an 80% yield of 4-chloro-3-trifluoromethylanisole, b.p. 113° at 39 mm.

4-Chloro-3-trifluoromethylphenoxyacetic Acid.—A mixture of 3.93 g. of 4-chloro-3-trifluoromethylphenol and 3.78 g. of chloroacetic acid was dissolved in a solution of 2.4 g. of sodium hydroxide in 25 ml. of water. This was heated eight hours on a steam-bath, acidified with dilute hydrochloric acid and extracted with ether. The ether extract was then extracted with sodium bicarbonate solution and the bicarbonate solution acidified; yield 3.05 g., m.p. 133–134.5° from benzene.

2-Chloro-5-trifluoromethylphenol.—This phenol, its intermediates and derivatives listed in Table II were made in a similar fashion.

2,6-Dichloro-3-trifluoromethylphenol.—The chlorination of 2-chloro-5-trifluoromethylphenol did not occur at an appreciable rate in carbon tetrachloride at room temperature. To a suspension of 6.3 g. of 2-chloro-5-trifluoromethylphenol in 250 ml. of concentrated hydrochloric acid was added a solution of 1.35 g. of potassium chlorate in 25 ml. of water. Shaking the stoppered flask vigorously seemed to result in complete absorption of the chlorine formed. After 15 minutes the reaction mixture was diluted with two parts of water and extracted with ether. Distillation of the ether extract gave a small fraction, b.p. 85–98° at 20 mm., and about 4 g., b.p. 98–110° at 20 mm. A small amount of Skellysolve A was added to the higher boiling fraction and extensive cooling with a Dry Ice–methylene chloride-bath was resorted to. The solid which precipitated amounted to 2.1 g., m.p. 53–54°. Hydrolysis of this phenol with concentrated sulfuric acid gave 2,4-dichloro-3-hydroxybenzoic acid whose properties are indicated in Table II. Methylation of this phenol in the ordinary way with dimethyl sulfate gave 2,4-dichloro-3-methoxybenzoic acid,[3] m.p. 162–163°.

2,4-Dichloro-3-trifluoromethylphenol.—A solution of 20 g. of 4-chloro-3-trifluoromethylphenol in 250 cc. of carbon tetrachloride was prepared and chlorine was bubbled through the solution for three hours at room temperature. The chlorine saturated solution was allowed to stand three hours more and was then distilled under reduced pressure. There resulted 21.5 g. of product, b.p. 119–121° at 34 mm., n^{25}D 1.5094. This oil was chilled till it crystallized and then filtered cold. The resultant crystals were recrystallized from Skellysolve A to give 10 g. of large well-shaped crystals, m.p. 33–34°, n^{25}D 1.5105. From the uncrystallized portion of the product a nitrobenzyl ether, m.p. 176.5–178°, of more 2,4-dichloro-3-trifluoromethylphenol was prepared. The oil was evidently contaminated with the isomeric compound preventing further crystallization.

Chlorination of 3-Trifluoromethylphenol.—Chlorine gas was passed into a solution of 210 g. of 3-trifluoromethylphenol in 400 cc. of carbon tetrachloride quite rapidly until an excess of gas had been added. The reaction mixture was allowed to stand a few hours then distilled under reduced pressure. There resulted 256 g. of crude product, b.p. 97–130° at 29 mm. This was carefully fractionated and a 140-g. cut, b.p. 114–116° at 29 mm., taken. On standing, more than one-half of this crystallized in large crystals m.p. 54° from Skellysolve A. This was identical with the 2,6-dichloro-3-trifluoromethylphenol described above.

The uncrystallized portion was converted to a *p*-nitrobenzyl ether and a small amount of 2,4-dichloro-3-trifluoromethylphenyl-4′-nitrobenzyl ether, m.p. 176–177°, resulted.

In a similar fashion, 3-trifluoromethylphenol was treated with only one mole of chlorine. The reaction was not clean cut since some dichlorinated material and some unchlorinated material resulted; a cut boiling at 70–72° at 13 mm., n^{25}D 1.4770 was taken. This fraction analyzed well for monochloro-3-trifluoromethylphenol (Cl, calcd. 18.04; found 17.89%) but was evidently a mixture of two isomers. Hydrolysis with sulfuric acid gave 4-chloro-3-hydroxybenzoic acid,[8] m.p. 220° and another material, m.p. 153–157° which resisted further purification. This is undoubtedly 2-chloro-3-hydroxybenzoic acid,[9] m.p. 157–158°. This mixture was treated with sodium hydroxide and chloroacetic acid and a clean-cut product, m.p. 135–136°, resulted (*Anal.* Calcd.: C, 42.45; H, 2.36. Found: C, 42.71; H, 2.56). However a mixed melting point with 4-chloro-3-trifluoromethylphenoxyacetic acid showed a sharp depression (m.p. 108–112°), and neither was it identical with 2-chloro-5-trifluoromethylphenoxyacetic acid, m.p. 105–106°. Hence this derivative must be 2-chloro-3-trifluoromethylphenoxyacetic acid.

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(8) P. H. Beyer, *Rec. trav. chim.*, **40**, 621 (1921).

(9) G. Mazzara and V. Bertozzi, *Gazz. chim. ital.*, **30**, II, 84 (1900).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Reactions of Some Triarylsilanes with Methyllithium and Phenylisopropylpotassium

BY ROBERT A. BENKESER AND FRANK J. RIEL

The reaction of tri-*p*-chlorophenylsilane, tris-(*p*-trifluoromethylphenyl)-silane, tri-*p*-tolylsilane and tri-*p*-anisylsilane, with methyllithium was investigated. In all cases the corresponding triarylmethylsilane was formed. Tri-*o*-tolylsilane reacts with phenylisopropylpotassium in a manner similar to tri-*o*-tolylmethane in that all three methyl groups are metalated. When the metalated product is carbonated, a silane tricarboxylic acid is formed. The acid can be esterified to form a triethyl ester. Treatment of the metalated product with methyl iodide forms tri-*o*-ethylphenylsilane. When tri-*p*-tolylsilane and triphenylsilane are treated with phenylisopropylpotassium, disproportionation occurs with the formation of tetra-*p*-tolylsilane and tetraphenylsilane, respectively. On the other hand tri-*p*-tolylmethylsilane reacts with phenylisopropylpotassium to form tri-*p*-ethylphenylmethylsilane upon treatment of the metalated product with methyl iodide.

In attempting the preparation of a compound containing a silicon–metal bond, Gilman[1] and Meals[2] independently discovered that triethylsilane will react with methyl- or *n*-butyllithium according to the equation

$$\mathrm{Et_3SiH + R'Li \longrightarrow Et_3SiR' + LiH}$$

This reaction was later extended by Gilman[3] to triphenylsilane and various other organolithium compounds.

The formation of lithium hydride in this reaction indicates that the silicon–hydrogen bond is broken with the elimination of a hydride ion.[4] This suggests that if electron attracting groups were attached to the silicon atom the electron pair making up the silicon–hydrogen bond might be sufficiently displaced toward the silicon atom that the hydride ion would no longer be formed in this reaction. To investigate this hypothesis the reactions of tri-*p*-chlorophenylsilane and tris-(*p*-trifluoromethylphenyl)-silane with methyllithium were studied. For the purpose of comparison, the reactions of tri-*p*-tolylsilane, and tri-*p*-anisylsilane with methyllithium were also investigated. All of the para substituted silanes reacted with methyl-

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(1) H. Gilman and S. P. Massie, THIS JOURNAL, **68**, 1128 (1946).

(2) R. N. Meals, *ibid.*, **68**, 1880 (1946).

(3) H. Gilman and H. W. Melvin, Jr., *ibid.*, **71**, 4050 (1949).

(4) F. P. Price, *ibid.*, **69**, 2600 (1947).

lithium to produce the corresponding triarylmethylsilanes in comparable yields. Apparently the electronic effect of a single substituent in the benzene ring is not sufficient to alter the course of this reaction. Table I gives the physical constants and other pertinent data with regard to these starting silanes. Table II lists the triarylmethylsilanes obtained in the reaction with methyllithium.

TABLE I

TRIARYLSILANES (R_3SiH)

R	M.p.,[a] °C.	Crystallization solvent	Yield, %	Anal., Calcd.	% Si Found
p-$\mathrm{CH_3C_6H_4}$–	82.5–83.5	95% ethanol + methanol	37	9.27	9.10
p-$\mathrm{CH_3OC_6H_4}$–	75.5–76	95% ethanol + methanol	40	8.01	7.95
p-$\mathrm{ClC_6H_4}$–	80–81	95% ethanol	51	7.74	7.65
p-$\mathrm{CF_3C_6H_4}$–	82–83	95% ethanol	38	6.03	6.13

[a] All melting points are corrected.

TABLE II

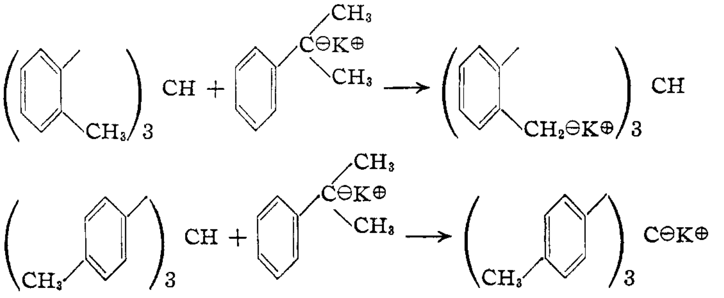
TRIARYLMETHYLSILANES (R_3SiCH_3)

R	M.p.,[a] °C.	Crystallization solvent	Yield, %	Anal., Calcd.	% Si Found
p-$\mathrm{CH_3C_6H_4}$–	91–93	95% ethanol	61	8.86	8.60
p-$\mathrm{CH_3OC_6H_4}$–	133–134.5	95% ethanol	47	7.69	7.68
p-$\mathrm{ClC_6H_4}$–	83–85	95% ethanol	58	7.43	7.21
p-$\mathrm{CF_3C_6H_4}$–	106–107.5	95% ethanol	64	5.85	5.75

[a] All melting points are corrected.

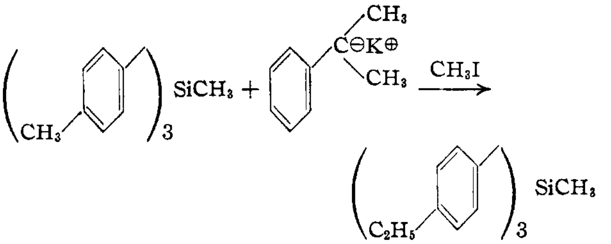
In order to test the effect of a more vigorous metalating agent the reaction between phenylisopropylpotassium and tri-*o*-tolyl- and tri-*p*-tolylsilane was investigated.

This approach offered an interesting comparison with carbon chemistry since Bartlett and Jones[5] previously observed that tri-*o*-tolylmethane reacts with phenylisopropylpotassium to form a product which after carbonation was identified as triphenylmethane-2,2′,2″-triacetic acid. On the other hand a similar reaction with tri-*p*-tolylmethane gave tri-*p*-tolylacetic acid.



Thus in the case of the ortho isomer metalation occurs in the side chain while with the para compound it occurs on the central carbon atom. If the same relationship would hold true with the corresponding silicon compounds one might expect that a silicon organometallic would form if tri-*p*-tolylsilane were treated with phenylisopropylpotassium.

Actually it was found that tri-*o*-tolylsilane reacts like tri-*o*-tolylmethane with metalation occurring on the three methyl groups. This was shown by coupling the metalated product with methyl iodide to form tri-*o*-ethylphenylsilane (mixed m.p.). The metalated product can also be carbonated to form an impure acid which is probably triphenylsilane-2,2′,2″-triacetic acid. This acid can be esterified with ethanol to form a pure triethyl ester. Tri-*p*-tolylsilane reacted in a much more complicated manner and only tetra-*p*-tolylsilane was isolated from the reaction. In order to obtain some information as to the course of this reaction, tri-*p*-tolylmethylsilane was treated with phenylisopropylpotassium, and after treatment with methyl iodide, tri-*p*-ethylphenylmethylsilane (mixed m.p.) was obtained in good yield



This would seem to indicate that both metalation of the methyl groups and cleavage of the tolyl groups occur in the case of tri-*p*-tolylsilane. Triphenylsilane seems to react in a similar manner with phenylisopropylpotassium since tetraphenylsilane is formed.

Experimental

Triarylsilanes.—All of these silanes were prepared by the reaction of the appropriate Grignard reagent with trichlorosilane.

In a typical experiment a saturated ether solution containing 115 g. (0.6 mole) of *p*-chlorobromobenzene was added to 15 g. (0.62 mole) of magnesium in 100 ml. of ether. After stirring for 30 minutes the mixture was cooled in an ice-bath, and 24.2 g. (0.18 mole) of trichlorosilane was added. After four hours of refluxing the solution was cooled and then hydrolyzed by pouring into cracked ice and dilute hydrochloric acid. The ether layer was separated, washed with water, dried over anhydrous sodium sulfate and then the solvent was removed. The residue was distilled and the fraction boiling at 230–236° (3 mm.) was collected. Recrystallization from 95% ethanol gave 37.0 g. (57%) of tri-*p*-chlorophenylsilane; m.p. 79.5–81°. A second crystallization from the same solvent gave 33.15 g. (51%); m.p. 80.5–81°.

Table I lists all the triarylsilanes prepared by this procedure.

Triarylmethylsilanes.—In a typical experiment a solution of methyllithium (0.0415 mole) in ether was added dropwise with stirring to a solution of 15.0 g. (0.0415 mole) of tri-*p*-chlorophenylsilane in 100 ml. of ether. The immediate formation of a white precipitate was observed. After the addition was complete the product was allowed to stir for one hour and then was hydrolyzed by pouring into a mixture of cracked ice and dilute hydrochloric acid. The ether layer was separated, washed twice with water, dried, and the solvent removed. The solid residue was crystallized twice from 95% ethanol to give 9.05 g. (58%) of tri-*p*-chlorophenylmethylsilane melting at 83–85°. (See Table II for the triarylmethylsilanes prepared by this procedure.)

Reaction of Tri-*o*-tolylsilane with Phenylisopropylpotassium.—Phenylisopropylpotassium was prepared by the procedure described by Ziegler.[6] The yield determined by differential titration[7] was 46%.

A solution containing 0.0446 mole of phenylisopropylpotassium was added to a solution of 4.53 g. (0.0149 mole) of tri-*o*-tolylsilane in 75 ml. of ether. After standing for 36 hours at room temperature the product was carbonated by

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(5) P. D. Bartlett and J. E. Jones, *ibid.*, **64**, 1837 (1942).

(6) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).

(7) H. Gilman and A. H. Haubein, THIS JOURNAL, **66**, 1515 (1948).

pouring onto crushed Dry Ice; after warming to room temperature the aqueous solution was filtered and acidified. A thick gummy solid separated out, from which the water was decanted. The residue was suspended in benzene and then boiled for a few minutes after which it was allowed to evaporate to a small volume at room temperature. A solid residue was collected and suspended in petroleum ether. Acetone was added until most of the solid had dissolved. This suspension was filtered hot and boiled until most of the acetone had evaporated. The solid which separated was collected and the above purification process was repeated. The final product melted at 158–165° and could not be purified further.

In another experiment a solid was obtained which melted at 135–150°. The neutral equivalent was 162 (neutral equivalent of triphenylsilane-2,2′,2″-triacetic acid is 145). This product was refluxed for two days in high boiling petroleum ether and filtered while hot. The loss in weight was 0.5 g. and the solid residue had a neutral equivalent of 158. A sample of this product was recrystallized twice from an ethanol–water mixture to give a small amount of product melting at 220–223° and having a neutral equivalent of 148.

In still another experiment the acidic solid obtained after carbonation was recrystallized from an ethanol–water mixture. Only an intractable oil was obtained.

Esterification of the Acid Produced from Tri-*o*-tolylsilane and Phenylisopropylpotassium.—A 4.4-g. sample of the acid prepared in the manner just described was dissolved in 25 ml. of ethanol which had previously been saturated with hydrogen chloride. This solution was refluxed for three hours and then cooled in an ice-bath. The solid which separated out was filtered off and air-dried. It weighed 3.46 g. (66% calculated as the ethyl ester of triphenylsilane-2,2′,2″-triacetic acid). After one crystallization from 95% ethanol 1.9 g. (36%) of large crystals was collected melting at 103.5–106.5°. A small sample after another crystallization from ethanol melted at 106–107°.

Anal. Calcd. for $C_{30}H_{34}O_6Si$: Si, 5.41. Found: Si, 5.23.

Tri-*o*-ethylphenylsilane.—Phenylisopropylpotassium (0.059 mole) in ether was added to a solution of 5.13 g. (0.0169 mole) of tri-*o*-tolylsilane in ether. After 36 hours 8.4 g. (0.059 mole) of methyl iodide was added. The product was hydrolyzed and the ether layer was concentrated to a small volume. The residue was distilled and a fraction boiling at 158–173° (1 mm.) was collected. After standing overnight the material solidified. This product weighed 3.75 g. (65%) and after one crystallization from ethanol melted at 78–79°. The melting point was not depressed when mixed with an authentic sample of tri-*o*-ethylphenylsilane prepared by treating *o*-ethylphenyllithium with trichlorosilane.

Anal. Calcd. for $C_{24}H_{28}Si$: Si, 8.14. Found: Si, 8.02.

Reaction of Tri-*p*-tolylsilane with Phenylisopropylpotassium.—A solution of phenylisopropylpotassium (0.044 mole) in ether was added to 50 ml. of an ethereal solution containing 3.28 g. (0.0126 mole) of tri-*p*-tolylsilane. After the addition was complete the product was allowed to stand at room temperature for 36 hours. At the end of this time a brick red solid had separated out, and the ether solution had a dark red color. The entire product was carbonated by pouring jetwise onto a stirred slush of powdered Dry Ice and ether. Upon warming to room temperature 50 ml. of water was added and then concentrated hydrochloric acid, whereupon a white gum separated out which could not be solidified. When an attempt was made to esterify this material by a procedure similar to the one described above an oil was obtained which also could not be solidified.

In another experiment 0.0545 mole of phenylisopropylpotassium in ether was added to 4.73 g. (0.0155 mole) of tri-*p*-tolylsilane in 50 ml. of ether. After 36 hours 7.73 g. (0.0545 mole) of methyl iodide was added. The color of the solution was completely discharged and a white solid separated out. The addition of water produced two clear layers. The organic layer was separated, dried over anhydrous sodium sulfate and the solvent distilled off. An attempt was made to distil the residue at 1 mm.; however, the material in the flask decomposed because of the high temperatures required. (Tri-*p*-ethylphenylsilane boils around 185–200° (1 mm.) and can be distilled without decomposition.)

In still another experiment 0.0578 mole of phenylisopropylpotassium was added to 5.02 g. (0.0165 mole) of tri-*p*-tolylsilane in ether. After standing for 24 hours the product was hydrolyzed with water. After working up in the usual manner, 0.6 g. of a crystalline solid was obtained which melted at 223–225°. This material was identified as tetra-*p*-tolylsilane by a mixed melting point with an authentic sample prepared from *p*-tolyllithium and silicon tetrachloride. No other pure product could be isolated.

Reaction of Phenylisopropylpotassium with Tri-*p*-tolylmethylsilane.—An ethereal solution of phenylisopropylpotassium containing 0.0538 mole of the organometallic was added to a solution of 4.9 g. (0.0154 mole of tri-*p*-tolylmethylsilane in 50 ml. of ether. After 24 hours 7.65 g. (0.0538 mole) of methyl iodide was added. The product was then hydrolyzed by the addition of water and the organic layer was separated and dried over anhydrous sodium sulfate. After removal of the solvent the residue was distilled and 2.9 g. (61%) of a fraction boiling at 175–195° (1 mm.) was collected. After standing one week the product solidified. It was recrystallized by making a saturated alcohol solution at room temperature and then cooling it in an ice-bath for twelve hours. It melted at 50–50.5° and was not depressed by mixing with an authentic sample of tri-*p*-ethylphenylmethylsilane (see below).

Tri-*p*-ethylphenylmethylsilane.—A solution of 6.24 g. (0.046 mole) of trichlorosilane in ether was added to an ether solution of *p*-ethylphenylmagnesium bromide prepared from 32.0 g. (0.18 mole) of *p*-bromoethylbenzene. After the addition was complete the product was refluxed for one hour, cooled and then hydrolyzed by pouring into a mixture of cracked ice and dilute hydrochloric acid. The organic layer was separated, washed twice with water, dried and the solvent distilled off. The residue was distilled and the fraction boiling at 160–210° (1 mm.) was collected. Upon redistillation the fraction boiling at 184–200° (1 mm.) was collected. This amounted to 8 g. (51%) but would not solidify.

A solution of methyllithium containing 0.02 mole of the organometallic was added dropwise to 6.88 g. (0.02 mole) of the tri-*p*-ethylphenylsilane prepared above. A white precipitate began to separate out immediately. After the addition was complete the product was stirred for one hour, after which it was hydrolyzed by the addition of water. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate and the solvent was removed. The residue solidified on cooling. After one crystallization from ethanol it weighed 1.8 g. (25%) and melted at 47–48°.

Anal. Calcd. for $C_{25}H_{30}Si$: Si, 7.80. Found: Si, 7.64.

Reaction of Triphenylsilane with Phenylisopropylpotassium.—An ethereal solution of phenylisopropylpotassium containing 0.0453 mole of the organometallic was added to a solution of 11.8 g. (0.0453 mole) of triphenylsilane in ether. After standing for 36 hours the product was carbonated and worked up in the usual manner. There was isolated 1.97 g. (26%) of phenyldimethylacetic acid and 5.65 g. of tetraphenylsilane (mixed m.p.). No other crystalline product could be isolated.

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