evolution. Near the end of the experiment a very fine precipitate appeared. Isolation of the precipitate gave 0.23 g. of a powdery material which was affected by moisture in the air but failed to dissolve completely in dilute hydrochloric acid. Upon ether extraction of an oil suspended in the acid solution and washing with sodium carbonate, 0.1 g. of trichloroethyl benzoate was obtained.

Reaction of Aluminum Chloride and Trichloroethyl Benzoate.—In the apparatus previously described 0.40 g. (0.003 mole) of aluminum chloride and 47 ml. of carbon tetrachloride were mixed and brought to 50°. Trichloroethyl benzoate (2.54 g., 0.010 mole) was added all at once to the reaction vessel. Over a period of 90 minutes, 0.0015 mole of gas was evolved. The reaction solution became homogeneous during this period and slightly discolored. After cooling, the solution was filtered under nitrogen to remove a few dark particles remaining and returned to the reaction vessel. Upon reaching reaction temperature, a mixture of 1.49 g. (0.010 mole) of trichloroethanol and 1.40 g. (0.010 mole) of benzoyl chloride was added all at once. Hydrogen chloride evolution was rapid at first and then tapered off. In a period of 2 hours, 0.010 mole of gas was titrated. After working up the product in the manner previously described, a yield of 90% of trichloroethyl benzoate was recovered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Formation of Tetraarylsilanes from the Reactions of Triarylsilylmetallic Compounds.[1] II. Reactions with Triarylsilanes

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Triarylsilylmetallic compounds react at room temperature with triarylsilanes to give high yields of tetraarylsilanes. The only by-products of the reaction, other than hydrolysis products of the unconsumed reagents, are hydrogen and an inorganic silica-like material. The course of the reaction has been investigated but it has been found impossible under the present conditions to establish whether the aryl group migrates from the silane or from the silylmetallic compound, due to the fact that hydrogen–metal interconversion between the silylmetallic and the silane occurs. The sodium or potassium reagents are equally effective in this reaction, but with triphenylsilyllithium, the reaction is slower and takes predominantly an alternative route.

A number of examples have been reported from this Laboratory[1] and by other workers[2,3] of the isolation of tetraphenylsilane from reactions involving phenylsilanes, particularly triphenylsilylmetallic compounds. When this same product was isolated from several investigations in which we were engaged, either as a major product, or as a minor contaminant, the present study was undertaken to attempt to account for its formation.

An extensive investigation has revealed the following facts. The formation of tetraphenylsilane, as a specific example of what appears to be a general reaction, in reactions of triphenylsilylmetallic compounds either with triphenylsilane, or with a variety of compounds containing active hydrogen, is due to the reaction of the triphenylsilylmetallic reagent with triphenylsilane. If this latter species is not a reagent in the reaction, then it is formed by metalation of the hydrocarbon species by part of the triphenylsilylmetallic compound, with the concomitant formation of triphenylsilane, which then reacts with the remaining triphenylsilylmetallic reagent. This latter phase of the investigation, namely, the reactions of triarylsilylmetallic compounds with hydrocarbons, and the reactions of triarylmethylmetallic compounds with triarylsilanes, is discussed more fully in the accompanying paper.

A superficial examination of the reaction of triphenylsilylmetallic compounds with triphenylsilane might suggest that the reaction could be described by the equation

$$(C_6H_5)_3SiK + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_4Si + \text{"other products"} \quad (1)$$

However, an examination of the products of the reactions of a number of triarylsilylmetallic reagents with several triarylsilanes, as listed in Table I, indicated that the course of the reaction cannot be that described by equation 1. In the first place, yields of tetraphenylsilane in excess of 100%, as based on this equation, have been obtained. Secondly, were the simple migration of an aryl group the only reaction occurring, then diphenylsilyl derivatives should constitute the bulk of the "other products," whereas none are actually obtained. Instead, other than the isolation of some triphenylsilyl derivatives, which can be accounted for as recovered reagents, or derivatives of these, the other product isolated appears to be a largely crystalline, inorganic solid, containing a relatively high percentage of silicon. A similar product has been reported by Benkeser and Foster,[3] and by Hauser and Hance.[3a]

The isolation of this inorganic silicon-containing compound suggests that the end product of the reaction of triphenylsilylmetallic compounds with triphenylsilane is silane (SiH_4) or some simple derivative, and this in turn suggests a sort of chain mechanism for the course of the reaction. The first step of this chain is the transfer of an aryl group from one reagent to the other to yield a tetraarylsilane and a diarylsilyl derivative. This diarylsilyl derivative is evidently more susceptible to further aryl migration than is the original triaryl derivative, so that it successively transfers the two remaining aryl groups, yielding in the end silane (SiH_4), or a metalated derivative of silane, and 3 moles of tetraarylsilane, as depicted in the following equations. Since it is uncertain at present as to whether the silane or the silylmetallic compound is

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[1] For paper I of this series, see H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2509 (1953).

[2] R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 4200 (1952); R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

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

[3a] C. R. Hauser and C. R. Hance, *ibid.*, **74**, 1856 (1952).

TABLE I

REACTIONS OF TRIARYLSILYLMETALLIC COMPOUNDS WITH TRIARYLSILANES[a]

R = C_6H_5, R' = *p*-$CH_3C_6H_4$, R" = *o*-$CH_3C_6H_4$

Run	Triarylsilylmetallic	Triarylsilane	Solvent	Products and yield (%)[b]
1	R_3SiK	R_5SiH	Ether[c]	R_4Si (55), $R_3SiOSiR_3$ (12), and silicious mat. accounting for 31.5% of tot. Si introduced as reagents
2	R_3SiK	R_2SiH	Ether	R_4Si (46), R_3SiH (12), R_3SiOH (8)
3	R_3SiK	R_3SiH	Et–bz[d]	R_4Si (50), R_3SiOH (18)
4	R_3SiK	R'_3SiH	Ether	R_4Si (14), R'_3SiR (16), R_3SiOH (5), R'_4Si (1.3)
5	R_3SiK	R''_3SiH	Ether	R''_3SiH (77), R_3SiOH (13.5), $R_3SiOSiR_3$ (8), $R_3SiCOOH$ (11)
6	R_3SiK	R_3SiH	Ether	R_4Si (49), R_3SiOH (3), $R_3SiOSiR_3$ (1)
7	R_3SiK	R_3SiH	GDME[e]	R_4Si (36)
8	R'_3SiK	R_3SiH	Ether	R'_3SiR (14.5), R_4Si (12)
9	R''_3SiK	R_3SiH	Ether	R_4Si (11), R''_3SiH (8), R_3SiOH (8)
10	R_3SiK	R'_4Si	Ether	R'_4Si (81 rec.), R_3SiOH (37)
11	R_3SiNa	R_3SiH	GDME	R_4Si (40), R_3SiOH (20)
12	R_3SiLi	R_3SiH	GDME	R_6Si_2 (14), R_4Si (11), R_3SiH (63 rec.)

[a] Unless otherwise mentioned, all reactions were run with equimolar amounts of the silane and silylmetallic reagent at room temperature for 4 days. [b] Yields are calculated on the basis of the % of total silicon represented, except recovered reagents which are expressed as % recovery. [c] Reaction was stirred 5 days. [d] Ether–benzene. The reaction mixture was refluxed at 74°, the excess ether being distilled off. [e] Ethylene glycol dimethyl ether.

the reagent involved in the transfer of the aryl group, the equations have been written assuming that the aryl group migrates from the silylmetallic compound. This assumption will be discussed later in this paper.

$$R_3SiH + R_3SiK \longrightarrow R_4Si + R_2SiHK \qquad (2)$$

$$R_3SiH + R_2SiHK \longrightarrow R_4Si + RSiH_2K$$

$$R_3SiH + RSiH_2K \longrightarrow R_4Si + SiH_3K \xrightarrow{H_2O} [SiH_4] \xrightarrow{H_2O} H_4SiO_4 + H_2$$

That this mechanism is more nearly correct is borne out by the fact that neither mono- nor disubstituted silanes are isolated from the reaction, and that a carefully hydrolyzed reaction mixture not only gives rise to the evolution of a gas which, after passage through sulfuric acid to remove any organic components burns with a blue flame and then explodes, a behavior characteristic of hydrogen, but also gives rise to a silicious material. This material contained 23.5% silicon after drying. Silicic acid contains 29.2% silicon, and silica contains 46.7% silicon; infrared and X-ray diffraction spectra indicate that the material contained, in all probability, both these compounds. The material as originally isolated was alkali-soluble but acid-insoluble, although after some days of air drying it became only partially alkali-soluble.

The reaction scheme as proposed above cannot be entirely correct since it indicates that 3 moles of triphenylsilane and 1 mole of triphenylsilylpotassium give rise to 3 moles of tetraphenylsilane. Hence when 1 mole of the silane is treated with 1 mole of the silylpotassium reagent, the maximum yield of tetraphenylsilane should be one mole, whereas actually, yields as high as 1.1 moles per mole of the silane have been obtained. This suggests that a certain amount of hydrogen–metal interconversion (metalation) between the reagents, or between a reagent and some of the products or intermediates, must be occurring, a fact that is borne out quite clearly by the results of run 9. Here tri-*o*-tolylsilylpotassium was treated with triphenylsilane. While only a small amount of tetraarylsilane was actually formed, and a mixture of products difficult to separate was obtained, a small amount of tri-*o*-tolylsilane was obtained, which could only have arisen through a hydrogen–metal exchange between the tri-*o*-tolylsilylpotassium and the triphenylsilane to yield tri-*o*-tolylsilane and triphenylsilylpotassium, since the reaction mixture was carbonated prior to hydrolysis. The other reaction product obtained, other than tetraphenylsilane, was triphenylsilanol, which conceivably arose as the hydrolysis product of triphenylsilanecarboxylic acid, derived by carbonation of triphenylsilylpotassium.[4]

The mechanism of reaction described by equations 2 further does not account for the mechanism of migration of the aryl group. In their closely related work on the reaction of sodium with triphenylsilane at elevated temperatures, Benkeser and Foster[3] postulate a reaction wherein phenylsodium is cleaved from triphenylsilane and that the diphenylsilylsodium [$(C_6H_5)_2SiHNa$] thus formed reacts further with sodium with the elimination of further phenyl groups, so that a silicious material much like that reported here is obtained. The phenylsodium formed in these reactions then couples with the triphenylsilane to yield tetraphenylsilane. If this last step is the correct manner in which the tetrasubstituted silane is formed, then this mechanism applied to our system implies that the phenyl groups are cleaved from triphenylsilylpotassium, which is the only other reagent present. Attempts to demonstrate the presence of phenylpotassium in the reaction mixtures derived from treatment of triphenylsilane with triphenylsilylpotassium by carbonation of aliquots of the reaction mixture during and at the end of the reaction have consistently failed. The failure to isolate benzoic acid might, however, be due to a very transitory existence of the reactive phenylpotassium under the conditions of the reaction. However, it is difficult to conceive how phenylpotassium could arise from triphenylsilylpotassium. Consequently, while this mode of formation cannot be excluded, it seems unlikely in the present case.

Attempts to determine from which reagent the aryl group migrated by treating an aryl silane with a silylmetallic compound bearing a different aryl group did not clarify the problem. Thus treatment of tri-*p*-tolylsilane with triphenylsilylpotassium yielded the unsymmetrical tri-*p*-tolylphenylsilane,

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(4) R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

together with both tetraphenyl- and tetra-*p*-tolylsilane, indicating that both phenyl and *p*-tolyl groups migrated. Similarly, when triphenylsilane was treated with tri-*p*-tolylsilylpotassium, tri-*p*-tolylphenylsilane was again isolated together with some tetraphenylsilane, but no tetra-*p*-tolylsilane or triphenyl-*p*-tolylsilane was found. The uncertainty from these results as to which aryl group migrates can best be explained on the basis that hydrogen–metal interconversion between the silane and the silylmetallic reagent probably occurs, so that both species of silane and of silylmetallic compound are probably present. The findings reported earlier in this paper in connection with tri-*o*-tolylsilylpotassium and triphenylsilane bear out the validity of this postulation.

$$\begin{tikzcd}
(C_6H_5)_3SiK + (p\text{-}CH_3C_6H_4)_3SiH \arrow[r, shift left] \arrow[d] & (C_6H_5)_3SiH + (p\text{-}CH_3C_6H_4)_3SiK \arrow[l, shift left] \arrow[d] \\
\begin{array}{l}(C_6H_5)_4Si\ (14\%)\\ (p\text{-}CH_3C_6H_4)_3SiC_6H_5\ (16\%)\\ (p\text{-}CH_3C_6H_4)_4Si\ (1.3\%)\end{array} & \begin{array}{l}(C_6H_5)_4Si\ (12\%)\\ (p\text{-}CH_3C_6H_4)_3SiC_6H_5\ (14.5\%)\end{array}
\end{tikzcd}$$

In all of the products isolated from the above experiments, with the exception of the small amount of tetra-*p*-tolylsilane, there can be little doubt that it is a phenyl group which has migrated, and this would seem to confirm the postulate that an equilibrium between the two possible silanes and silylmetallic reagents must exist. It appears that under the conditions of these experiments, there is considerable preference for the migration of a phenyl group than for the migration of a *p*-tolyl group.

The presence of an *o*-tolyl group in these reactions seems to exert considerable effect on the reaction. When tri-*o*-tolylsilylpotassium was treated with triphenylsilane, the reaction occurred only to the extent of 11%. In contrast, when tri-*o*-tolylsilane was treated with triphenylsilylpotassium, the silane was recovered unchanged in 77% yield, and the absence of any tetrasubstituted silane indicated that no reaction occurred. Recent studies[5] have shown that tri-*o*-tolylsilanes are sterically hindered, and it appears probable that the failure of a reaction to occur in this case is yet another example of the steric hindrance in these compounds.

That the variety of products obtained from the reaction of triphenylsilylpotassium with tri-*p*-tolylsilane did not arise from the reaction of the silylmetallic reagent with a tetrasubstituted silane was confirmed by treating tetra-*p*-tolylsilane, under the same conditions, with one equivalent of triphenylsilylpotassium. The tetra-*p*-tolylsilane was recovered unchanged in 81% yield, and the only other product of the reaction was triphenylsilanol, derived from hydrolysis of triphenylsilanecarboxylic acid,[4] obtained by carbonation of the reaction mixture.

With these findings of the behavior of triarylsilylpotassium compounds with triarylsilanes, it was of interest to investigate the behavior of the other silylmetallic reagents, triphenylsilylsodium and triphenylsilyllithium, under these conditions. Difficulties in reproducing the conditions of the reactions were encountered, as well as uncertainties as to the actual course of the reaction. While triphenylsilylpotassium can easily be prepared in diethyl ether, no way of preparing triphenylsilylsodium or -lithium in this solvent is as yet known, although each of these reagents can be prepared in fair yield in ethylene glycol dimethyl ether. This necessary change of medium for the reaction further complicates results, inasmuch as it is known that some reaction between the triphenylsilylmetallic reagent and the solvent occurs, so that the amount of triphenylsilylmetallic reagent after 4 days stirring at room temperature will be somewhat reduced independently of any reaction with triphenylsilane.

With the above restrictions in mind, the results are nevertheless of interest. Under the same time and temperature conditions, but in a different solvent than in the experiments described earlier, triphenylsilylpotassium and triphenylsilylsodium both react with triphenylsilane to give relatively high and essentially equal yields of tetraphenylsilane. However, triphenylsilyllithium, by contrast, yields only a small amount of tetraphenylsilane but a considerable amount of hexaphenyldisilane together with some recovered starting materials. This apparently anomalous behavior of triphenylsilyllithium will be referred to in more detail in the accompanying paper, where a similar result is obtained in the reaction of triphenylmethylsodium with triphenylsilane in an ether–benzene mixture boiling at 74°.

From the results reported above it appears that the reaction between triphenylsilylpotassium or -sodium and triphenylsilane are qualitatively and quantitatively similar, but that with triphenylsilyllithium, the reaction is not only appreciably slower, but also largely takes a different course. The coupling of triphenylsilyllithium with triphenylsilane to form hexaphenyldisilane is not unexpected, since the treatment of triphenylsilane with organolithium compounds is a well-recognized method of preparing tetrasubstituted silanes.[6] Actually, it seems surprising that triphenylsilylpotassium and triphenylsilylsodium do not couple with triphenylsilane to yield hexaphenyldisilane instead of reacting in the complex manner described above to yield tetraphenylsilane.

Experimental[7]

Reagents.—Triphenylsilylpotassium[8] was prepared by treatment of hexaphenyldisilane (usually 5.0 g., 0.00965 mole) with 1:5 sodium–potassium alloy in a total of 50 ml. of ether. After amalgamation, the triphenylsilylpotassium suspension was decanted from the amalgam by siphoning under nitrogen, and two 50-ml. ether washings were used to remove the rest of the material from the amalgam. To this material was added the triarylsilane as a solid.

Tri-*p*-tolylsilylpotassium was prepared similarly from hexa-*p*-tolyldisilane. This latter material was prepared in 72% yield by refluxing in 40 ml. of xylene a mixture of 7.2 g. (0.0214 mole) of tri-*p*-tolylchlorosilane (obtained from treatment of silicon tetrachloride with 3 equivalents of *p*-tolyllithium) and 2.3 g. (0.1 g. atom) of sodium for 18

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[5] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950); H. Gilman and G. N. R. Smart, *ibid.*, **16**, 424 (1951).

[6] H. Gilman and H. W. Melvin, THIS JOURNAL, **71**, 4050 (1949); H. Gilman and S. P. Massie, Jr., *ibid.*, **68**, 1128 (1946).

[7] All reactions involving organometallic compounds were carried out in a dry, oxygen-free nitrogen atmosphere. Melting points are uncorrected.

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

hours. The reaction was hydrolyzed, the material filtered and recrystallized from toluene to melt at 354–356°. A mixed melting point with an authentic sample of hexa-*p*-tolyldisilane was not depressed.

The preparations of triphenylsilylpotassium, triphenylsilylsodium and triphenylsilyllithium in ethylene glycol dimethyl ether were carried out according to published procedures.[9] The organometallic reagents were separated from the excess unconsumed metals by means of a transfer pipet. It was assumed that the reactions were quantitative. The solutions were diluted with solvent to approximate the concentrations employed in the runs with diethyl ether.

Tri-*o*-tolylsilylpotassium was prepared by treating 5.7 g. (0.0169 mole) of tri-*o*-tolylchlorosilane in 40 ml. of ether with 2 ml. of sodium–potassium alloy. The reaction mixture was stirred for 24 hours, during which time the mixture became yellow colored. The mixture was amalgamated with mercury and the tri-*o*-tolylsilylpotassium was decanted off under nitrogen as before.

Preparation of Tri-*p*-tolylsilane.—To a suspension of 1.0 g. (0.026 mole) of lithium aluminum hydride in 150 ml. of ether was added slowly in portions 16.8 g. (0.05 mole) of tri-*p*-tolylchlorosilane. The reaction was stirred for 24 hours, and then was carefully hydrolyzed with wet ether, followed by 100 ml. of 5% aqueous hydrochloric acid. The ether layer was removed, dried over sodium sulfate and then evaporated to dryness under reduced pressure. The residue was recrystallized from petroleum ether (b.p. 60–70°) to yield 11.6 g. (77%) of tri-*p*-tolylsilane, m.p. 81–83°. The infrared spectrum was consistent with the anticipated structure.

Anal. Calcd. for $C_{21}H_{22}Si$: C, 83.5; H, 7.29. Found: C, 83.2; H, 7.25.

General Method.—All reactions were run with approximately equimolar amounts of the organometallic reagent and the organosilane. The concentration of each reagent was approximately 0.125 molar, regardless of the solvent employed. The reactions were stirred at a moderate rate at room temperature for 4 days (except for run 1 which was 5 days), at the end of which time they were worked up. In some cases the reaction mixture was carbonated with a Dry Ice–ether slurry prior to hydrolysis with water, in others the reaction mixture was hydrolyzed directly, and in a few cases the reaction mixture was treated with excess benzyl chloride. None of these methods of stopping the reaction had any profound effect on the results, although in two cases where the carbonation procedure was used, excess triphenylsilylmetallic reagent was isolated as triphenylsilanecarboxylic acid, whereas direct hydrolysis of this reagent usually yields a mixture of triphenylsilane and triphenylsilanol. More specific details are best given by describing several examples.

Yields of Products.—Due to the unknown mechanism of the reaction the amounts of all products isolated from the reactions of triarylsilylmetallic compounds with triarylsilanes are reported both in terms of the moles of materials obtained, and by a percentage yield, the percentage yield being based on the percentage of the total silicon introduced as reagents which the isolated material represents. Thus % yield = g. atom of Si in compound/total g. atom of Si in reagents.

Reaction of Triphenylsilylpotassium with Triphenylsilane (Run 1).—This run deviated slightly from the general method employed, with respect to time and method of hydrolysis. Triphenylsilylpotassium, prepared from 5.18 g. (0.01 mole) of hexaphenyldisilane in 150 ml. of ether was treated with 5.2 g. (0.02 mole) of triphenylsilane. The mixture was stirred for a total of 5 days. In the first few hours the reaction slowly became red, but after the first 24 hours the color changed to red-brown, which it remained for the rest of the reaction period. The mixture was hydrolyzed with 100 ml. of "wet" ether discharging the color of the mixture. A considerable volume of gas was liberated. Some of this was passed through concentrated sulfuric acid to remove any ether vapor, and some of the residual gas was collected. It burned with a blue flame, and then detonated, a behavior characteristic of hydrogen.

When gas evolution had ceased and the color of the reaction mixture was a dirty white, the solids were filtered off and washed with ether. The solid material was refluxed with three 100-ml. portions of benzene. These colorless clear extracts yielded, on concentration, a total of 6.75 g. (0.02 mole, 50%) of tetraphenylsilane, m.p. 229–231°, identified by mixed melting point.

The residual material remaining after the benzene extractions was a sirupy, alkaline, gray liquid. This was carefully neutralized with 10% hydrochloric acid, which precipitated a gray-white solid. This was filtered off and air-dried for 2 days. Immediately after the precipitation this material was completely soluble in alkali, and was reprecipitated by acid, but after the 2 days drying period, it was only partially soluble in alkali. It then weighed 1.05 g. and was found to contain 33.0% silicon. (Calcd. for SiO_2: Si, 46.7; for H_4SiO_4: Si, 29.2.) This material did not burn in a strong flame, but did blacken slightly, before turning white. An infrared spectrum failed to detect the presence of phenylsilicon absorption, but absorption characteristic of hydroxyl groups and of silica were present. The material isolated represents 31.5% of the silicon introduced into the reaction in the form of reagents.

The X-ray diffraction pattern of this silicious material indicated that it contained a small amount of sodium chloride, and that the remaining material was largely crystalline (unlike silicic acid), but the interplanar spacings could not be correlated with any of the published data for silicon dioxide or for any silicon-containing compound. Further leaching of the material with 10% hydrochloric acid, followed by extensive washing with water and ethanol removed the sodium chloride, but the X-ray diffraction pattern was not altered other than that the lines characteristic of sodium chloride were not present. The white solid, silicon content 23.5%, did not blacken when placed in a strong flame.

The ether layer originally separated from the reaction mixture was evaporated to dryness, and the solid remaining was treated with petroleum ether (b.p. 60–70°). An insoluble residue weighing 0.7 g. (0.0021 mole, 5%) was filtered off and identified as tetraphenylsilane by its melting point of 228–231°, and mixed melting point with an authentic sample. The petroleum ether filtrate deposited a total of 1.3 g. (0.0024 mole, 12%) of hexaphenyldisiloxane, m.p. 223–225°, identified by mixed melting point and infrared spectrum.

Reaction of Triphenylsilylpotassium with Tri-*p*-tolylsilane (Run 4).—The amalgamated triphenylsilylpotassium prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane in a total of 150 ml. of ether was treated with 5.7 g. (0.0019 mole) of solid tri-*p*-tolylsilane. The reaction was stirred at room temperature for 4 days during which time it became red colored and considerable precipitate appeared to form. The reaction mixture was then carbonated and the mixture was filtered without hydrolyzing.

The ether was removed from the filtrate under reduced pressure, and the resulting 5.7 g. of white solid was extracted with 50 ml. of hot petroleum ether (b.p. 60–70°). The 1.3 g. of insoluble residue melted from 152–188°. Several recrystallizations from benzene eventually yielded 0.1 g. (0.00026 mole, 0.7%) of tri-*p*-tolylphenylsilane, m.p. 172–183°, which did not depress the mixed melting point of an authentic specimen, and 0.2 g. (0.0006 mole, 1.6%) of tetraphenylsilane, m.p. 227–230°, identified by mixed melting point.

The petroleum ether extract from above deposited three crops of material on concentration. Crop 1, which weighed 2.5 g. and melted from 150–166° was recrystallized from 3:1 ethanol–ethyl acetate. The first 0.6 g. of needles deposited melted from 185–196°, and successive recrystallizations from petroleum ether (b.p. 77–115°) and petroleum ether (b.p. 60–70°) followed by sublimation at reduced pressure eventually gave 0.2 g. (0.00051 mole, 1.3%) of crude tetra-*p*-tolylsilane, m.p. 205–210°, whose mixed melting point with authentic tetra-*p*-tolylsilane, m.p. 231–233°, was 215–221°, but whose mixed melting points with tetraphenylsilane or tri-*p*-tolylphenylsilane were all depressed below 200°. The infrared spectrum agreed with the proposed structure, but indicated the presence of some tetraphenylsilane. The second fraction of crop 1 weighed 1.05 g. (0.0028 mole, 7%) and melted from 170–182°, and did not depress the mixed melting point with authentic tri-*p*-tolylphenylsilane, m.p. 180–182°. Recrystallization from ethyl acetate failed to raise or sharpen the melting point. The filtrate from the second fraction of crop 1, together with crops 2 and 3, each of which melted over the range 165–180°, were combined and recrystallized from petroleum ether (b.p. 77–115°); a total of 1.3 g. (0.0034 mole, 9%) of tri-*p*-

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

tolylphenylsilane was obtained which melted from 173–182°, the mixed melting point with an authentic sample being 178–182°. The infrared spectra of this material and of that described above indicated the probable presence of a small amount of tetraphenylsilane as a contaminant.

The mother liquors from crop 3 above were evaporated to dryness under reduced pressure and the resulting gum was treated with piperidine and alkali to convert the triphenylsilane present to triphenylsilanol.[10] After the evolution of hydrogen was complete, the solution was poured into water, and the solid which precipitated was filtered, dried, and recrystallized from petroleum ether (b.p. 60–70°). A total of 0.55 g. (0.0020 mole, 5%) of triphenylsilanol, m.p. 148–150°, was obtained and was identified by mixed melting point.

The residue from the original filtration after carbonation was treated with water and dilute alkali. An insoluble material was filtered off and after recrystallization from benzene weighed 1.8 g. (0.0054 mole, 14%), melted at 230–232°, and was shown to be tetraphenylsilane by a mixed melting point determination with an authentic specimen, m.p. 230–232°. A mixed melting point with tetra-*p*-tolylsilane, m.p. 231–233°, was depressed to 199–205°.

The actual yields of the tetrasubstituted silanes reported here were undoubtedly higher since considerable less-pure material was recovered, but appreciable difficulty in separating the compounds was experienced.

Reaction of Triphenylsilylpotassium with Tri-*o*-tolylsilane (Run 5).—To the 150 ml. of amalgamated triphenylsilylpotassium suspension prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane and sodium–potassium alloy was added as a solid 5.7 g. (0.019 mole) of tri-*o*-tolylsilane. The suspension was stirred for 4 days during which time it became red-brown in color, although little reaction appeared to occur. The reaction mixture was carbonated with Dry Ice and then filtered without hydrolyzing.

The ether filtrate was evaporated to dryness under reduced pressure and the residue taken up in petroleum ether (b.p. 60–70°). The first fraction weighed 1.2 g. and melted from 134–150°. Recrystallization yielded a total of 0.9 g. (0.0033 mole, 8.5%) of triphenylsilanol, m.p. 148–150°, which did not depress the mixed melting point with an authentic specimen.

The succeeding four fractions obtained by concentration of the mother liquors weighed 4.4 g. (77% rec.), melted at 88–90°, and were shown to be tri-*o*-tolylsilane by a mixed melting point determination with an authentic specimen.

The gray residue remaining from the original filtration of the ether layer was treated with water and dilute sodium hydroxide. A residue weighing 1.2 g. was filtered off and, after recrystallization from petroleum ether (b.p. 60–70°), weighed 0.85 g. (0.0015 mole, 8%) and melted at 221–223°. It was identified as hexaphenyldisiloxane by mixed melting point determination.

A white solid separated from the clear aqueous filtrate over a period of two hours. It was filtered off, dried, and after recrystallization weighed 0.5 g. (0.0018 mole, 5%), and was shown to be triphenylsilanol by its melting point 147–149°, which was not altered by admixture with an authentic sample of triphenylsilanol.

The aqueous alkaline filtrate from above was carefully acidified precipitating a white solid. This was dried, weighed 1.3 g. (0.0043 mole, 11%) and melted at 177–178° with evolution of a gas. A mixed melting point with authentic triphenylsilanecarboxylic acid was not depressed.

Reaction of Tri-*p*-tolylsilylpotassium with Triphenylsilane (Run 8).—To 6.0 g. (0.01 mole) of hexa-*p*-tolyldisilane in 10 ml. of ether was added 2 ml. of 1:5 sodium–potassium alloy. The reaction mixture rapidly became yellow and was diluted with an additional 40 ml. of ether. After stirring for 24 hours, the suspension was treated with mercury to remove the excess alloy and the tri-*p*-tolylsilylpotassium was siphoned from the amalgam, using two 50-ml. washings of ether to remove all the material. To this yellow suspension was added 5.2 g. (0.02 mole) of solid triphenylsilane. The suspension became dark brown during the 4 days stirring. The reaction mixture was carbonated, and the insoluble residue filtered off.

The ether filtrate was evaporated to dryness under reduced pressure and the residue treated with hot petroleum ether (b.p. 60–70°). A small amount of insoluble material was filtered off and recrystallized from benzene to yield 0.25 g. (0.0074 mole, 2%) of tetraphenylsilane, m.p. 230–232°, identified by mixed melting point. From the petroleum ether solution was obtained, after further recrystallization from ethyl acetate, a total of 2.2 g. (0.0058 mole, 14.5%) of tri-*p*-tolylphenylsilane, m.p. 174–183°, which did not depress the mixed melting point of an authentic specimen. An infrared spectrum indicated that a small amount of tetraphenylsilane was probably also present. Considerable additional but less pure material was also recovered.

The insoluble residue from the original reaction mixture was treated with aqueous alkali, and the insoluble material was removed, dried, and recrystallized from benzene. A total of 1.3 g. (0.0039 mole, 10%) of tetraphenylsilane, m.p. 230–232°, was obtained, which was identified by a mixed melting point determination.

Reaction of Triphenylsilylsodium with Triphenylsilane (Run 11).—The triphenylsilylsodium prepared from 5.0 g. (0.00965 mole) of hexaphenyldisilane and 2.0 g. of sodium in 50 ml. of ethylene glycol dimethyl ether was treated with 4.7 g. (0.018 mole) of triphenylsilane in 80 ml. of the ether. The reaction became dark over a period of 4 days, and a precipitate rapidly formed. The reaction mixture was hydrolyzed with water, a gas which burned with a blue flame being evolved. The reaction mixture was filtered, and the residue was recrystallized from benzene. A small amount of benzene-insoluble silicious material was filtered off and the benzene filtrate deposited a total of 4.45 g. (0.0135 mole, 38%) of tetraphenylsilane, m.p. 229–231°, identified by mixed melting point with an authentic specimen.

The ether–aqueous filtrate from above was extracted thrice with ether, the ether layers were dried over sodium sulfate, and the ether was then removed under reduced pressure. The solid which remained was treated with petroleum ether (b.p. 60–70°) and 0.4 g. of insoluble material was filtered off. This was recrystallized from benzene, to yield 0.2 g. (0.0006 mole, 2%) of tetraphenylsilane, m.p. 228–230°, identified by mixed melting point.

The petroleum ether solution above deposited a total of 1.95 g. (0.0071 mole, 20%) of triphenylsilanol, m.p. 149–151°, which did not depress the melting point of authentic triphenylsilanol.

Reaction of Triphenylsilyllithium with Triphenylsilane (Run 12).—Triphenylsilyllithium was prepared by treating 5.0 g. (0.00965 mole) of hexaphenyldisilane in 5 ml. of ethylene glycol dimethyl ether with excess (1.5 g.) finely cut lithium. The reaction started in about 1 minute as evidenced by the formation of a yellow color. After 2 hours stirring, an additional 45 ml. of the ether was added. After a total of 6 hours stirring, the reaction appeared to be complete, there being no undissolved solid present in the flask. An aliquot representing 0.016 mole (assuming 100% reaction) was removed and treated with 4.16 g. (0.016 mole) of triphenylsilane in 80 ml. of the ether. The reaction was stirred for 4 days. In the first few hours the reaction mixture turned red in color and a white precipitate formed. The reaction mixture was carbonated, and then hydrolyzed with water. The insoluble residue was filtered off. This 1.6 g. of material was refluxed with 50 ml. of benzene, and filtered hot. The 1.2 g. (0.0023 mole, 14%) of insoluble hexaphenyldisilane so isolated melted at 359–361°, and did not depress the mixed melting point when admixed with an authentic sample. The benzene filtrate deposited 0.3 g. (0.00089 mole, 3%) of tetraphenylsilane, m.p. 229–231°, identified by mixed melting point.

The original aqueous glycol dimethyl ether filtrate was thrice extracted with ether and the combined ether extracts were dried over sodium sulfate. The ether was removed under reduced pressure, and the gummy residue was treated with petroluem ether (b.p. 60–70°). From the 0.5 g. of insoluble material which melted from 152–217° was obtained by recrystallization from benzene 0.15 g. (0.00045 mole, 1%) of tetraphenylsilane, m.p. 227–230°, identified by mixed melting point, and some crude unidentified material. The petroleum ether filtrate failed to deposit any solid, so the solvent was removed under reduced pressure and the residue was distilled at 0.03 mm. to yield a total of 2.65 g. (0.0104 mole, 63% recovery) of triphenylsilane, b.p. 116–120°, which crystallized when seeded with authentic triphenylsilane, and which then melted at 41–44°, and which did not depress the mixed melting point with an authentic sample.

Acidification of the original ether-extracted aqueous layer

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

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

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[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.

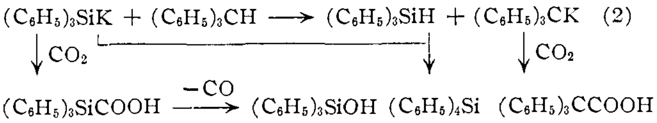
The previous paper in this series[1] described the reaction of triarylsilylmetallic compounds with triarylsilanes in which high yields of tetraarylsilanes are formed. Specifically, it was found that both triphenylsilylpotassium and triphenylsilylsodium react with triphenylsilane to yield, after hydrolysis, 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.



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

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).