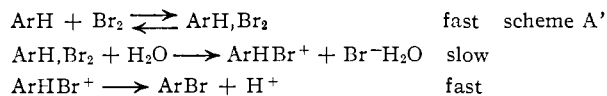


as iodine-catalyzed bromination of benzene, has no hydrogen isotope effect.³⁰ The lack of any appreciable basic catalysis by sodium acetate supports this view.³¹ The other mechanism involves the preliminary formation of a complex, as in scheme A, with water acting as the electrophilic reagent in the second step instead of bromine (scheme A')



A third scheme (scheme C) permitted by the kinetic data is similar to scheme A', except that the first step is slow and rate-controlling, and the second is fast. This scheme is less likely than the other two, because complex formation is usually considered to be instantaneous.

There is nothing in the present data that necessitates the postulation of a complex, as in scheme A', but neither is there any evidence against it. The medium may be polar enough to allow a simultaneous attack of bromine and the breaking of the

(30) L. Melander, *Arkiv. Kemi*, **2**, 213 (1950).

(31) This observation corrects a previous statement by one of us (ref. 8, footnote 4). The increase in rate caused by NaAc in 85% acetic acid is probably a salt effect.

bromine-bromine bond. An argument in favor of an initially formed complex can be based on the reasoning that high-order bromination, according to the available evidence, most likely involves a complex, and that it is consistent to view the changes in order as a gradual process, in which the solvent or neutral salts^{12,32} eventually can take the place of the second bromine molecule. The fact that the first- but not the second-order (in bromine) rate is reduced in deuterated acetic acid or 90% acetic acid⁴ speaks for a fairly close participation of the solvent molecules in the transition state of the first-order reaction, although this in itself is no unique proof of the "complex" mechanism.

Acknowledgment.—The generous help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged. We are also indebted to Professor P. W. Robertson and Dr. P. B. D. de la Mare for critically reading the manuscript and to Dr. G. Zimmerman for many helpful discussions.

(32) See ref. 9, N. E. Brezhneva and S. Z. Roginsky, *Acta Physicochim. U.R.S.S.*, **12**, 209 (1940), and L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **78**, 4549 (1956), for the role of ZnCl_2 , which may, however, also act by changing the nature of the substituting agent. BRYN MAWR, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Reaction of Triphenylsilylpotassium with Organic Halides, a Case of Halogen-Metal Interconversion¹

BY A. G. BROOK AND SAUL WOLFE²

RECEIVED AUGUST 16, 1956

Investigation of the products obtained from the reactions of triphenylsilylpotassium with a variety of organic halides indicates that as well as the normal coupling reaction, halogen-metal interconversion also occurs. The fate of the halogen-metal exchange products, whose presence in the reaction mixture was demonstrated indirectly by subsidiary experiments, depends on the order of addition of the reagents. These exchange products do not appear to contribute significantly to the over-all yield of coupling product.

Evidence for the participation of the halogen-metal interconversion reaction in the reaction of organosiliconmetallics with an organic halide has been reported recently.³ Despite the frequent occurrence of this reaction in organic chemistry, this appears to be the only reported evidence for the occurrence of this reaction in organosilicon chemistry. Recent studies in this Laboratory on the coupling of triphenylsilylpotassium with a variety of organic halides has shown that these reactions are far from clean and the products formed seem to indicate that halogen-metal interconversion plays an important role.

Although triphenylsilylpotassium is a highly reactive organometallic reagent, the yield of coupled product from the reaction with organic halides, in our own work as well as that reported by others,⁴

is surprisingly low, rarely exceeding 50%, although all the silylmetallic reagent appears to be consumed. It has generally been assumed that cleavage of the solvent, hydrolysis and incomplete formation of the silylmetallic from the starting material, hexaphenyldisilane, accounted for the fate of the remainder of the reagents and for the by-products isolated.

Since it was felt that halogen-metal exchange might account for some of the by-products isolated, we have reinvestigated the products formed between triphenylsilylpotassium and a variety of halides. In each case, unless otherwise mentioned, 0.038 mole of triphenylsilylpotassium in about 150 ml. of ether was allowed to react with 0.038 mole of halide, also in ether. The results with bromobenzene, which was most thoroughly studied, will be interpreted, and it will be shown that the other halides follow closely the same behavior.

Table I shows the products and yields obtained when triphenylsilylpotassium reacts with bromobenzene. As can be seen, except for the coupling product tetraphenylsilane, the nature and yields

(1) Presented in part at the 39th Conference of the Chemical Institute of Canada, Montreal, May, 1956.

(2) Dept. of Chemistry, University of Ottawa, Ontario. Holder of a Research Council of Ontario Scholarship, 1954-1955.

(3) A. G. Brook, H. Gilman and L. S. Miller, *THIS JOURNAL*, **75**, 4759 (1953).

(4) R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951); R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952); H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

of the other products depend on the order of addition of the reagents. When the halide is added to the metallic (normal addition), the chief by-product is hexaphenyldisilane. In addition, small amounts of benzene and the "hydrolysis products," triphenylsilanol and hexaphenyldisiloxane, are formed. On the other hand, when the silylmetallic is added to the halide (inverse addition), no hexaphenyldisilane is formed, considerably greater amounts of hydrolysis products are obtained and instead of benzene, biphenyl is formed in approximately the corresponding yield.

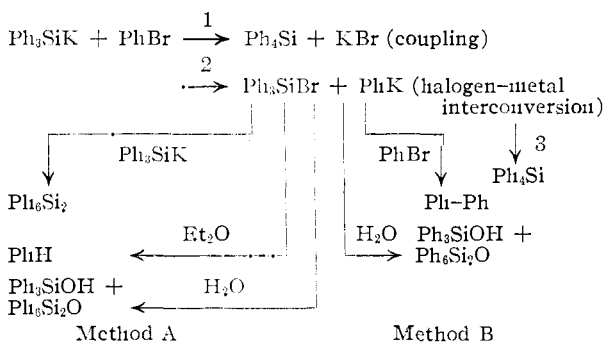
TABLE I
PRODUCTS AND YIELDS FROM THE REACTION OF TRIPHENYLSILYLPOTASSIUM WITH BROMOBENZENE

Product	Yield, %		Product	Yield, %	
	Method A ^a	Method B ^b		Method A ^a	Method B ^b
Ph ₄ Si	55	61	Ph ₆ Si ₂ O	4	34
Ph ₆ Si ₂	22	0	PhH	9	Trace
Ph ₃ SiOH	5	1	Ph-Ph	0	8

^a Addition of bromobenzene to triphenylsilylpotassium. Addition of triphenylsilylpotassium to bromobenzene.

The formation of these products under the different reaction conditions may be explained on the basis of two main reaction processes (1 and 2) and various subsequent reactions, depending on the conditions.

Figure 1 outlines the reactions proposed to explain the observed results.



Triphenylsilylpotassium and bromobenzene react either to form tetraphenylsilane and potassium bromide (1) or by halogen-metal interconversion (2), to yield triphenylbromosilane and phenylpotassium. In the case of the addition of the halide to the metallic (method A) these products, at least initially, are being formed in the presence of an excess of triphenylsilylpotassium. Hence it seems reasonable to account for the formation of hexaphenyldisilane as due to reaction of the triphenylbromosilane, formed by halogen-metal exchange, with triphenylsilylpotassium, a reaction found to occur slowly but in good yield (run 1, Table II).

The benzene isolated is assumed to be formed from cleavage of the solvent ether by the phenylpotassium formed from halogen-metal exchange. Experiments confirming this conclusion will be described later. The "hydrolysis products," triphenylsilanol and hexaphenyldisiloxane, isolated are due to hydrolysis of the triphenylbromosilane not consumed by reaction with triphenylsilyl-

potassium, by the water used in working up the reaction.

When the silylmetallic is added to the organic halide (method B), the same two primary reactions again occur. In this case however, the halogen-metal exchange products are formed initially in the presence of excess bromobenzene. Under these conditions the phenylpotassium formed by halogen-metal exchange can couple (probably inefficiently) with bromobenzene to form biphenyl, and hence little benzene is formed.

The triphenylbromosilane formed by halogen-metal exchange has no triphenylsilylpotassium to react with; hence no hexaphenyldisilane is formed and the triphenylbromosilane accumulates in the reaction flask, producing greater yields (35%) of hydrolysis products from this mode of addition than are obtained by normal addition (9%).

One further possible reaction is that the halogen-metal interconversion products themselves couple to form tetraphenylsilane (3), a reaction experimentally possible under similar conditions (run 2, Table II). In fact it is conceivable that all the tetraphenylsilane isolated from these reactions is produced by this reaction. However, as will be demonstrated later, the recombination of the exchange products does not materially contribute to the over-all yield of tetraphenylsilane.

It is necessary to demonstrate that halogen-metal interconversion is actually occurring in order to justify the above argument. The nature of these products does not permit of their ready isolation. However, from several reactions of triphenylsilylpotassium with chlorobenzene (which gives analogous results to those with bromobenzene, run 3, Table II) which were worked up without hydrolysis, crude triphenylchlorosilane, identified by X-ray diffraction and infrared absorption measurements, was isolated, which must have been formed by halogen-metal interconversion (e.g., run 4, Table II).

Additional evidence for the formation of triphenylbromosilane was also sought. According to the previous arguments, when triphenylsilylpotassium is added to bromobenzene, triphenylbromosilane accumulates in the reaction flask; under these conditions no hexaphenyldisilane is formed. If, therefore, on completion of the reaction excess triphenylsilylpotassium were added, it should react with the triphenylbromosilane to form hexaphenyldisilane, where none was normally obtained. When this experiment was carried out, a 10.4% yield of hexaphenyldisilane was isolated (run 5, Table II), strong evidence for the presence of triphenylbromosilane.

The high reactivity of phenylpotassium precludes its direct isolation, and attempts to demonstrate its presence in the reaction system by carbonation failed to yield any benzoic acid. Hence, it must rapidly react with the solvent diethyl ether. This was qualitatively shown by adding phenylpotassium in benzene to one volume of ether; carbonation after 6 minutes indicated 71% of the phenylpotassium had been destroyed.

The presence of phenylpotassium in the system was indirectly demonstrated by the addition of tri-

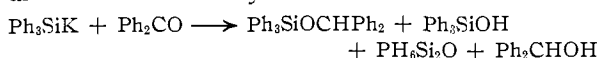
TABLE II
 COUPLING REACTIONS OF ORGANOMETALLICS AND HALIDES

Run ^a	Organometallic reagent	Mole	Halide	Mole	Time, hr.	Products and yields, ^b %
1	Ph ₃ SiK	0.020	Ph ₃ SiCl	0.020	14	Ph ₆ Si ₂ (69), ^c Ph ₁₀ Si ₂ O (13) ^c
2	PhK	.020	Ph ₃ SiBr	.020	22	Ph ₄ Si (72), Ph ₆ Si ₂ O (9), Ph ₃ SiOH (9)
3	Ph ₃ SiK	.040	PhCl	.040	12	Ph ₄ Si (72), Ph ₆ Si ₂ (7), Ph-Ph (6)
4	Ph ₃ SiK ^d	.038	PhCl ^d	.038	12	Ph ₄ Si (52), Ph ₆ Si ₂ (7), Ph ₃ Si ₂ O (15), Ph ₂ Si(OH) ₂ (0.5), Ph ₃ SiCl (4)
5	Ph ₃ SiK	.038	PhBr	.019	48	Ph ₄ Si (70), Ph ₆ Si ₂ (10.4), Ph ₃ SiOH (19), Ph-Ph (10), Ph ₃ SiH (trace)
6	Ph ₃ SiK	.038	Ph ₂ CO	.038	16	Ph ₃ SiOCHPh ₂ (21), Ph ₃ SiOH (41), Ph ₂ CHOH (18), Ph ₂ CO (27)
7	Ph ₃ SiK	.040	PhBr Ph ₂ CO	.038 .040	12	Ph ₃ COH (23), Ph ₄ Si (10), Ph ₃ Si ₂ O (22), PhBr (8), Ph ₃ -SiOH (15), Ph ₂ CO (31), and unstable unknown compd.
8	Ph ₃ SiK	.020	Ph ₃ SiCl PhBr	.020 .019	13	Ph ₄ Si (50), Ph ₆ Si ₂ O (35), ^c Ph ₃ SiOH (28) ^c
9	Ph ₃ SiK ^d	.038	PhBr ^d	.038	16	Ph ₄ Si (55), Ph ₆ Si ₂ (27)
10	PhK	.025	PhBr Ph ₃ SiCl	.026 .026	12	Ph ₄ Si (50), PhBr (52), Ph-Ph (4)
11	C ₆ H ₁₁ MgBr	.041	Ph ₃ SiCl	.041	39 ^e	Ph ₃ SiH (44), Ph ₃ SiOH (51), C ₆ H ₁₀ (22)

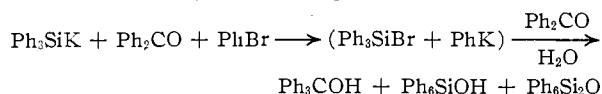
^a Ether was the solvent for all runs except 2 and 10, where benzene was used. ^b Yields are based on moles of Ph₃SiK or halide, whichever is appropriate, unless otherwise mentioned. ^c Yields are based on total silicon. ^d Reagents added simultaneously over 1-2 hr. to 100 ml. of ether. ^e After 15 hr. reflux, the ether was replaced with xylene, and the mixture was refluxed at 100° for 24 hr.

phenylsilylpotassium to a mixture of one equivalent each of bromobenzene and benzophenone. It was hoped that the benzophenone might react with the phenylpotassium to form triphenylcarbinol before it reacted with the ether solvent.

The reaction between triphenylsilylpotassium and benzophenone has been investigated by Gilman and Wu^b and in the present research (run 6, Table II). In general it is a complex reaction in which the major products formed are triphenylbenzhydroxysilane, triphenylsilanol, hexaphenyldisiloxane and benzhydrol.



In neither study was any triphenylcarbinol detected, although the reaction mixture was carefully scrutinized in the present study. But when triphenylsilylpotassium was added to the mixture of benzophenone and bromobenzene (run 7, Table II), a 23% yield of triphenylcarbinol was isolated, which could reasonably have come only from the reaction of phenylpotassium with benzophenone. Evidently the benzophenone very efficiently captures the phenylpotassium, since in the system triphenylpotassium-bromobenzene it is estimated that halogen-metal interconversion occurs to about 40% of the reagents.



It was stated that the main source of tetraphenylsilane in these reactions was from direct coupling of the reagents and that coupling of the halogen-metal interconversion products (3) is a relatively unimportant reaction. Two different experiments support this statement. In the first, triphenylsilylpotassium was added to an equivalent each of triphenylchlorosilane and bromobenzene (run 8, Table II). If the halogen-metal exchange

products were coupling to form tetraphenylsilane, then this system should favor formation of tetraphenylsilane, due to the increased concentration of triphenylhalosilane, and minimize destruction of the phenylpotassium by reaction with the solvent. Hence an increased yield of tetraphenylsilane would have been expected, but no significant change was observed.

In the second experiment, equivalents of triphenylsilylpotassium and bromobenzene simultaneously and at equal rates were added to a large volume of ether (run 9, Table II), a system designed to favor the destruction of phenylpotassium and hence to decrease the yield of tetraphenylsilane, if it were being formed by reaction of phenylpotassium with triphenylbromosilane. No significant change in the yield of tetraphenylsilane was observed. It is therefore concluded that recombination of the halogen-metal exchange products is not an important reaction in this system.

During the course of this investigation numerous incidental experiments were carried out to gain insight into the reaction. These, and the experiments previously described, are summarized in Table II. Of particular interest were the qualitative experiments on the relative rates of reaction of triphenylsilylpotassium with bromobenzene and triphenylchlorosilane (run 8) and of phenylpotassium with the same reagents (run 10). In each case, as judged by the yields, the faster reaction involved coupling of one organosilicon species with one organic species: *i.e.*, triphenylsilylpotassium reacted more rapidly with bromobenzene than with triphenylchlorosilane, whereas phenylpotassium reacted more rapidly with triphenylchlorosilane than with bromobenzene. Evidently the coupling of an organosilicon reagent with an organic compound is preferred to the coupling of two organic or two organosilicon compounds.

The preceding interpretation is applicable, with minor variations, to the reactions of triphenylsilylpotassium with the other halides investigated:

(5) H. Gilman and T. C. Wu, *THIS JOURNAL*, **75**, 2935 (1953).

benzyl chloride, cyclohexyl bromide and methylene bromide and chloride. Table III summarizes the products and yields obtained by both direct and inverse addition.

TABLE III

REACTION PRODUCTS FORMED FROM TRIPHENYLSILYL POTASSIUM AND ORGANIC HALIDES

PhCH ₂ Cl	C ₆ H ₁₁ Br	CH ₂ Cl ₂			
A. Addition of Halide to Silylmetallic					
Ph ₃ SiCH ₂ Ph	60	Ph ₃ SiC ₆ H ₁₁	0	Ph ₃ SiCH ₂ Cl	0
Ph ₆ Si ₄	25	Ph ₆ Si ₂	56	Ph ₆ Si ₂	62
		Ph ₃ SiOH	2	Ph ₃ SiOH	11
		Ph ₆ Si ₂ O	24	Ph ₆ Si ₂ O	4
PhCH ₂ CH ₂ -	25	(C ₆ H ₁₁) ₂	2	Ph ₃ SiCH ₃	Trace
Ph		C ₆ H ₁₁ Br	31	C ₂ H ₂	Trace
		C ₆ H ₁₂	Trace		
B. Addition of Silylmetallic to Halide					
Ph ₃ SiCH ₂ Ph	40	Ph ₃ SiC ₆ H ₁₁	0	Ph ₃ SiCH ₂ Cl	0
Ph ₆ Si ₂	7	Ph ₆ Si ₂	80	Ph ₆ Si ₂	0
		Ph ₃ SiH	6	Ph ₃ SiOH	20
Ph ₆ Si ₂ O	21	Ph ₆ Si ₂ O	10	Ph ₆ Si ₂ O	50
		C ₆ H ₁₀	9	Ph ₃ SiCl	9
PhCH ₂ CH ₂ -	15	(C ₆ H ₁₁) ₂	37		
Ph		C ₆ H ₁₁ Br	5		
		C ₆ H ₁₂	14		

Comparison of these results with Table I indicates that benzyl chloride behaves rather similarly to bromobenzene. The yield of coupling product is in the range 40–60%, and normal addition yields much hexaphenyldisilane, whereas inverse addition yields almost none. On the other hand, whereas with normal addition bromobenzene yields benzene, benzyl chloride yielded bibenzyl rather than the anticipated toluene. This difference was probably due to the fact that there appeared to be an induction period before reaction began, so that excess benzyl chloride may have been present in the system at all times. Thus any benzylpotassium formed probably coupled with benzyl chloride forming the bibenzyl isolated; the efficacy of benzyl chloride as a coupling reagent for organometallics is well known, as in its use in the double titration procedure for organolithium compounds.⁶ The yields of hydrolysis products also parallel the findings with bromobenzene.

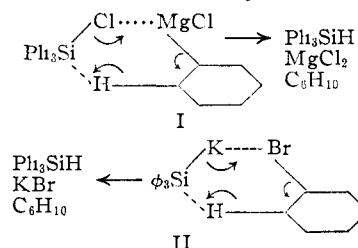
The reactions with cyclohexyl bromide were unusual in that no coupling product, triphenylcyclohexylsilane, was obtained. Nor could triphenylcyclohexylsilane be prepared by more conventional methods such as treatment of triphenylchlorosilane with cyclohexylmagnesium bromide (run 11, Table II). The failure to form this product presumably is due to steric effects, as have been encountered previously in attempts to prepare tetracyclohexylgermane.⁷

Cyclohexene, triphenylsilane and triphenylsilanol, undoubtedly formed by hydrolysis of triphenylsilane during the working up of the reaction, were isolated from the attempted synthesis of triphenylcyclohexylsilane. The formation of these products indicates the participation of the β -

hydrogen of the cyclohexane ring in a "quasi-ring" complex I as illustrated, and suggests that the failure to form triphenylcyclohexylsilane is due to steric hindrance toward attack by the cyclohexyl group on the silicon atom. No such restriction would be expected toward attack by hydrogen. Such a reaction is analogous to the "reduction" reaction of a Grignard reagent on a sterically hindered ketone.⁸

Since the coupling reaction of triphenylsilylpotassium with cyclohexyl bromide does not occur, the halogen-metal exchange reaction becomes more significant. Very high yields of hexaphenyldisilane were obtained from both methods of addition of the reagents, and cyclohexyl bromide was recovered in each case. A high yield of bicyclohexyl was isolated from inverse addition; from normal addition correspondingly high yields of cyclohexane were presumably formed, but difficulties in the isolation of this product from the solvent were encountered. The cyclohexene and triphenylsilane isolated from inverse addition are undoubtedly formed *via* the complex II, analogous to the "reduction" reaction previously described. Other than the absence of the coupling reaction and the resulting effects produced on the over-all reaction, the results with cyclohexyl bromide can be related to those obtained with bromobenzene.

The reactions of triphenylsilylpotassium with methylene dichloride or methylene dibromide are



similar to the one described above in that no coupling product is obtained. In related studies under different conditions, using liquid ammonia as solvent, Kraus and Nutting have reported that coupling occurred between triphenylgermysodium and methylene chloride.⁹ In the present study although no coupling product was obtained, the yields of hexaphenyldisilane and "hydrolysis" products were in accord with our previous interpretations. However, no account has been made of the fate of the methylene group, except for the formation of acetylene, isolated as copper acetylide, and triphenylmethylsilane, a compound analogous to one reported by Kraus and Nutting.⁹ No ethylene or ethylene dichloride, which might have been expected as reaction products, was detected, and it must be presumed that the methylene group of the methylene halide was converted into volatile or low-boiling products which escaped detection. From the inverse addition of triphenylsilylpotassium to methylene chloride, triphenylchlorosilane was isolated, indicating that halogen-metal exchange was occurring in this system.

(6) H. Gilman and A. H. Haubein, *THIS JOURNAL*, **66**, 1515 (1944).

(7) O. H. Johnson and W. H. Nebergall, *ibid.*, **71**, 1720 (1949); **71**, 4022 (1949).

(8) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 147–157.

(9) C. A. Kraus and H. S. Nutting, *THIS JOURNAL*, **54**, 1622 (1932)

The formation of certain products in these reactions seems to indicate that radical processes are not involved in these systems. Thus the formation of biphenyl from the system triphenylsilylpotassium-bromobenzene cannot be due to the coupling of phenyl radicals, which under these conditions would be expected to cleave the ether solvent and form benzene.¹⁰ Although the mechanism of halogen-metal interconversion is not well understood, it is generally considered to involve association of the reagents through dipole interaction.¹¹ In the present study these dipoles are Si-K and C-X. Since silicon is electropositive to both carbon and halogen, it is probable that two dipolar complexes, I and II, may be formed, which would lead to coupling and halogen-metal interconversion, respectively.



Hence these two processes should be mutually independent, an observation which seems to be borne out by the experimental results.

The relative extents of the two reactions is probably governed to a large extent by the electronegativities of the radicals R_3Si and R_3C .¹¹ Evidently the radicals ClCH_2 -, Ph_3C -,³ and possibly C_6H_{11} -, are too weakly electronegative¹² to favor the formation of complex I, and hence the coupling reaction does not occur.

From these studies it is concluded that halogen-metal interconversion can occur as a major reaction path in the reaction of silylmetallics with organic halides. Since the halogen-metal exchange process fails to yield significant amounts of coupling product under the experimental conditions, the yields are lower than are obtained by treatment of the corresponding silyl halide with an organometallic reagent. Hence the latter method appears to be the preferred one, particularly since the halogen-metal interconversion process gives rise to a variety of products which frequently are difficult to separate.

Experimental¹³

The experiments carried out in this study are summarized in Tables I, II and III. All experiments listed in Tables I and III involved equimolar quantities of silylmetallic and halide (usually 0.038 mole of each) each in approximately equal volumes of ether added one to the other over a period of 0.5 to 2 hr. These runs usually were stirred from 16-24 hours, although frequently the reaction appeared to be complete on or shortly after addition was complete, as indicated by the absence of Color Test I.¹⁴ The yields reported in Tables I and III are frequently composites of a number of runs carried out under identical conditions but worked up differently to facilitate isolation of the different products. The following will serve as typical examples of the techniques used.

(10) W. A. Waters, "The Chemistry of Free Radicals," Oxford Press, Oxford, 1946, p. 146.

(11) R. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 341.

(12) M. S. Kharasch and A. L. Flenner, *THIS JOURNAL*, **54**, 674 (1932).

(13) All experiments involving organometallic reagents were carried out in a dry oxygen-free nitrogen atmosphere. Melting points are not corrected.

(14) H. Gilman and F. Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

Addition of Bromobenzene to Triphenylsilylpotassium.—To a suspension of 0.038 mole of amalgamated triphenylsilylpotassium¹⁵ in 150 ml. of ether was added over 40 minutes a solution of 6.0 g. (0.038 mole) of bromobenzene in 75 ml. of ether. The system changed from yellow-brown to red-brown and became slightly warm. Color Test I was positive immediately after addition was complete but was negative after 1 hr. of stirring. After 24 hr. of stirring, 50 ml. of water was added and the reaction mixture was worked up.

The aqueous phase together with the insoluble precipitate were separated from the orange-colored ether layer, which was dried over anhydrous sodium sulfate. The insoluble solid was separated from the aqueous phase; the solid was purified by refluxing with 100 ml. of benzene in which it was largely insoluble and yielded 2.33 g. (22%) of hexaphenyldisilane on filtration, m.p. 358-359°, identified by mixed melting point with an authentic specimen. From the benzene filtrate, on evaporation and then recrystallization, was obtained a total of 4.80 g. (36%) of tetraphenylsilane, m.p. 229-231°, and 0.40 g. (4%) of hexaphenyldisiloxane, m.p. 225-227°, both identified by mixed melting points with authentic samples.

The solvent was distilled from the dried ether layer. The distillate was carefully fractionated to remove the ether and the 2.20 ml. of liquid residue, n_D^{20} 1.3965, was treated at 0° with excess 1:1 sulfuric acid-fuming nitric acid. Dilution with water gave 0.58 g. of *m*-dinitrobenzene, m.p. 89-91° after recrystallization from ethanol, representing a 9% yield of benzene from the bromobenzene.

The solid residue remaining after removal of the solvent described above was recrystallized from benzene. An additional 1.6 g. (14%) of tetraphenylsilane (total recovery 50%), m.p. 228-231°, was obtained. The filtrate was concentrated and petroleum ether (b.p. 60-70°) was added; a total of 0.50 g. (5%) of triphenylsilanol, m.p. 152-154°, and a trace of crude tetraphenylsilane were obtained and identified by mixed melting points.

Addition of Triphenylsilylpotassium to Bromobenzene.—A stirred suspension of 0.030 mole of amalgamated triphenylsilylpotassium in 125 ml. of ether was added over 1 hr. to a solution of 4.7 g. (0.030 mole) of bromobenzene in 100 ml. of ether. The system turned purple and then brown; after 30 minutes additional stirring, Color Test I was negative.

The reaction mixture was filtered without hydrolyzing it. The insoluble material was recrystallized from benzene, in which it was completely soluble and yielded a total of 4.0 g. (41%) of tetraphenylsilane, m.p. 229-231°, and 0.50 g. (6%) of hexaphenyldisiloxane, m.p. 218-222°, both compounds identified by mixed melting points.

The volatile solvents were removed from the filtrate above, and refractionation gave a very small residue which failed to give a crystalline *m*-dinitrobenzene derivative on nitration but which gave a positive color test for *m*-dinitrobenzene using alcoholic alkali and butanone.¹⁶

Recrystallization from benzene of the solid residue remaining after removal of the solvent yielded an additional 2.13 g. (21%, total recovery 62%) of tetraphenylsilane, m.p. 229-232°, and 2.75 g. (28%, total recovery 34%) of hexaphenyldisiloxane, m.p. 222-224°, identified by mixed melting points with authentic specimens. Chromatography of the mother liquor on an alumina column, followed by elution with petroleum ether (b.p. 40-60°), yielded 0.18 g. (8%) of biphenyl, m.p. 66-68° after recrystallization from methanol, and 0.09 g. (1%) of triphenylsilanol, m.p. 151-152°, both identified by mixed melting point determinations with authentic specimens.

Addition of Two Moles of Triphenylsilylpotassium to One Mole of Bromobenzene.—A suspension of 0.04 mole of amalgamated triphenylsilylpotassium in 200 ml. of ether was prepared, and a 20-ml. aliquot was added to water. No hexaphenyldisilane was isolated indicating that cleavage of the hexaphenyldisilane used to prepare the triphenylsilylpotassium was complete. The remainder of the suspension was added over 1 hr. to a solution of 3.0 g. (0.019 mole) of bromobenzene in 125 ml. of ether; after 48 hr. of stirring the reaction mixture was hydrolyzed with water.

The reaction mixture was worked up essentially as described above to yield 0.97 g. (10.4%, based on moles of silylmetallic) of hexaphenyldisilane, m.p. 355-357°, identified by mixed melting point with an authentic specimen, and

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

(16) B. H. Dolin, *Anal. Chem.*, **15**, 242 (1943).

3.90 g. (61%) of tetraphenylsilane, m.p. 227–229°, identified by mixed melting point. The ether layer on evaporation to dryness was recrystallized from benzene to yield an additional 0.62 g. (9%, total yield 70%) of tetraphenylsilane, m.p. 225–228°, and a total of 2.25 g. (19%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point. The remaining mother liquor was chromatographed on an alumina column, using petroleum ether (b.p. 60–70°) and then benzene as eluents, and from the fractions collected were isolated a trace of tetraphenylsilane and 1.74 g. of an oil, b.p. 120–140° at 0.3 mm., which appeared to be a mixture of biphenyl and triphenylsilane. Recrystallization of the pot-residue yielded 0.15 g. of an unidentified compound, m.p. 174–175°, with the empirical formula $C_{30}H_{26}Si_2$.

Anal. Calcd. for $C_{30}H_{26}Si_2$: C, 81.4; H, 5.89. Found: C, 81.37, 81.51; H, 5.76, 5.90.

A second run gave a 10% yield of biphenyl, as well as the above products.

Addition of Triphenylsilylpotassium to Bromobenzene and Benzophenone.—To a solution of 6.8 g. (0.037 mole) of benzophenone and 5.8 g. (0.037 mole) of bromobenzene in 100 ml. of ether was added over a period of 1 hr. a suspension of 0.037 mole of amalgamated triphenylsilylpotassium in 150 ml. of ether. The reaction mixture became green during the addition, but after addition was complete slowly changed to olive-green to orange to deep red over a period of 0.5 hr. Although Color Test I was negative immediately after addition was complete, the mixture was stirred a total of 12 hr. and was then hydrolyzed with water.

The mixture was filtered to remove a large quantity of white solid. This 6.3 g. of material started to melt at 165°, became red at 180° and was completely liquid at 350°. When an attempt was made to recrystallize the material from benzene, the suspension turned red and most of the solid dissolved, but after filtration no solid products could be isolated from the solution, and evaporation left a viscous oil.

Similar material (4.81 g.) isolated from a second run was treated with 250 ml. of warm (50°) chloroform. After brief stirring, the suspension was filtered. The residue, 1.08 g. (22% of the weight of the original material), was found to be hexaphenyldisilane, m.p. 355–358°, identified by mixed melting point. To the chloroform solution was added 250 ml. of cold absolute ethanol. This treatment precipitated 1.07 g. of white crystals, melting from 165–200°, which turned red at 180°. This material contained 6.1% silicon. Concentration of the mother liquor under reduced pressure led to the isolation of 1.89 g. of crude hexaphenyldisiloxane, m.p. 221–227°. Recrystallization of this material from benzene gave 1.32 g. of pure hexaphenyldisiloxane, m.p. 226–228°, identified by mixed melting point. The mother liquor on evaporation yielded an oil from which no recognizable material could be obtained.

Attempted further purification of the partially purified 1.07 g. of material described above from chloroform failed to improve the wide melting point range. Evaporation of the solvents led to recovery of 0.15 g. of triphenylsilanol, m.p. 149–151°, identified by mixed melting point. Cleavage of 0.3 g. of the compound in a system made up of 0.5 g. of potassium hydroxide, 10 ml. of ethanol, 3 ml. of water and 10 ml. of ethylene glycol monomethyl ether, refluxed for 14 hr. yielded only 0.12 g. of crude triphenylsilanol, m.p. 125–133°, which after recrystallization from petroleum ether, b.p. 90–100°, melted at 150–152°. No other fragment could be isolated. Hence the structure of the insoluble material has not been established, other than that it appears to contain a triphenylsilyloxy group.

The filtrate removed from the original precipitate was dried over anhydrous sodium sulfate and was evaporated to dryness under reduced pressure, the distillate being collected in a Dry Ice trap. Redistillation of the trap contents yielded 0.47 g. (8%) of bromobenzene, n_D^{20} 1.559. The residue was recrystallized from carbon tetrachloride to give a total of 1.24 g. (10%) of tetraphenylsilane, m.p. 231–233°, identified by mixed melting point, then 4.22 g. of crystals, m.p. 138–145°, and then 2.10 g. (22%) of hexaphenyldisiloxane, m.p. 227–229°, and finally 0.45 g. (5%) of triphenylsilanol, m.p. 149–152°, all compounds being identified by mixed melting point determinations with authentic specimens after recrystallization. The residue remaining was distilled at 112–140° (0.1 mm.), to yield 2.1 g. (31%) of

benzophenone, m.p. 47–49°, identified by mixed melting point.

The original 4.22 g. of crystals failed to depress the melting points of either triphenylcarbinol or triphenylsilanol. A 2.55-g. sample was refluxed for 12 hr. with 50 ml. of 98% formic acid, and after drowning the reaction mixture, the recovered solids were recrystallized from benzene to yield 1.03 g. (10%) of hexaphenyldisiloxane, m.p. 227–229°, identified by mixed melting point. Removal of the benzene from the filtrate and recrystallization of the residue from ethanol yielded 1.25 g. (23%) of triphenylmethane, m.p. 89–90°, which did not depress the mixed melting point with authentic triphenylmethane. Hence the original 4.22 g. of crystals must have consisted of approximately 54% triphenylcarbinol and 44% triphenylsilanol; this useful separation of these compounds has been described before by Gilman and Wu,¹⁷ and the material isolated corresponds to yields of 23% of triphenylcarbinol and 10% of triphenylsilanol, based on the original reagents.

When a 1.67-g. aliquot of the original 4.22 g. of mixed products was twice recrystallized, there was isolated 0.71 g. (18%, based on bromobenzene) of triphenylcarbinol, m.p. 158–161°, identified by mixed melting point with an authentic sample, and by the fact that the material was completely soluble in concentrated sulfuric acid to give a yellow solution; triphenylsilanol is not readily soluble in concentrated sulfuric acid, and the system is colorless.

Reaction of Phenylpotassium with Diethyl Ether.—A solution of 0.056 mole of phenylpotassium¹⁸ in 220 ml. of benzene was standardized by carbonation of a 25-ml. aliquot with Dry Ice; the yield of benzoic acid was 0.80 g. The remainder of the solution was added to an equal volume (195 ml.) of ether and aliquots were withdrawn and carbonated at known intervals. The yields of benzoic acid obtained, compared to the above, and including correction for dilution were as follows: 1 min., 54%; 3 min., 34%; 6 min., 29%; 10 min., 25%. After stirring for several hours the reaction mixture was hydrolyzed and worked up. The products isolated were phenol (2%), as tribromophenol, m.p. 86–88°, ethanol (19%), as the α -naphthylurethan, m.p. 78–80°, and biphenyl (16%), m.p. 65–68°, all identified by mixed melting point determinations with authentic samples. No unsaturated gases were evolved from the system that could be derivatized by passage through traps containing bromine in carbon tetrachloride or aqueous cuprous ammonium chloride.

Attempted Preparation of Triphenylcyclohexylsilane.—Cyclohexylmagnesium bromide was prepared in 84% yield from 8.15 g. (0.05 mole) of cyclohexyl bromide and 1.3 g. (0.055 g. atom) of magnesium in 50 ml. of ether. To this 0.041 mole of Grignard reagent was added 12.1 g. (0.041 mole) of triphenylchlorosilane dissolved in 30 ml. of ether and 30 ml. of xylene. After 15 hr. of reflux no apparent change had occurred and the solution gave a strong Color Test I. Thirty ml. of xylene was added to the system, and the ether was distilled off until the temperature was 100°. During this process the system became pale gray. After 24 hr. of reflux Color Test I was negative, and the reaction mixture was cooled and hydrolyzed with water and acid. The non-aqueous layer was separated, dried over anhydrous sodium sulfate, and roughly fractionated, the fraction boiling from 40–100° being saved. After removal of this fraction, the remaining solvent was removed under reduced pressure. Petroleum ether (b.p. 60–70°) was added to the residue, which precipitated 5.29 g. (47%) of triphenylsilanol, m.p. 149–152°, identified by mixed melting point with an authentic specimen. Concentration of the mother liquor yielded an additional 0.40 g. (4%) of triphenylsilanol, m.p. 148–150°.

The residue was distilled at reduced pressure to yield a total of 4.67 g. (44%) of triphenylsilane, b.p. 135–160° (0.1 mm.), which solidified to melt at 43–45°. A mixed melting point with an authentic specimen was not depressed. The identity of this material was confirmed by treating its piperidine solution with aqueous 5% potassium hydroxide.¹⁹ Hydrogen was evolved and triphenylsilanol, m.p. 150–152°, was the only product isolated.

The ether distilled off during replacement of the reaction solvent with xylene was combined with the material boiling

(17) H. Gilman and T. C. Wu, *THIS JOURNAL*, **75**, 2509 (1953).

(18) V. Sabatier and V. Mailhe, *Compt. rend.*, **139**, 343 (1904).

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

40–100° obtained during the working up of the reaction mixture. This material was carefully fractionated to yield 1.10 g. of material boiling at 77–83°. The identity of this material as cyclohexene was confirmed by preparation of the 1-chloromercuri-2-methoxycyclohexane derivative.²⁰ The material isolated weighed 4.0 g. (corresponding to 22%)

(20) J. Romeyn and G. F. Wright, *THIS JOURNAL*, **69**, 697 (1947).

cyclohexene) and melted at 113–114°; the mixed melting point with an authentic specimen was not depressed.

Acknowledgment.—This research was sponsored by a grant from the National Research Council of Canada.

TORONTO, CANADA

[CONTRIBUTION NO. 747 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

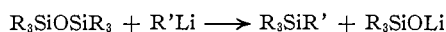
The Cleavage of *sym*-Diphenyldisiloxane by Organometallic Compounds

BY MACK C. HARVEY, WILLIAM H. NEBERGALL AND JOHN S. PEAKE

RECEIVED OCTOBER 8, 1956

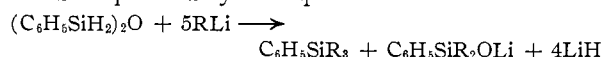
The cleavage of *sym*-diphenyldisiloxane by organolithium compounds, Grignard reagents and lithium aluminum hydride has been accomplished. With organolithium compounds the products are a tetrasubstituted silane and the lithium salt of a silanol. With Grignard reagents two reactions occur. The products from reaction I are an alkylphenylsilane and the halomagnesium salt of phenylsilanol, and from reaction II the products are phenylsilane and the halomagnesium salt of an alkylphenylsilanol. The latter reaction involves the alkylation of a silicon-hydrogen group and the reduction of the silicon-oxygen bond. *sym*-Diphenyldisiloxane is reduced by lithium aluminum hydride to phenylsilane.

It has been reported¹ that when a symmetrical hexasubstituted disiloxane is cleaved by an organolithium compound, one obtains as the products a tetrasubstituted silane and the lithium salt of a silanol.



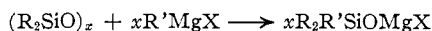
These authors likewise found that hexaphenyldisiloxane and hexa-*p*-tolylidisiloxane were cleaved by phenyllithium but not by methylolithium.

In the present investigation the cleavage of *sym*-diphenyldisiloxane by both phenyllithium and methylolithium was accomplished. Because an excess of these organolithium compounds was employed, the hydrogen atoms attached to silicon were replaced by alkyl groups, and the net reaction can be expressed by the equation

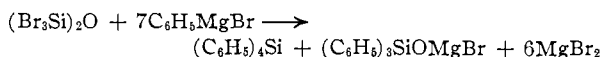


Subsequent hydrolysis of the lithium salt of the silanol gave triphenylsilanol when $R = C_6H_5$, and *sym*-tetramethyldiphenyldisiloxane, $[C_6H_5(CH_3)_2Si]_2O$, when $R = CH_3$.

Kipping and Hackford² found that Grignard reagents cleave cyclic siloxanes of the type $(R_2SiO)_x$, but not hexasubstituted disiloxanes



Similarly, Sauer³ found that dimethylsilicone, $[(CH_3)_2SiO]$, reacted with methylmagnesium iodide to form trimethylsilanol (after hydrolysis). Schumb and Saffer⁴ reported that no cleavage was observed in the reaction between hexachlorodisiloxane and phenylmagnesium bromide, but that when hexabromodisiloxane was treated in a similar manner, some cleavage of the silicon-oxygen bond resulted.



In the present work it was discovered that two reactions take place concurrently between Grignard reagents and *sym*-diphenyldisiloxane. One of these

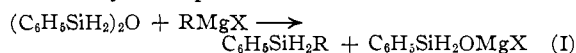
(1) H. Gilman, H. N. Benedict and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954).

(2) F. Kipping and J. Hackford, *J. Chem. Soc.*, **99**, 138 (1911).

(3) R. Sauer, *THIS JOURNAL*, **66**, 1707 (1944).

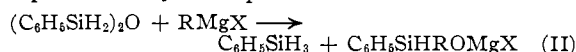
(4) W. Schumb and C. Saffer, *ibid.*, **61**, 363 (1939).

is the expected cleavage reaction, which is described by the equation

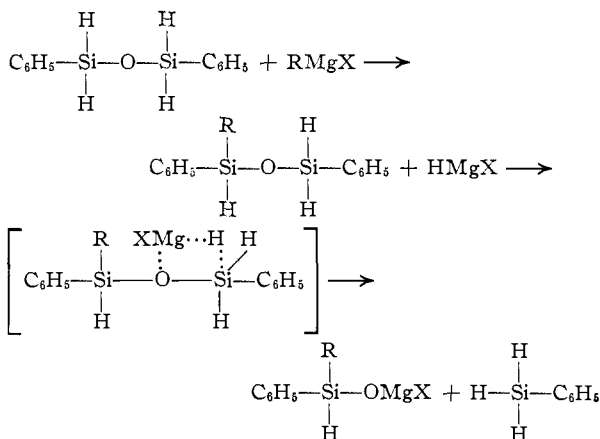


Hydrolysis of the magnesium salt should give rise to the original disiloxane. However it appears that one of the hydrogen atoms attached to silicon in the salt is hydrolyzed off, giving rise to high polymers of the type $(C_6H_5SiHO)_x$. In fact a considerable quantity of the trimer was isolated in an experiment in which phenylmagnesium bromide was the Grignard reagent employed.

The second reaction occurring between *sym*-diphenyldisiloxane and Grignard reagents may be represented by the equation



Hydrolysis converts the magnesium salt to the corresponding tetrasubstituted disiloxane, $(C_6H_5SiHR)_2O$. This reaction is the first reported example of the alkylation of the Si-H group by Grignard reagents. It may be that the alkylation step in this reaction results in the formation of halomagnesium hydride,⁵ $HMgX$, which then proceeds to reduce the Si-O bond, as indicated in the mechanism



(5) C. Miles, U. S. Patent 2,432,921, June 20, 1944; *C. A.*, **42**, 2278 (1948).