

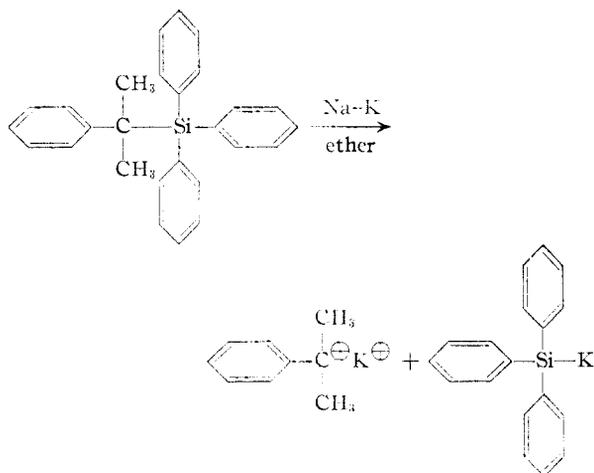
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

**The Preparation and Reactions of Triphenylsilylpotassium**BY ROBERT A. BENKESER AND ROLAND G. SEVERSON<sup>1</sup>

Triphenylsilylpotassium has been prepared by the cleavage of phenylisopropyltriphenylsilane with a sodium-potassium alloy (1:5) in ethyl ether. This compound couples with trimethylchlorosilane, triethylchlorosilane and bromobenzene to form 1,1,1-triphenyl-2,2,2-trimethyldisilane, 1,1,1-triphenyl-2,2,2-triethyldisilane and tetraphenylsilane, respectively. It reacts with hydrogen chloride to form triphenylsilane, and can be carbonated to form an unstable substance thought to be triphenylsilanecarboxylic acid. This latter material loses carbon monoxide readily to form triphenylsilanol. Further studies in this field are now in progress.

**Introduction.**—In 1933 Kraus and Eatough<sup>2</sup> reported the preparation of triphenylsilyllithium and triphenylsilylsodium. One year later triethylsilyllithium was made by Kraus and Nelson.<sup>3</sup> These classical experiments represent the only successful preparation of organometallics of silicon compounds. Of necessity these workers were restricted to small scale reactions since their procedure required the use of a high vacuum system along with starting materials that in some cases were expensive and difficult to make. Both from the standpoint of chemical theory, and because of their potential usefulness in the synthesis of new types of compounds, these silicon organometallics are of considerable importance. Several workers<sup>4</sup> have reported unsuccessful attempts to prepare these reactive silicon intermediates by methods which normally produce organometallics with carbon compounds.

At this time we are reporting the preparation of triphenylsilylpotassium<sup>5</sup> by the cleavage of phenylisopropyltriphenylsilane with sodium-potassium alloy in ethyl ether<sup>6</sup>:



(1) A portion of this paper is abstracted from the doctoral dissertation of Roland G. Severson, Purdue University, 1951.

(2) C. A. Kraus and H. Eatough, *THIS JOURNAL*, **55**, 5008 (1933).

(3) C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934).

(4) (a) C. Eaborn, *J. Chem. Soc.*, 2755 (1949); (b) H. Gilman and S. P. Massie, Jr., *THIS JOURNAL*, **68**, 1128 (1946); (c) R. N. Meals, *ibid.*, **68**, 1880 (1946).

(5) It is entirely possible that this substance is contaminated with some triphenylsilylsodium. However, it has been shown that sodium-potassium alloy cleavages of this type generally result in almost exclusive formation of the potassium compound. See H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 319 (1936). For this reason we refer to the compound as triphenylsilylpotassium.

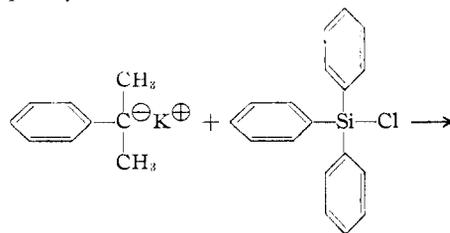
(6) We are not ready to say that this cleavage leads to the exclusive formation of triphenylsilylpotassium. However, based upon the yield of triphenylsilane obtained upon hydrolysis, it would seem that at least a 50% yield of this cleavage product is realized.

The size of our runs are limited only by the availability of the starting material, since the apparatus used is no more elaborate than that commonly employed in a Grignard or organolithium preparation.

**Discussion.**—It seemed that the most promising approach to the problem of preparing an organometallic of a silicon compound (wherein the metal is bonded to silicon) would consist in cleaving an organosilane with a reagent that would leave a metal atom attached to the silicon. A cleaving agent like *n*-butyllithium is not successful in accomplishing this, since the final product in these cleavages usually has the butyl radical attached to the silicon.<sup>7</sup> On the other hand sodium-potassium alloy seemed ideally suited for this purpose since it is very reactive and has been successfully used in similar cases.<sup>8</sup> It also seemed desirable to attempt a cleavage of a silicon-carbon bond rather than of a silicon-germanium or silicon-tin bond, since compounds with these groupings are usually difficult and expensive to prepare in quantity.

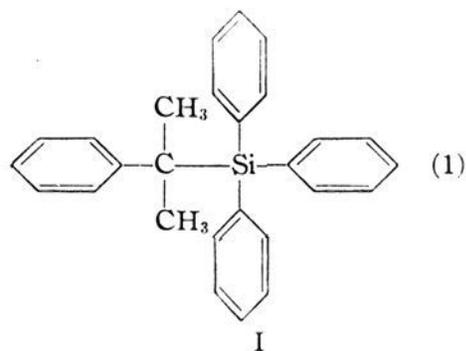
From theoretical considerations, for a molecule to undergo ready cleavage at a central silicon-carbon bond it should possess two characteristics: (1) the silicon-carbon bond must be weakened by the steric interference of bulky groups attached to both the silicon and carbon atom, (2) the fragments formed after cleavage should possess structures that will allow resonance stabilization. This latter consideration seemed more important in the case of the carbon fragment, since the contribution of the resonance forms in the silicon portion appeared questionable. The compound which seemed to fulfill both of these requirements was phenylisopropyltriphenylsilane (see Fig. 1).

**Experimental.**—The phenylisopropyltriphenylsilane used in these reactions was prepared by the coupling of phenylisopropylpotassium with triphenylchlorosilane

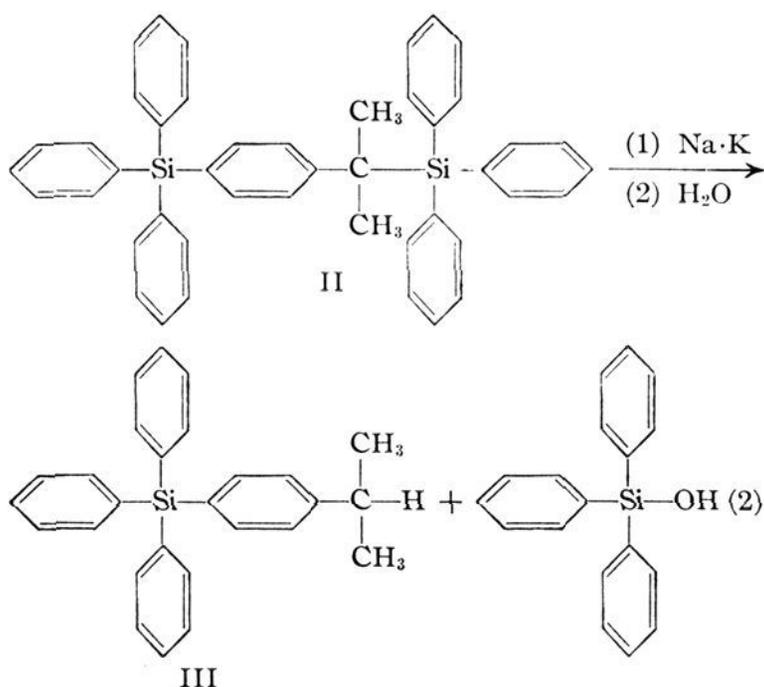


(7) H. Gilman, R. A. Benkeser and G. E. Dunn, *THIS JOURNAL*, **72**, 1689 (1950).

(8) J. B. Conant and B. S. Garvey, Jr., *ibid.*, **49**, 2599 (1927).



This reaction is complicated by the formation of a white crystalline by-product which melts at 221–222° and has a molecular weight between 600–700. This material has been identified as  $\alpha,p$ -bis-(triphenylsilyl)-cumene (II) since it can be cleaved with sodium–potassium alloy to form triphenylsilanol and triphenyl-(*p*-isopropylphenyl)-silane (III) upon subsequent hydrolysis. Compound



III was identified by a mixed melting point with an authentic sample prepared by treating triphenylchlorosilane with *p*-isopropylphenyllithium. The origin of compound II has not been ascertained, but it might be conjectured that it arises from a metalation of phenylisopropyltriphenylsilane (I) by unreacted phenylisopropylpotassium followed by coupling of the metalated product with triphenylchlorosilane. It seems reasonable that if

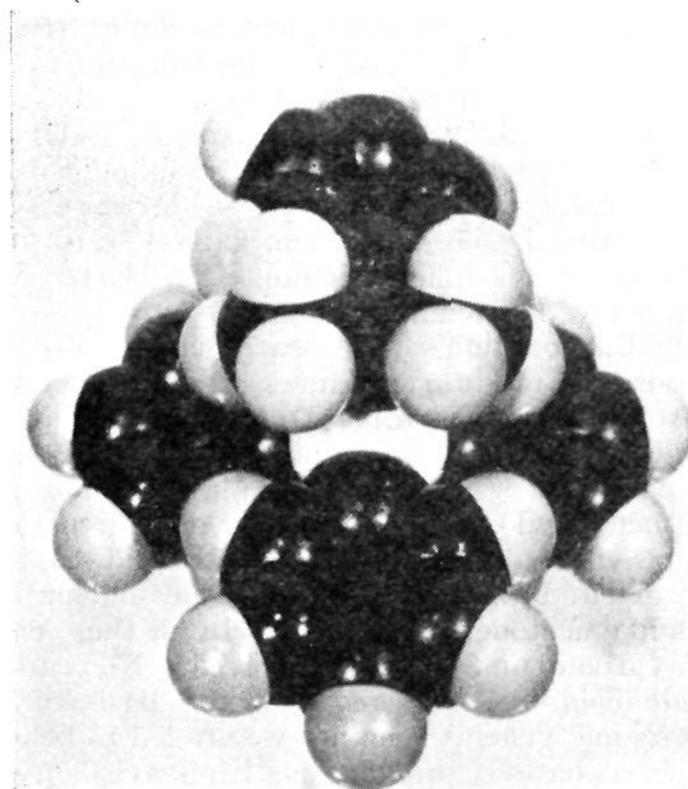
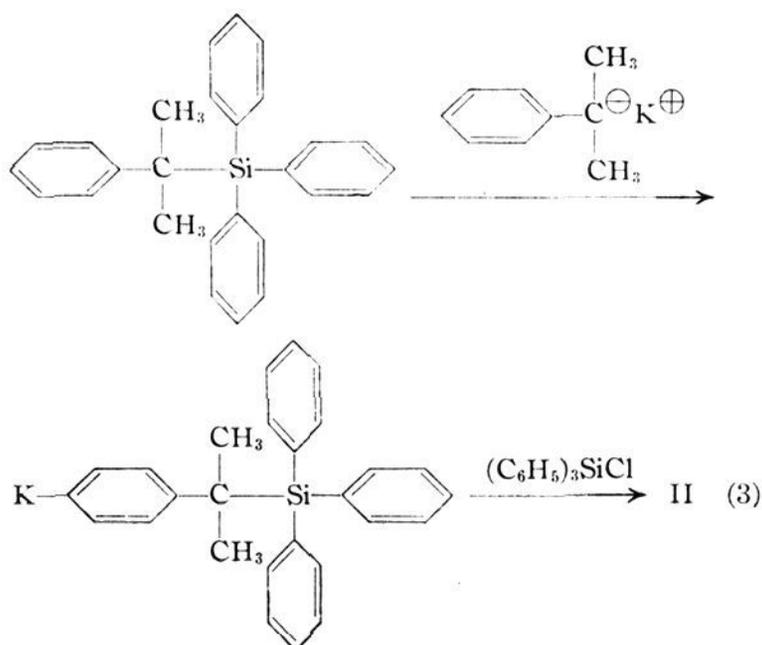
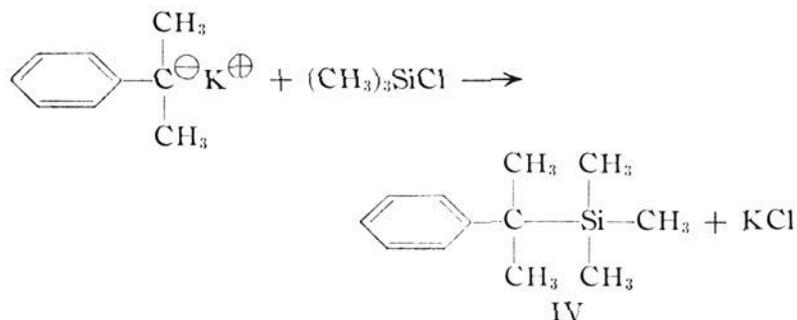


Fig. 1.—Phenylisopropyltriphenylsilane.

Reaction 3 does occur it would seriously compete with Reaction 1, since it is not hampered by the steric factors which tend to inhibit the latter.

Phenylisopropyltrimethylsilane (IV) was also prepared by the reaction of phenylisopropylpotassium with trimethylchlorosilane. It is in-



teresting that this compound did not undergo any appreciable cleavage with sodium–potassium alloy under the conditions employed. A possible explanation for the failure of this compound to react may be the lack of resonance stabilization in the trimethylsilyl fragment compared with the triphenylsilyl group. This hypothesis is now under investigation.

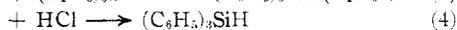
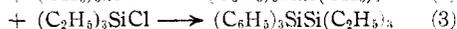
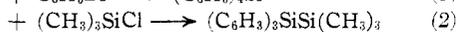
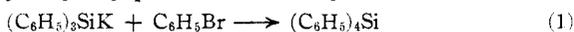
**Reactions of Triphenylsilylpotassium.**—The following reactions were carried out with triphenylsilylpotassium in order to establish its identity as well as to investigate its chemical properties.

(a) **With Hydrogen Chloride.**—It was found that the ordinary methods of hydrolysis which employ either acid, alcohol or water must be used with caution on triphenylsilylpotassium because of the unreacted alloy which usually remains in the cleavage mixture. Also these methods result in the formation of triphenylsilanol rather than triphenylsilane probably as the result of the quantitative conversion of the silane by the basic hydrolysate. However, it is possible to destroy the excess alloy and the organometallics present without violence by the introduction of hydrogen chloride diluted with dry, oxygen-free nitrogen. Triphenylsilane is formed as the product of this reaction.

(b) **Coupling.**—Trimethylchlorosilane, triethylchlorosilane and bromobenzene were all found to couple with triphenylsilyl potassium to form 1,1,1-triphenyl-2,2,2-trimethyldisilane, 1,1,1-triphenyl-2,2,2-triethylidisilane and tetraphenylsilane, respectively. The unsymmetrical disilanes were characterized by cleaving them with base to form hydrogen and triphenylsilanol. The latter was identified by a mixed m.p.

(c) **Carbonation.**—The carbonation of triphenylsilyl potassium produces a white crystalline solid, which is stable at room temperature, but, when heated, decomposes to form carbon monoxide and a mixture of triphenylsilanol and hexaphenyldisiloxane. This decomposition can also be effected by treatment with acid, and to some extent by merely dissolving the solid in solvents like acetone and ethanol. In all these cases only carbon monoxide is evolved. No carbon dioxide could be detected. On the basis of its analysis and general behavior we are led to believe this carbonation product is triphenylsilane-carboxylic acid. Further investigation of the structure and reactions of this interesting compound is now under way.

**Results.**—The equations summarize our findings on some of the chemical reactions of triphenylsilyl potassium in ethyl ether



It is of interest that reactions 2 and 3 above represent the only feasible way of preparing unsymmetrical disilanes at the present time.

### Experimental

The following reactions were all carried out under dry oxygen-free nitrogen, in ether which had been previously dried with *n*-butylmagnesium bromide or phenylmagnesium bromide. The ether was distilled directly from the Grignard mixture to the reaction flask without allowing it to come in contact with the atmosphere.

**Phenylisopropyltriphenylsilane and  $\alpha,\beta$ -Bis-(triphenylsilyl)-cumene.**—To 13.8 g. (0.047 mole) of triphenylchlorosilane<sup>9</sup> in 150 ml. of anhydrous ether was added 940 ml. of an ether solution containing 0.047 mole of phenylisopropylpotassium.<sup>10,11</sup> This mixture was stirred vigorously at room temperature for 20 hours. The reaction mixture, which was still red at the end of this time, was hydrolyzed by the addition of water. The colorless ether layer was removed, washed with water and dried over anhydrous sodium sulfate. This solution was combined with a similar solution obtained from the reaction of 13.5 g. (0.046 mole) of triphenylchlorosilane and 860 ml. of an ether solution containing 0.046 mole of phenylisopropylpotassium. The ether was removed by distillation and the residue was distilled giving, after some fore-run, 18.4 g. of colorless oil, b.p. 205–240° at 1 mm., and 10.4 g. of a glassy pot residue. The oil, which solidifies on stirring with a small amount of ethanol, was crystallized twice from 95% ethanol giving 10.5 g. (30%) of white crystals, m.p. 119–120°.

*Anal.* Calcd. for  $C_{27}H_{26}Si$ : Si, 7.41. Found: Si, 7.36, 7.60.

(9) Purchased from the Dow Corning Company, Midland, Michigan.

(10) K. Ziegler and B. Schnell, *Ann.*, **487**, 227 (1924).

(11) The titer of this solution can be determined either by a differential titration (H. Gilman and A. H. Haubein, *THIS JOURNAL*, **66**, 1515 (1944)) or by weighing the phenyldimethylacetic acid obtained by carbonation.

The pot residue from the distillation was crystallized twice from a mixture of xylene and petroleum ether (b.p. 90–100°) giving 4.3 g. (14.5%) of white crystals, m.p. 221–222°. This material was later identified as  $\alpha,\beta$ -bis-(triphenylsilyl)-cumene.

*Anal.* Calcd. for  $C_{45}H_{40}Si_2$ : Si, 8.81; mol. wt., 637. Found: Si, 8.74, 8.73; mol. wt. (Rast), 680.

**Cleavage of  $\alpha,\beta$ -Bis-(triphenylsilyl)-cumene.**—To 350 ml. of anhydrous ether was added 3 ml. of sodium-potassium alloy (1:5) and 6.3 g. (0.0099 mole) of  $\alpha,\beta$ -bis-(triphenylsilyl)-cumene. This mixture was stirred vigorously at reflux temperature for 20 hours and at room temperature for 25 hours. During this time the mixture became red and a dark precipitate appeared. Hydrolysis was effected by the careful addition of water. The clear, colorless ether layer was removed, washed with water and dried over sodium sulfate. Removal of the ether by distillation left a residue which partially crystallized on cooling. This material was dissolved in 95% ethanol and, after allowing a small amount of oil to deposit, 1.25 g. (33%) of a white solid, m.p. 110–115°, was obtained. Two additional crystallizations from 95% ethanol gave 0.68 g. (18%) of white crystals, m.p. 120–121°. This material was shown to be triphenyl-(*p*-isopropylphenyl)-silane by a mixed melting point with an authentic sample.

*Anal.* Calcd. for  $C_{27}H_{26}Si$ : Si, 7.41. Found: Si, 7.72.

The alcohol solutions from these crystallizations were distilled under reduced pressure to remove the solvent. The residue was crystallized from petroleum ether (b.p. 90–100°) giving 1.8 g. (66%) of material, melting at 148–150°. An additional crystallization from petroleum ether gave 0.98 g. (36%) of triphenylsilanol (mixed m.p.), m.p. 151–152°.

**Triphenyl-(*p*-isopropylphenyl)-silane.**—*p*-Isopropylphenyllithium was prepared from 12.9 g. (0.065 mole) of *p*-bromocumene<sup>12</sup> and 1 g. (0.14 g. atom) of lithium in 200 ml. of ether. To the resulting mixture was added 12 g. (0.041 mole) of triphenylchlorosilane in ether. When the spontaneous reflux had stopped, the mixture was refluxed 4 hours, cooled and hydrolyzed with dilute hydrochloric acid. The ether layer was removed, washed with water and dried over sodium sulfate. The ether was removed by distillation and the residue was crystallized from 95% ethanol, giving 11.9 g. (77%) of white crystals, m.p. 117–121°. Recrystallization from petroleum ether (b.p. 90–100°) gave 8.8 g. (57%) of white crystals, m.p. 120–121°. This material showed a depressed mixed melting point with phenylisopropyltriphenylsilane but no depression when mixed with material obtained from the cleavage of  $\alpha,\beta$ -bis-(triphenylsilyl)-cumene.

*Anal.* Calcd. for  $C_{27}H_{26}Si$ : Si, 7.41. Found: Si, 7.63.

**Phenylisopropyltrimethylsilane.**—To 12 g. (0.11 mole) of trimethylchlorosilane in 150 ml. of anhydrous ether was added 414 ml. of a phenylisopropylpotassium solution. Stirring was continued for one hour after completion of the addition and the colorless mixture was then hydrolyzed by the addition of water. The ether layer was removed, washed with water and dried over sodium sulfate. After removal of the ether by distillation, the residue was distilled at atmospheric pressure giving 5.34 g. (80% based on a saturated solution of phenylisopropylpotassium) of colorless liquid, b.p. 220–221°. The following constants were determined:  $n_D^{20}$  1.5059;  $d_4^{20}$  0.8906;  $M_{RD}$  calcd., 63.93;  $M_{RD}$  found, 64.14.

*Anal.* Calcd. for  $C_{12}H_{20}Si$ : Si, 14.59. Found: Si, 14.59.

**Attempted Cleavage of Phenylisopropyltrimethylsilane.**—To 200 ml. of anhydrous ether was added 3 ml. of sodium-potassium alloy (1:5) and 3.8 g. (0.02 mole) of phenylisopropyltrimethylsilane. This mixture was stirred vigorously for 30 hours at room temperature, in addition to 20 hours at reflux temperature. At the end of this time no color had developed, indicating that little or no cleavage had occurred.

**1,1,1-Triphenyl-2,2,2-trimethyldisilane.**—To 300 ml. of anhydrous ether was added 2 ml. of sodium-potassium alloy (1:5) and 4 g. (0.011 mole) of phenylisopropyltriphenylsilane. This mixture was stirred vigorously for 4 hours at

(12) G. F. Hennion and V. R. Pieronek, *ibid.*, **64**, 2751 (1942). See also J. W. Copenhaver, M. F. Roy and C. S. Marvel, *ibid.*, **57**, 1311 (1935).

room temperature. At the end of this time the solution appeared dark red in color and contained a suspended black precipitate. To this mixture was added a solution of 3 g. (0.028 mole) of trimethylchlorosilane in 25 ml. of anhydrous ether. During the first part of the addition the red color disappeared, leaving a black precipitate which decolorized on completion of the addition. This left a white solid suspended in a colorless ether layer. The latter was carefully decanted from the excess alloy. Water was added and the ether layer was removed, washed with water and dried over anhydrous sodium sulfate. Removal of the ether by distillation left an oil which was partially distilled at atmospheric pressure, giving 0.6 g. (30%) of phenylisopropyl-trimethylsilane, b.p. 215–225°,  $n_D^{20}$  1.5057. The residue from this distillation solidified on cooling to room temperature. It was recrystallized from a mixture of methanol and ethanol giving 1.78 g. (51%) of white crystals, m.p. 101–103°. An additional recrystallization from 95% ethanol gave 1.1 g. (31%) of white crystals, m.p. 103–104°.

*Anal.* Calcd. for  $C_{21}H_{24}Si_2$ : Si, 16.88. Found: Si, 16.47.

A small sample of this material was warmed in alcoholic sodium hydroxide until the evolution of hydrogen had ceased. The resulting solution was neutralized with dilute hydrochloric acid and then diluted with water. This caused precipitation of a white solid which was collected, washed with water and dried. This material, m.p. 148–150°, showed no depression in a mixed melting point with authentic triphenylsilanol.

**1,1,1-Triphenyl-2,2,2-triethylsilane.**—To 300 ml. of anhydrous ether was added 2 ml. of sodium-potassium alloy (1:5) and 3 g. (0.008 mole) of phenylisopropyltriphenylsilane. This mixture was stirred vigorously for 9 hours at room temperature. To the resulting black mixture was added 3 g. (0.02 mole) of triethylchlorosilane dissolved in 15 ml. of anhydrous ether. The mixture which was colorless when the addition was complete, was carefully decanted away from the excess alloy. Water was added and the colorless ether layer was removed, washed with water, and dried over anhydrous sodium sulfate. Removal of the ether left an oil which resisted attempts at crystallization. This oil was distilled at 1 mm. and 1.83 g. of material, b.p. 200–205°, was collected. Recrystallization from a pentane-ethanol mixture at Dry Ice temperatures gave 1.1 g. (37%) of white crystals. Two additional crystallizations from 95% ethanol gave 0.8 g. (27%) of white crystals, m.p. 92.5–93.5°.

*Anal.* Calcd. for  $C_{24}H_{30}Si_2$ : Si, 14.98. Found: Si, 14.88.

A small sample of this material was treated with alcoholic sodium hydroxide and boiled for 20 minutes. This mixture was cooled, neutralized with dilute hydrochloric acid and diluted with water. This gave a white solid which, on crystallization from petroleum ether (90–100°), gave triphenylsilanol (mixed melting point), m.p. 149–150°.

**Tetraphenylsilane.**—To 300 ml. of anhydrous ether was added 2 ml. of sodium-potassium alloy (1:5) and 3 g. (0.008 mole) of triphenyl-(phenylisopropyl)-silane. This mixture was stirred vigorously at room temperature for 7 hours and then 3.5 g. (0.022 mole) of bromobenzene in 15 ml. of anhydrous ether was added to the nearly black reaction mixture. After 5 minutes the mixture was a light brown in color. Water was added carefully, giving two colorless layers with a white solid which remained suspended in the ether layer. This ether layer was removed and washed with water. The resulting ether layer, still

containing this suspended solid, was distilled to remove the ether. Pentane was added to the residue. Filtration gave 1.9 g. of white solid which on crystallization from xylene gave 1.04 g. (39%) of white crystals, m.p. 226–229°. An additional crystallization from xylene gave 0.93 g. of needles, m.p. 228–230°. A mixed melting point of this material with tetraphenylsilane showed no depression.

**Triphenylsilane.**—To 300 ml. of anhydrous ether was added 2.5 ml. of sodium-potassium alloy (1:5) and 7.6 g. (0.02 mole) of phenylisopropyltriphenylsilane. This mixture was vigorously stirred at room temperature for 12 hours. Anhydrous hydrogen chloride, diluted with dry, oxygen-free nitrogen, was then passed over the surface of the stirred mixture until the color and the excess alloy no longer remained. Dilute hydrochloric acid was then added and the ether layer was removed, washed with water and dried over sodium sulfate. The ether was removed by distillation and the residue was distilled at 1.5 mm. with 3.73 g. (72%) of material, b.p. 153–163°, being collected. This material solidified on standing. Recrystallization from 95% ethanol gave 1.56 g. (30%) of white crystals, m.p. 43–44°, and 0.93 g. (18%), m.p. 40–43°. This material was identified as triphenylsilane by a mixed melting point with an authentic sample.

**Triphenylsilanecarboxylic Acid.**—To 300 ml. of anhydrous ether was added 5 g. (0.013 mole) of phenylisopropyltriphenylsilane and 2 ml. of sodium-potassium alloy (1:5). This mixture was stirred vigorously for 12 hours at room temperature and was then poured under nitrogen into a Dry Ice-ether slurry. As much of the excess metal as possible was left in the reaction flask during this operation. When the carbonated mixture had warmed to room temperature, it was washed with two 40-ml. portions of water. The basic aqueous extract was filtered and then acidified with hydrochloric acid. Filtration gave 1.4 g. (65%) of phenyl-dimethylacetic acid, m.p. 74–76°. The ether solution was dried over anhydrous sodium sulfate and was then allowed to evaporate. This gave a white solid residue which was washed with petroleum ether, giving 2.4 g. of material which evolved carbon monoxide<sup>13</sup> at about 135°. No carbon dioxide could be detected. When a sample of this material was added to acetone or ethanol, carbon monoxide<sup>13</sup> was again given off. No gas was evolved when the material was added to petroleum ether or benzene. This material contained 9.73% of silicon. A sample in acetone was treated with two drops of dilute hydrochloric acid to complete its decomposition. After filtration, water was added and the white precipitate was collected, dried, and washed with petroleum ether. The product, melting at 149–150°, was shown to be triphenylsilanol by a mixed melting point with an authentic sample. After several attempts it was possible to obtain from a mixture of petroleum ether and acetone a white crystalline sample of the material which decomposed at 169° with the evolution of carbon monoxide.

*Anal.* Calcd. for  $C_{19}H_{18}O_2Si$ : C, 75.0; H, 5.30; Si, 9.22. Found: C, 75.5; H, 5.47; Si, 9.29.

**Acknowledgment.**—The authors are deeply grateful to the Research Corporation whose financial assistance made this research possible.

LAFAYETTE, INDIANA

RECEIVED AUGUST 21, 1950

(13) The carbon monoxide was detected by a Mine Safety Appliances Carbon Monoxide Tester, No. D.S.-47133, Mine Safety Appliances Co., Pittsburgh, Pa.