85.1; H, 5.87; Si, 4.50.

The hexaphenyldisilane isolated from this and similar runs is believed not to be uncleaved material from the preparation of the triphenylsilylpotassium, but may be formed as proposed by Wittenberg, *et al.*

Structural Evidence for 2-Triphenylsiloxytetraphenylethanol.—The compound had an infrared spectrum consistent with the proposed structure including OH absorption (2.8 μ) and Si–O absorption (9.4 μ).

When 0.4 g. (0.00064 mole) of the compound was treated with 2.5 ml. of glacial acetic acid and a trace of iodine under the same conditions by which benzpinacol is converted to β-benzopinacolone,[19] there was obtained, after brief refluxing and cooling, 0.15 g. (67%) of β-benzopinacolone, m.p. 179–180°, which did not depress the mixed melting point with an authentic specimen.

When 0.5 g. (0.0008 mole) of the compound III was refluxed for 40 min. in 25 ml. of ethanol and 5 ml. of 10% aqueous sodium hydroxide, and the reaction mixture was drowned in water, acidified and ether extracted, evaporation of the ether extracts yielded an oily solid which was dissolved in hot petroleum ether (b.p. 60–70°). From this was obtained 0.90 g. (41%) of triphenylsilanol, m.p. 151–153°, and 0.14 g. (95%) of benzhydrol, m.p. 67–68.5°, identified by mixed melting points. The oily mother liquor was treated with 2,4-dinitrophenylhydrazine and a yellow 2,4-dinitrophenylhydrazone of benzophenone was obtained in 66% yield, m.p. 237–238°.

Thermal Decomposition of 2-Triphenylsiloxytetraphenylethanol.—To 10 ml. of cold xylene was added 0.5 g. of pure compound III, and the mixture was placed on a hot-plate. After about 1 min., and before reflux began, the colorless solution turned a pale pink and at reflux temperature was a dark pink. After about 2 min. the solution became colorless again. The xylene was removed under reduced pressure at 50° and recrystallization of the oily residue from

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[11] D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem.*, **24**, 1349 (1959).

[12] H. Gilman and T. C. Wu, THIS JOURNAL, **76**, 2502 (1954).

[13] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 2680 (1958).

[14] H. Gilman and C. W. Gerow, *ibid.*, **77**, 5740 (1955).

[15] A. G. Brook and N. V. Schwartz, unpublished results.

[16] A. G. Brook and C. M. Warner, unpublished results.

[17] All experiments involving organometallics or sodium–potassium alloy were carried out in a dry, oxygen-free, nitrogen atmosphere in sodium-dried solvents.

[18] H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 3404 (1951).

[19] W. E. Bachmann, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 73.

ethanol gave 0.18 g. (51%) of benzhydryloxytriphenylsilane, m.p. 81–83°, identified by mixed melting point with an authentic specimen. The mother liquor was concentrated and then treated with 2,4-dinitrophenylhydrazine reagent, giving, after recrystallization, 0.19 g. (66%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 237–238°, identified by mixed melting point. Samples of benzhydryloxytriphenylsilane or of 2-triphenylsiloxytetraphenylethanol treated with the same reagent under the same conditions failed to yield a hydrazone derivative.

Reaction of 2-Triphenylsiloxytetraphenylethanol with Sodium.—To a solution of 2.0 g. (0.0032 mole) of 2-triphenylsiloxytetraphenylethanol in 38 ml. of 1:1 ether–benzene was added 0.23 g. (0.01 g. atom) of sodium metal. The surface of the metal rapidly became blue. After being shaken for 2 min. the entire mixture was deep blue in color. After standing for 5.5 hr. without change, two-thirds (25 ml.) of the deep blue solution was added to excess Dry Ice. On reaching room temperature, the carbonation mixture was washed with water and after acidification of the aqueous layer with HCl it was extracted with ether. On removal of the ether there remained a solid residue which was recrystallized from water yielding 0.05 g. (10%) of benzilic acid, m.p. 150–152°, which was identified by mixed melting point with an authentic sample. The original organic layer from the carbonation was dried over anhydrous magnesium sulfate. Removal of the solvent gave an oil which was crystallized from ethanol to give 0.85 g. (90%) of benzhydryloxytriphenylsilane, m.p. 79–82°, which was identified by mixed melting point. The mother liquor was treated with 2,4-dinitrophenylhydrazine reagent to yield 0.5 g. (68%) of crude benzophenone 2,4-dinitrophenylhydrazone melting from 200–205°. Recrystallization raised the melting point to 236–239°.

The remaining one-third of the original mixture was still blue after 25 hr. and it was carbonated and worked up as described above. The aqueous washing of the carbonation, on acidification, became slightly cloudy but did not yield an isolable quantity of benzilic acid. The other products obtained were benzhydryloxytriphenylsilane, 0.3 g. (64%), and benzophenone as its 2,4-dinitrophenylhydrazone, 0.25 g. (68%).

Similarly, to 1.0 g. (0.0016 mole) of the compound III in 20 ml. of dry ether was added about 0.0075 g. (0.00032 g. atom) of sodium. In 1 min. the surface of the sodium was intensely blue, but swirling the solution removed the color. No hydrogen appeared to be evolved. After 30 min. the entire medium was deep blue and after 1.25 hr. the blue color began to fade to a pale yellow. After a total of 1.5 hr., 14 ml. (two-thirds) of the solution was poured into dilute acid, ether extracted, and worked up to yield 0.41 g. (87%) of benzhydryloxytriphenylsilane, m.p. 82–84°, identified by mixed melting point. The mother liquor on treatment with 2,4-dinitrophenylhydrazine reagent yielded 0.26 g. (67%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 236–238°, identified by mixed melting point.

The remaining one-third of the reaction mixture was stirred an additional hour. The sodium, not noticeably changed in size, was removed, and the ether was removed directly under reduced pressure. Treatment of this oil with hot petroleum ether (b.p. 90–100°) gave 0.13 g. (55%) of benzhydryloxytriphenylsilane, m.p. 81–82°. The mother liquor was not further worked up.

Similar results were obtained when the reaction was carried out at −70° over 6 hr.

When comparable runs of 1.0 g. (0.0016 mole) of III in 20 ml. of ether or 20 ml. of purified carbon tetrachloride were treated with excess sodium for 16 hr., 0.59 g. (83%) of benzhydryloxytriphenylsilane was obtained from the run in ether but 0.84 g. (84%) of III was recovered from the run in carbon tetrachloride and no benzhydryloxytriphenylsilane was detected. In the latter case the sodium did not become blue at all, but did seem to be slightly coated with a gray-white film.

When the original reaction, but with excess sodium, was carried out for extended periods of time (*e.g.*, 16 hr.) at room temperature an ether-insoluble precipitate formed (sodium triphenylsilanolate) and much of the sodium disappeared. Hydrolysis and work-up gave 7% of triphenylsilanol, m.p. 150–152°, and reduced yields (25%) of benzhydryloxytriphenylsilane. These results are attributable to cleavage of benzhydryloxytriphenylsilane by sodium.[4]

Synthesis of 2-Triphenylsiloxytetraphenylethanol from Triphenylchlorosilane and Benzophenone Ketyl.—To 3.64 g. (0.02 mole) of benzophenone in 50 ml. of ether was added 0.46 g. (0.02 g. atom) of sodium and this was refluxed until all the sodium had dissolved. The blue suspension was cooled in a Dry Ice–acetone-bath to about −70° and a solution of 2.94 g. (0.01 mole) of triphenylchlorosilane in 50 ml. of dry ether was added with stirring. After 2 hr. stirring at −70°, the mixture, which was still blue, was drowned in dilute acid. The ether extracts, after drying, were concentrated under reduced pressure and the resulting oil yielded 0.15 g. (8%) of benzpinacol, m.p. 175–185°, and 0.4 g. (15%) of triphenylsilanol, m.p. 149–151°, both identified by mixed melting point, and 0.3 g. of material, m.p. 121–133°, which after several recrystallizations from benzene-petroleum ether (b.p. 60–70°) yielded 0.1 g. (1.5%) of material, m.p. 130–133°, which did not depress the mixed melting point with 2-triphenylsiloxytetraphenylethanol and which had an identical infrared spectrum.

From the oily mother liquors was isolated by vacuum distillation 1.85 g. (51%) of benzophenone, m.p. 42–46°, identified by mixed melting point.

When a similar reaction, except that the benzophenone ketyl was made with sodium–potassium alloy and the reaction was run at room temperature, was carried out over 2.5 hr., by which time the blue color had faded, the products were 41% hexaphenyldisiloxane, m.p. 222–225°; 16% benzhydryloxytriphenylsilane; and 16% recovered benzophenone. A similar reaction with 5-hr. stirring, by which time the deep blue color had faded to pale yellow, gave 61% of triphenylsilanol and 11% of benzhydryloxytriphenylsilane.

Reaction of Triphenylsiloxydiphenylmethylpotassium with Benzophenone.—To the triphenylsilylpotassium resulting from the cleavage of 5.2 g. (0.01 mole) of hexaphenyldisilane by excess sodium–potassium alloy was added over a 3-min. period 3.1 g. (0.017 mole) of benzophenone in 25 ml. of dry ether. The reaction mixture was allowed to stir for 2 min. longer and then was filtered through a sintered glass plate sealed in the bottom of the flask.[6] The red solid which remained was washed twice with dry ether and then was mixed with another 25 ml. of ether. To this suspension was added rapidly, with stirring, a second portion of 3.1 g. (0.017 mole) of benzophenone in 25 ml. of dry ether. The red solid seemed to dissolve and a deep blue solution was formed. After stirring for 5 min. longer a heavy white precipitate formed and stopped the stirrer. The solution from which this solid precipitated remained blue. At this point the mixture was hydrolyzed in dilute HCl and after extraction of the aqueous layer with ether the extracts were combined, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure leaving a viscous oil. Petroleum ether (b.p. 90–100°) was added to the oil causing it to solidify. There was obtained 7.25 g. (58%) of 2-triphenylsiloxytetraphenylethanol (III) melting from 126–133°. Recrystallization of this material from chloroform–petroleum ether raised the melting point to 130–134° and a mixed melting point with authentic III was not depressed. The mother liquor from the crude III after concentration was treated with 2,4-dinitrophenylhydrazine reagent and yielded 1.8 g. (29%) of crude benzophenone 2,4-dinitrophenylhydrazone melting from 200–212°. Recrystallization of this material raised the melting point to 236–239° and its mixed melting point with an authentic sample was not depressed.

Determination of the Equivalent Weight of Triphenylsiloxydiphenylmethylpotassium.—The metallic, triphenylsiloxydiphenylmethylpotassium (IV) was prepared and isolated as described above in the tared flask. After a thorough washing of the solid with dry ether, it was freed from solvent by evacuating the flask to 0.6 mm. pressure until the flask reached constant weight. The solid then was hydrolyzed by sucking distilled water into the evacuated flask. The hydrolysate then was washed with ether to remove most of the organic material. The aqueous portion was made up to 250 ml. in a volumetric flask and 25-ml. samples of this alkaline solution were titrated with standardized 0.1 *N* HCl; calcd. for $C_{31}H_{25}OSiK$, equiv. wt., 480, found 457, 494. The ether layer from the hydrolysis after being dried and the solvent removed yielded a colorless oil which was dissolved in hot EtOH. There was obtained from this solution, on cooling, 2.2 g. (30%) of crude benzhydryloxytriphenylsilane, melting from 76–83°. Recrystallization of this material raised the melting point to 83.5–84.5° and its mixed melting point with an authentic sample was not depressed.

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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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.

$$\mathrm{Ph_3SiOCPh_2K + PhCH_2Cl \longrightarrow}$$

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

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

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).