gave no immediate precipitate, but a small amount of silicious material slowly precipitated over a period of 3 or 4 days.

Acknowledgments.—We are indebted to Mr. G. A. Guter of this Laboratory for preliminary investigations, to Dr. R. E. Rundle and Mr. F. Hollenbeck for the X-ray determination, and to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared studies.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Formation of Tetraarylsilanes from the Reactions of Triarylsilylmetallic Compounds. III. Reactions with Triarylmethanes

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Triarylsilylmetallic compounds have been found to metalate triarylmethanes, and if an excess of the metallic reagent is present, it reacts further with the triarylsilane formed to yield a tetraarylsilane. This behavior explains the recently reported anomalous formation of tetraphenylsilane from the reactions of triphenylsilylpotassium with a variety of compounds containing active hydrogen. Although no reaction occurs between equimolar amounts of triphenylsilane and triphenylmethylsodium at room temperature, at 60° or higher a reaction has been found to take place with the formation of hexaphenyldisilane and triphenylmethane.

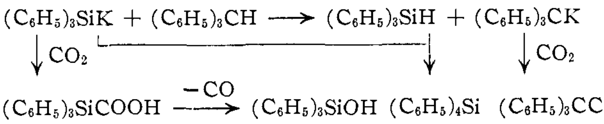
The previous paper in this series[1] described the reaction of triarylsilylmetallic compounds with triarylsilanes in which high yields of tetraarylsilanes are formed. Specifically, it was found that both triphenylsilylpotassium and triphenylsilylsodium react with triphenylsilane to yield, after hydrolysis, tetraphenylsilane, hydrogen and a silicic acid-like material. The results reported in the present paper are a logical extension of the previous work, since under similar conditions it has been found that a similar reaction occurs between triphenylsilylpotassium and either triphenylmethane or tri-*p*-tolylmethane, again with the formation of appreciably high yields of tetraphenylsilane. The results presented here also account for the formation of tetraphenylsilane from the reaction of triphenylsilylpotassium with phenylacetylene, triphenylcarbinol, benzhydrol, benzyl alcohol or triphenylsilanol, as described in paper I of this series.[2]

The findings of the present investigation are as follows. Any triarylsilylmetallic compound reacts with a triarylmethane (and by analogy with any compound containing an active hydrogen atom) to yield rapidly and practically quantitatively, a mixture of the corresponding triarylsilane and the metal salt of the triarylmethane.

$$R_3SiM + R'_3CH \text{ (or } R''H) \longrightarrow R_3SiH + R'_3CM \text{ (or } R''M) \quad (1)$$

Thus, for example, when triphenylsilylpotassium is treated with one equivalent of triphenylmethane (run 1, Table I), triphenylsilane and triphenylmethylpotassium are rapidly formed, for when an aliquot of the reaction mixture was carbonated 40 minutes after the addition of the reagents was begun, triphenylacetic acid, triphenylmethane, triphenylsilane and triphenylsilanol, derived from triphenylsilanecarboxylic acid by hydrolysis,[3] were obtained.

Whether or not the system described by equation 2 is an equilibrium system has not been established, but if this is true, which seems unlikely, the equilibrium certainly lies far over in the direction of the products triphenylsilane and triphenylmethylpotassium, for when the reaction was carbonated after 4.5 days stirring at room temperature, an almost quantitative yield of triphenylacetic acid and a high yield of triphenylsilane were obtained.



$$\begin{tikzcd}[column sep=small]
(C_6H_5)_3SiK \arrow[d, "CO_2"] & + (C_6H_5)_3CH \arrow[r] & (C_6H_5)_3SiH \arrow[d] & + (C_6H_5)_3CK \arrow[d, "CO_2"] \\
(C_6H_5)_3SiCOOH \arrow[r, "-CO"] & (C_6H_5)_3SiOH & (C_6H_5)_4Si & (C_6H_5)_3CCOOH
\end{tikzcd} \quad (2)$$

Since the only function of the triphenylmethane in the above reaction is that it supplies a hydrogen atom to the triphenylsilylmetallic reagent to form triphenylsilane, it is readily apparent that any compound containing an active hydrogen atom can fulfill this purpose, and so similar metalation reactions must occur with any compound which contains an active hydrogen atom when it is treated with a triphenylsilylmetallic compound as has actually been observed.[2]

Since the system triarylsilylmetallic–triarylmethane is capable of producing a triarylsilane, it would be expected that the reaction described in the previous paper between a triarylsilylmetallic compound and a triarylsilane would occur, if both these reagents were present, so that a tetraarylsilane would be produced.[1] This has been found to be the case. When triphenylsilylpotassium was treated over 4.5 days with one equivalent of triphenylmethane (run 1), a small yield (3%) of tetraphenylsilane was obtained. Under similar conditions, but where the molar ratio of triphenylsilylpotassium to triphenylmethane was 2.5:1 (run 2), a considerably higher yield (26%) of tetraphenylsilane was obtained. This variation in yield is explained readily if the system described by equation 2 is not an equilibrium system, as has been suggested already, since in the case where equimolar amounts of triphenylsilylpotassium and triphenylmethane are present, all of the former reagent would be consumed in metalating the triphenylmethane, and there would be none of it available to react with the triphenylsilane produced, to yield tetraphenylsilane. However, in the case where there is an excess

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[1] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 2333 (1954).

[2] H. Gilman and T. C. Wu, *ibid.*, **75**, 2509 (1953).

[3] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

TABLE I

REACTION OF TRIPHENYLSILYLMETALLIC COMPOUNDS WITH TRIARYLMETHANES ($R = C_6H_5$, $R' = p\text{-}CH_3C_6H_4$)

Run	Triphenylsilylmetallic	Triarylmethane	Moles, metallic/Moles, methane	Solvent	Temp. °C.	Time, days	Products and yields (%)
1	R_3SiK	R_3CH	1:1	Ether	35	40 min.	R_3CCOOH (54), R_3CH (26) R_3SiOH (37), R_3SiH (39)
						4.5	R_3CCOOH (95), R_4Si (3) R_6Si_2 (7), R_3SiH (64)
2	R_3SiK	R_3CH	2.5:1	Ether	25	4	R_4Si (26), R_3SiH (10) R_3SiOH (11), $R_3SiCOOH$ (9) R_3CCOOH (77)
3	R_3SiK	R_3CH	1.5:1	Ether	25	6	R_3SiH (41), R_4Si (17) R_3CCOOH (76)
4	R_3SiK	R_3CH	1:1	GDME^a–benzene	74	4	R_4Si (7), R_3CCOOH (23) R_3SiOH (41), R_3CH (26)
5	R_3SiK	R'_3CH	2:1	Ether	25	4	R_4Si (43), R'_3CH (37) R'_3CCOOH (10)
6	R_3SiK	R'_3CH	1:1	Ether–benzene	75	4	R_4Si (32), R'_3CCOOH (3) R'_3CH (57), R_3SiOH (11) R_6Si_2O (6)
7	R_3SiNa	R_3CH	1:1	GDME	25	4 hr	R_3CCOOH (41), R_3CH (25) R_3SiH (30)
					25	5	R_3CCOOH (4), R_3CH (77) R_3SiOH (36), R_3SiH (16)
8	R_3SiLi	R_3CH	1.4:1	GDME	25	1	R_3CCOOH (37)
				GDME–benzene	75	3	R_3SiH (70), R_3CH (70)

[a] GDME = ethylene glycol dimethyl ether.

of triphenylsilylpotassium, only one mole is consumed in metalating the triphenylmethane, and the additional material is available to react with the mole of triphenylsilane produced, to yield the expected tetraphenylsilane. This explanation of the variation in yields of tetraphenylsilane actually obtained under these different conditions suggests that the situation described by equation 2 is not an equilibrium system, or otherwise it would be expected that high yields of tetraphenylsilane would be obtained in all cases, through shifting of the equilibrium.

Further confirmation of this conclusion was obtained when it was found that no reaction occurred when approximately equimolar amounts of triphenylmethylsodium and triphenylsilane were stirred at room temperature for 3 days (run 10). Carbonation of the reaction mixture gave a 98% yield of phenylacetic acid and a 79% recovery of triphenylsilane, and no other products. When the reaction mixture was refluxed for 7 days at 74°, a 16% yield of tetraphenylsilane was obtained. A lower yield of this product was obtained when a 1.35:1 molar ratio of triphenylsilane to triphenylmethylsodium was refluxed at 60° for 7 days.

That the hydrogen-donating compound plays no part in the formation of tetraarylsilanes in reactions of triarylsilylmetallic reagents with these compounds, has been demonstrated by treatment of triphenylsilylpotassium with tri-*p*-tolylmethane. The only tetraarylsilane obtained was tetraphenylsilane, and no silane derivatives containing a *p*-tolyl group were isolated, indicating that the migrating aryl group which forms the tetraarylsilane does not arise from the triarylmethane or other hydrogen donor.

The formation of tetraphenylsilane from the reactions of triphenylsilylsodium or triphenylsilyllithium with triphenylmethane apparently does not occur under the conditions of the experiments outlined in Table I. This might have been anticipated, since in the case of triphenylsilylsodium (run 7), where the molar ratio of the silylmetallic compound and the triphenylmethane was 1:1, all of the triphenylsilylsodium would have been consumed in metalating the triphenylmethane, so that none would be available to react with the triphenylsilane formed. That no tetraphenylsilane was formed in the reaction of triphenylsilyllithium with triphenylmethane, where the molar ratio was 1.4:1 (run 8), so that the previous argument would not apply, is accounted for by the findings in the preceding paper[1] that no appreciable reaction between triphenylsilyllithium and triphenylsilane occurs under similar conditions. The failure to isolate any triphenylacetic acid (or its hydrolysis product) by carbonation of the colorless reaction mixture obtained after three days refluxing in a mixture of benzene and ethylene glycol dimethyl ether is undoubtedly due to reduction of the organometallic reagents under these conditions. Unpublished studies by Dr. K. M. Tai of this Laboratory have shown that under similar conditions triphenylsilyllithium rapidly decomposes, and unpublished studies by Dr. A. H. Haubein of this Laboratory have shown that triphenylmethyllithium is also rapidly decomposed under similar conditions. Hence the isolation of triphenylsilane and triphenylmethane as the only products of the reaction is not unexpected.

Although no reaction occurs between triphenylmethylsodium and triphenylsilane at room temper-

TABLE II

REACTION OF TRIMETHYLMETHYLMETALLIC COMPOUNDS WITH TRIPHENYLSILANE ($R = C_6H_5$)

Run	Reagent	Moles, metallic / Moles, silane	Solvent	Temp., °C.	Time, days	Products and yields (%)
9	R_3CNa	0.74:1	Ether–benzene	60	7	R_6Si_2 (50), R_4Si (6), R_6Si_2O (8), R_3SiOH (5), R_3SiH (16), R_3CCOOH (39), R_3CH (47)
10	R_3CNa	0.94:1	Ether then ether–benzene	25	3	R_3CCOOH (98), R_3SiH (79)
				74	7	R_6Si_2 (61), R_4Si (16), R_3CCOOH (33), R_3CH (44)
11	R_3CLi	1:1	Ether–benzene	25	1	R_3CCOOH (22), R_3SiH (46)
				75	3	R_3CH (36), R_3SiH (85), R_3SiOH (6)
12	R_3CMgCl	1:1	Ether–benzene	75	4	R_3SiH (87), R_3CCOOH (30), R_3CH (33)

ature over a period of at least three days (run 10), when the temperature is raised to 60° or 75° a new reaction occurs, in which hexaphenyldisilane and triphenylmethane are the chief products. The formation of hexaphenyldisilane was quite unexpected since the treatment of triarylsilanes with organolithium compounds[4] (and also apparently with organosodium compounds[5]) constitutes a well-recognized method for the preparation of tetraarylsilanes. The reaction of triarylsilanes with Grignard reagents to form tetraarylsilanes is not generally successful.[4a] Hence it might have been predicted that the product of the reaction of triphenylsilane with triphenylmethylsodium or triphenylmethyllithium would have been triphenylmethyltriphenylsilane,[6] rather than hexaphenyldisilane.

The mechanism of the formation of this hexaphenyldisilane is not known, but it seems possible at the elevated temperatures at which this product is formed that some reversal of the reaction depicted by equation 2 might occur, and that the small amounts of triphenylsilylsodium thus formed would then couple with the triphenylsilane under these conditions according to equation 3 to yield, as well as the tetraphenylsilane already described, some hexaphenyldisilane. Evidence that this postulate is correct is obtained in Table I where, at room temperature, no hexaphenyldisilane is obtained from the reaction of triphenylsilylpotassium with triphenylmethane (run 1), but in refluxing ether over a similar period of time a small yield (7%) of hexaphenyldisilane is obtained (run 2), accompanying the main product, tetraphenylsilane.

$$(C_6H_5)_3SiH + (C_6H_5)_3CNa \rightleftarrows (C_6H_5)_3SiNa + (C_6H_5)_3CH \quad (3)$$

$$(C_6H_5)_3SiNa + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + NaH + (C_6H_5)_4Si$$

The formation of this hexaphenyldisilane appears to be a reaction characteristic of the system triphenylmethylsodium–triphenylsilane, since none of this product is obtained when triphenylsilane is treated under similar conditions with either triphenylmethyllithium (run 11) or triphenylmethylmagnesium chloride (run 12). The failure of the compound to be formed from triphenylmethyllithium is probably due to the instability of this reagent under the conditions of the reaction (74°), as was suggested also for the failure to isolate tetraphenylsilane. However, it should be noted that in the previous paper[1] a low yield (14%) of hexaphenyldisilane was obtained from the reaction of triphenylsilyllithium with triphenylsilane at room temperature. In the case of the triphenylmethylmagnesium chloride, where carbonation of the reaction mixture at the end of 4 days yielded some triphenylacetic acid, showing that the reagent was at least partially stable under the conditions of the reaction, failure to isolate any hexaphenyldisilane (or triphenylmethyltriphenylsilane, the coupled product of the Grignard reagent and the silane) is probably due to the inherent unreactiveness of the Grignard reagent toward silanes, as compared with the corresponding lithium or sodium derivatives.[4a]

Experimental[7]

Reagents.—The following organometallic reagents were prepared according to published procedures: triphenylsilylpotassium,[8] triphenylsilylsodium,[9] triphenylsilyllithium,[9] triphenylmethylsodium,[10] triphenylmethyllithium[6] and triphenylmethylmagnesium chloride.[11]

General Method of Runs.—The details of the runs are listed in Tables I and II. With the exception of run 7, the concentration of the organometallic reagent in all runs was approximately 0.13 *M*. In run 7 the concentration of the organometallic reagent was 0.42 *M*. To the solution or suspension of the organometallic compound was added the other reagent, usually as a solid; with the moderate stirring used, this reagent invariably dissolved within a few minutes. When aliquots were removed at room temperature, prior to raising the temperature of the reaction mixture, they were drowned in a Dry Ice–ether slurry. When reactions in which mixtures of benzene and ether were employed as solvents were raised to elevated temperatures, the excess ether was permitted to distil off in a nitrogen atmosphere and the volume of ether collected was replaced by an equal volume of benzene. More specific details of the experimental techniques are given in the detailed description which follows of several of the runs.

Yields are calculated on the basis of the reagent from which the product arose. Thus the yields of all silicon-containing compounds are based on the moles of silicon-containing reagent employed.

Reaction of Triphenylsilylpotassium with Triphenylmethane (Run 1).—Triphenylsilylpotassium[8] was prepared from 10 g. (0.0193 mole) of hexaphenyldisilane, and to this material after amalgamation and removal from the amalgam, was added over a period of 25 minutes a solution of 9.4 g. (0.0386 mole) of triphenylmethane in 100 ml. of ether.

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[4] (a) H. Gilman and H. W. Melvin, THIS JOURNAL, **71**, 4050 (1949); (b) H. Gilman and S. P. Massie, Jr., *ibid.*, **68**, 1128 (1946); R. N. Meals, *ibid.*, **68**, 1880 (1946).

[5] R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).

[6] For the preparation of this compound see A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953).

[7] All melting points are uncorrected. All reactions involving organometallic compounds were carried out in an atmosphere of dry oxygen-free nitrogen.

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

[9] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 278 (1954).

[10] W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

[11] H. Gilman and E. A. Zoellner, THIS JOURNAL, **51**, 3493 (1929).

Shortly after the addition was started the heterogeneous system became reddish-brown in color and, if the stirrer was stopped, the supernatant liquid was found to be of a pale red color. By the time the addition was complete the reaction mixture was dark red. Forty minutes after the addition was started, a 25-ml. aliquot of the suspension was carbonated with Dry Ice. The remaining material was stirred at room temperature overnight, and then under reflux for an additional 4 days.

When the carbonated aliquot of the reaction mixture had warmed to room temperature, it was filtered without hydrolyzing and washed with ether. The residual solids were treated with water in which they almost completely dissolved, and the aqueous mixture was ether extracted. The ether layer after drying and removal of the ether, left a white solid, melting from 115–130°, which after recrystallization from petroleum ether (b.p. 60–70°), yielded 0.15 g. (14%) of white solid which melted at 149–151° and which did not depress the mixed melting point with an authentic sample of triphenylsilanol. The aqueous layer was acidified precipitating a white solid, which after drying was recrystallized from ethanol to yield 0.6 g. (54%) of triphenylacetic acid, m.p. 265–268°, which did not depress a mixed melting point with an authentic specimen.

The original ether filtrate obtained after removal of the insoluble carbonation products, was evaporated to dryness under reduced pressure, yielding a white solid. The solid was dissolved in a hot benzene–petroleum ether (b.p. 60–70°) solution. The first fraction melted from 71–80°, and was recrystallized from ethanol to yield 0.25 g. (26%) of triphenylmethane, m.p. 87–90°, identified by mixed melting point. The second fraction, obtained by adding additional petroleum ether to the filtrate from the first fraction, yielded 0.35 g. of very crude triphenylsilanol, melting from 60–137°. It was recrystallized from petroleum ether (b.p. 60–70°) and the 0.25 g. (23%) of material isolated melted 145–150°, and failed to depress the mixed melting point with an authentic specimen. The third fraction was obtained by concentrating under reduced pressure the petroleum ether solution after removal of the second fraction. To this oil was added a small amount of petroleum ether (b.p. 28–38°). The solution was then cooled in a Dry Ice–acetone-bath, and a white solid slowly crystallized out. This 0.3 g. (39%) of triphenylsilane melted at 37–39°, and after recrystallization from petroleum ether (b.p. 28–38°) with cooling in an ice-bath, melted at 42–45° and did not depress the mixed melting point with an authentic sample.

The main reaction mixture after a total of 114 hours stirring was carbonated, and worked up as described for the aliquot above. From the residue, which was treated with water after removal of the ether layer, was isolated a 7% yield of insoluble hexaphenyldisilane, m.p. 360–363° (mixed melting point), and a 95% yield of triphenylacetic acid, m.p. 269–271° (mixed melting point). The ether layer was concentrated under reduced pressure to yield a viscous oil which was distilled directly under reduced pressure. The main fraction boiled at 154–156° at 1.3 mm. pressure and weighed 4.6 g. (64%). On seeding with authentic triphenylsilane it crystallized, and melted at 43–45°, and did not depress the melting point of triphenylsilane when mixed with it. From the residue in the flash after distillation was isolated 0.3 g. (3%) of tetraphenylsilane, m.p. 230–232°, identified by mixed melting point.

Reaction of Triphenylsilylpotassium with Tri-*p*-tolylmethane (Run 6).—To the amalgamated triphenylsilylpotassium[8] prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane in 55 ml. of ether was added 5.6 g. (0.0196 mole) of tri-*p*-tolylmethane and 200 ml. of ether. The ether was distilled off and replaced by benzene until the temperature was 75°, and the reaction mixture was then refluxed for 4 days. At the end of this time, the reaction was carbonated with a Dry Ice–ether slurry, and the mixture worked up.

The ether layer was separated from the clear aqueous layer and dried over sodium sulfate. The ether was removed under reduced pressure and the resulting gum was treated with ethanol. An insoluble residue of tetraphenylsilane weighing 2.1 g. (32%) was filtered off which melted at 229–232°, and which did not depress the melting point when admixed with an authentic sample. The ethanol filtrate was evaporated to dryness and the residue was taken up in hot petroleum ether (b.p. 60–70°). From this solution was deposited 0.6 g. (11%) of triphenylsilanol, m.p. 148–151°, identified by mixed melting point. The mother liquor was distilled at 184–187° (2 mm.) and solidified on standing. This tri-*p*-tolylmethane weighed 3.2 g. (57%) and melted at 61–63°. The mixed melting point with an authentic specimen was not depressed. A residue remained in the distillation flask. This was removed with benzene which deposited 0.3 g. (6%) of hexaphenyldisiloxane, m.p. 221–225°, identified by mixed melting point.

The original aqueous layer was acidified and then extracted with ether. Removal of the ether left a residue which was recrystallized from glacial acetic acid to yield 0.2 g. (3%) of a crystalline acid, m.p. 223–225°, believed to be tri-*p*-tolylacetic acid (reported 226–228°)[12] on the basis of its infrared spectrum.

Reaction of Triphenylsilylsodium[9] with Triphenylmethane (Run 7).—A suspension of 5.0 g. (0.00965 mole) of hexaphenyldisilane in 10 ml. of ethylene glycol dimethyl ether was stirred with 1.5 g. (0.065 g. atom) of sodium. After about 2 hours the reaction slowly began to turn green and then yellow and then after about 4 hours became dark brown. An additional 40 ml. of the solvent was added and the reaction was stirred for a total of 24 hours, by which time no undissolved material remained. A 40-ml. aliquot (0.017 mole if 100% reaction) was removed in a transfer pipet and added to 4.15 g. (0.017 mole) of triphenylmethane. The reaction mixture immediately turned bright red, and after 4 hours stirring at room temperature a 10-ml. aliquot was carbonated in Dry Ice. The remaining bulk of the reaction was stirred a total of 5 days.

The carbonated aliquot was hydrolyzed with water, and the solution extracted twice with ether. The combined ether extracts, after drying over sodium sulfate, were concentrated under reduced pressure. The residue was taken up in petroleum ether (b.p. 60–70°) which deposited 2 crops totalling 0.25 g. (24%) of triphenylmethane, m.p. 92–94°, identified by mixed melting point. The mother liquors were treated with piperidine and alkali to convert the triphenylsilane to triphenylsilanol,[13] and after the evolution of hydrogen had ceased, the solution was poured into water. The 0.35 g. (30%) of triphenylsilanol which crystallized out melted at 149–151°, and a mixed melting point with an authentic sample was not depressed.

Acidification of the aqueous layer gave 0.5 g. (41%) of triphenylacetic acid, m.p. 265–267°, identified by mixed melting point.

The bulk of the reaction was carbonated after 5 days stirring at room temperature. A small amount of precipitate was filtered off after hydrolysis with water. The filtrate was thrice extracted with ether, and the combined ether extracts after drying over sodium sulfate were concentrated under reduced pressure. The residue was taken up in petroleum ether (b.p. 60–70°) and this solution on concentration yielded a total of 1.25 g. (36%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point, followed by 2.4 g. (77%) of triphenylmethane, which after recrystallization from petroleum ether (b.p. 60–70°) melted at 91–93°, and which was identified by mixed melting point. The mother liquors yielded 0.5 g. of oil which was treated as before with alkali and piperidine[13] to give 0.5 g. (16%) of triphenylsilanol, m.p. 148–150°.

Acidification of the aqueous layer yielded 0.15 g. (4%) of triphenylacetic acid, m.p. 265–270°, identified by mixed melting point.

Reaction of Triphenylmethylsodium with Triphenylsilane (Run 10).—Triphenylmethylsodium[10] (0.0658 mole) in ether, analyzed by the double titration method,[14] was added rapidly to 18.2 g. (0.07 mole) of triphenylsilane in 50 ml. of ether. The blood-red solution was stirred at room temperature for 3 days, at which time a 50-ml. aliquot was carbonated by adding it to a Dry Ice–ether slurry. After warming to room temperature the carbonated suspension was filtered, washed with ether, and the ether filtrate evaporated under reduced pressure to yield a viscous oil. When cooled in an ice-bath, this material crystallized almost completely, and was filtered and washed with a minimum of cold petroleum ether (b.p. 28–38°) to yield 2.3 g. (78.5%) of triphenylsilane, m.p. 41–44°, which did not depress the mixed melting point with an authentic sample.

The residue from the above filtration was dissolved in water, a trace of insoluble residue was filtered off, and the

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[12] J. Schmidlin and H. H. Hodgson, *Ber.*, **41**, 438 (1908).

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

[14] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

clear alkaline filtrate was acidified, precipitating a white solid. This material was recrystallized from ethanol to yield a total of 3.0 g. (98%) of triphenylacetic acid, m.p. 269–271°, which did not lower the melting point when admixed with authentic triphenylacetic acid.

To the remaining triphenylmethylsodium and triphenylsilane solution, after removal of the above aliquot, was added a total of 250 ml. of dry benzene while the ether was simultaneously distilled off until the boiling point was 74°. The solution was then refluxed for 7 days at this temperature, during which time a white solid slowly precipitated, although the red color did not change appreciably. The suspension was then cooled and carbonated with Dry Ice which discharged the red color, and it was worked up without hydrolysis. The insoluble material was filtered off and washed with ether which was added to the benzene filtrate. The residue was ground in water made slightly alkaline with potassium hydroxide, and then filtered. The residue after drying weighed 8.5 g. and melted from 358–364°. It was refluxed in 100 ml. of ethanol, and filtered to yield 8.3 g. (55%) of pure hexaphenyldisilane, m.p. 362–364°, which did not depress the mixed melting point with an authentic specimen. The alkaline filtrate was acidified, and the precipitate was filtered, dried and recrystallized from ethanol to yield 0.5 g. (3%) of triphenylacetic acid (mixed melting point) which melted at 268–270°.

The original benzene filtrate described above, to which the ether washings were added, precipitated a white solid, and the addition of more ether caused further solid to precipitate. This material (6.1 g.) was filtered off and recrystallized from dioxane. A small amount (0.9 g. or 6%) of insoluble hexaphenyldisilane, m.p. 360–362°, was filtered off. The dioxane solution deposited a total of 4.8 g. (28%) of a white solid melting from 301–312° with decomposition, which was shown to be sodium triphenylacetate, since after dissolving in dilute alkali and filtering, the solution was acidified to yield, after recrystallization from ethanol, pure triphenylacetic acid, m.p. 268–270°, which did not depress the melting point of an authentic specimen.

The clear yellow benzene–ether filtrate, following removal of the sodium triphenylacetate was evaporated to dryness under reduced pressure depositing a yellow solid. This was treated with 50 ml. of hot petroleum ether (b.p. 28–38°), and the suspension was filtered hot. The 4.3 g. of residue which melted from 168–270° was recrystallized from a 3:1 mixture of benzene and petroleum ether (b.p. 60–70°), to give 1.0 g. of insoluble residue and a pale yellow solution which slowly deposited a white solid. The insoluble residue was shown to be sodium triphenylacetate, for when dissolved in 5% alkali, filtered and reacidified, it yielded 0.5 g. (3%) of triphenylacetic acid, m.p. 268–271° (mixed melting point). The solid deposited from the benzene–petroleum ether solution weighed 3.2 g. (16%), melted from 220–227°, and after recrystallization from benzene–ethanol melted at 228–230°. Its infrared spectrum was identical with that of tetraphenylsilane, and a mixed melting point with this substance was not depressed.

The petroleum ether (b.p. 28–38°) extract from above on concentration deposited a total of 8.6 g. of pale yellow solid which melted from 65–80°. The mixed melting point with triphenylmethane was not depressed and melted from 84–90°, but an infrared spectrum indicated the presence of some triphenylsilane as well as triphenylmethane. Recrystallization from ethanol, followed by chromatography of a petroleum ether (b.p. 60–70°) solution of the material on a 3 × 30 cm. alumina column, followed by elution with about 1 liter of petroleum ether (b.p. 60–70°) eventually yielded 5.9 g. (44%) of pure triphenylmethane, m.p. 90–92°, which did not depress the mixed melting point with authentic triphenylmethane.

These yields represent a 77% recovery of the triphenylsilyl group and a 75% recovery of the triphenylmethyl group.

Reaction of Triphenylmethylsodium with Triphenylsilane (Run 9).—A similar reaction to the above was carried out with 0.04 mole of triphenylmethylsodium in 140 ml. of ether and 14.0 g. (0.054 mole) of triphenylsilane in 200 ml. of benzene. The ether was distilled off until the temperature was 60° and the reaction mixture was then stirred and refluxed at this temperature for 7 days. The reaction mixture was cooled, carbonated and in contrast to the run above was then hydrolyzed with water, and then worked up similarly to the above run.

The both water- and ether-insoluble hexaphenyldisilane filtered from the reaction mixture weighed 6.95 g. (50%) after purification, melted at 360–363°, and did not depress the mixed melting point with an authentic sample. Acidification of the alkaline layer, followed by recrystallization from ethanol, gave 4.45 g. (39%) of triphenylacetic acid (mixed melting point) which melted at 267–270°. The ether layer, after removal of the ether, was dissolved in petroleum ether (b.p. 28–38°) and was fractionated on a 4 × 40 cm. column of alumina, by eluting first with petroleum ether (b.p. 28–38°), then with 1:1 benzene–petroleum ether (b.p. 60–70°), and finally benzene. From the various fractions the following compounds were isolated and identified, after recrystallization, by mixed melting point determinations with authentic samples: 1.15 g. (8%) of hexaphenyldisiloxane, m.p. 220–223°; 0.70 g. (5%) of triphenylsilanol, m.p. 149–151°; 1.1 g. (6%) of tetraphenylsilane, m.p. 228–230°; and 8.2 g. of crude triphenylmethane, which undoubtedly contained some triphenylsilane, and which after several recrystallizations from ethanol weighed 4.6 g. (47%) and melted 89–92°. These products account for 85% of the triphenylsilyl group and 86% of the triphenylmethyl group.

Reaction of Triphenylmethyllithium[8] with Triphenylsilane (Run 11).—To 4.88 g. (0.02 mole) of triphenylmethane was added 0.04 mole of *n*-butyllithium[15] in 180 ml. of ether. The solution was refluxed for 44 hours, during which time a red precipitate formed. The addition of 100 ml. of benzene dissolved most of the precipitate. Carbonation of a 20-ml. aliquot of the suspension yielded after hydrolysis 0.3 g. (73%) of triphenylacetic acid, m.p. 267–269°.

To the remaining material was added 5.2 g. (0.02 mole) of triphenylsilane and an additional 100 ml. of benzene. After stirring for 24 hours at room temperature, a 100-ml. (0.0055 mole) aliquot was carbonated with Dry Ice. The reaction mixture was then heated to distil off the ether until the temperature was 75°, at which temperature the reaction was refluxed for 3 days.

The carbonated aliquot above was hydrolyzed with water, and the ether layer separated and dried over sodium sulfate. Removal of the ether left a gummy solid, mainly triphenylsilane, which was converted to triphenylsilanol by treatment with piperidine and alkali.[13] When hydrogen evolution had ceased, the material was poured into excess water, acidified, and the solid which crystallized out was filtered off and recrystallized from petroleum ether (b.p. 60–70°) to yield 0.7 g. (46%) of triphenylsilanol, m.p. 149–151°, identified by mixed melting point. This material represents a 46% recovery of the reagent triphenylsilane.

The aqueous layer from above was acidified and the acid which was precipitated was filtered off and recrystallized from ethanol to yield 0.35 g. (22%) of triphenylacetic acid, m.p. 266–268°, identified by a mixed melting point determination with an authentic sample.

The bulk of the reaction mixture after refluxing at 75° for 3 days was carbonated and worked up essentially as before. The ether layer was evaporated to dryness under reduced pressure and the residual material was dissolved in petroleum ether (b.p. 60–70°). After the separation of 1.25 g. (36%) of triphenylmethane, m.p. 91–93°, identified by mixed melting point, and of 0.25 g. (6%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point, the residual material was distilled at 1.5 mm. to yield 3.75 g. (85%) of triphenylsilane, b.p. 150–153°, which crystallized and melted at 42–44°. The melting point was not depressed by admixture with an authentic sample of triphenylsilane.

No material was obtained when the aqueous layer was acidified.

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[15] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).