principal product, **pentamethylphenyldisiloxane**,[10] b.p. 95–96° (15 mm.).

Methyldiphenylsilanol Sodium Salt.—To a solution of 8 g. of sodium hydroxide in 35 ml. of isopropyl alcohol and 35 ml. of methanol at 60° was added, with stirring, 41.0 g. of 1,3-dimethyltetraphenyldisiloxane, which dispersed readily. The resulting reaction mixture was partially dehydrated in solution by simultaneously adding 30 ml. of toluene portionwise and boiling off solvent, over a period of three hours, when the concentrated solution reached a temperature of 125°. The viscous residue was redispersed in about 10 ml. of methanol and again solvent was evaporated, concurrent with portionwise addition of 30 ml. of toluene, until the boiling temperature reached 130°. After a third methanol-toluene treatment with concentration to 130°, followed by cooling and addition of 5 ml. of methanol, the salt partially crystallized. The partially crystalline mass was redissolved by heating with 25 ml. of additional toluene. The warm solution was then filtered from a small amount of suspended carbonate and concentrated for a fourth time to 135°. Upon cooling the product was highly viscous, but crystallized rapidly and extensively upon seeding. This indicated that the dehydration was essentially complete. The crystals were separated and rinsed with 30–75° petroleum ether; yield 31 g. with neut. equiv. 233.5. A second crop of 5 g. of crystals was obtained upon further concentrating from the mother liquor, yielding a total of 76% of product.

Anal. Calcd. for $C_{13}H_{13}SiONa$: neut. equiv., 236.3; Si, 11.86; Na, 9.75. Found: neut. equiv., 238; Si, 10.17; Na, 9.54.

X-RAY POWDER PATTERN DATA

d, kX.	I/I_0	*d*, kX.	I/I_0	*d*, kX.	I/I_0
13.19	0.64	5.47	0.77	4.19	0.39
11.48	.62	5.10	1.00	3.93	.35
9.61	.40	5.85	0.58	3.27	.23
8.59	.67	4.72	.71	2.51	.31
8.35	.81	4.58	.83		
6.81	.31	4.46	.75		

Hydrolysis of a 5-g. sample of the salt with dilute acetic acid, using the procedure employed with the dimethylphenylsilanol salt, afforded 4.1 g. (96%) of **methyldiphenylsilanol**,[10] b.p. 165–168° (14 mm.), n^{25}D 1.579.

Anal. Calcd. for $C_{13}H_{14}SiO$: Si, 13.09; OH, 7.9; mol. wt., 214. Found: Si, 13.02; OH, 7.76, 7.74; mol. wt. (acetic acid), 227.

A 4.15-g. sample of the salt was added in small portions to 5.05 g. of triphenylchlorosilane in 25 g. of benzene. Concentration of the resulting clear mixture gave a transparent sodium chloride gel. The latter was coagulated by adding 25 g. each of diethyl ether and benzene, and refluxing four hours. It was then separated by filtration. The concentrated filtrate yielded 6.4 g. (79%) of prisms of **methylpentaphenyldisiloxane**,[10] m.p. 67.5–72.5°, from ethyl acetate. Recrystallization from petroleum ether and from acetone–ethanol gave purified disiloxane as prisms, m.p. 75.2–75.8°.

The salt was further characterized by reaction in toluene with an equivalent amount of trimethylchlorosilane to form **tetramethyl-1,1-diphenyldisiloxane**,[10] b.p. 155–158° (13 mm.), n^{25}D 1.519, in 83% yield.

Triphenylsilanol Sodium Salt.—To a slurry of 26.7 g. of hexaphenyldisiloxane and a solution of 4 g. of sodium hydroxide, in 20 ml. of isopropyl alcohol and 40 ml. of methanol, 30 ml. of toluene was added gradually with warming. Upon reaching 100° the disiloxane had dissolved. However, with further heating to 115°, solids began to separate; they were accordingly redissolved by adding 10 ml. of isopropyl alcohol. The solution was again concentrated until the appearance of solids, which were again dissolved as before. On the third concentration, crystallization was allowed to proceed to completion, with heating to 150° under reduced pressure. The solid product was redissolved in 40 ml. of toluene and 3 ml. of isopropyl alcohol, filtered from a trace of solids, concentrated to half its volume, and allowed to cool. The crystals, which deposited on standing, were rinsed with toluene and dried by warming *in vacuo;* yield 26 g. (81%). They carbonized without melting at 300–350° in a vacuum.

Anal. Calcd. for $C_{18}H_{15}SiONa$: neut. equiv., 298.4. Found: neut. equiv., 296.0, 298.9.

X-RAY POWDER PATTERN DATA

d, kX.	I/I_0	*d*, kX.	I/I_0
10.78	0.40	4.62	1.00
10.40	.44	4.15	0.13
9.83	.22	2.98	0.11
5.83	.19		

The salt, with neut. equiv. 303.8, was similarly prepared from triphenylsilanol. Hydrolysis of the salt with dilute acetic acid yielded 97% of the triphenylsilanol, m.p. 144.5–146.5°.

An 18-g. sample of the salt was allowed to react with 6.95 g. of trimethylchlorosilane in a toluene–ether solution to form 21.5 g. (98%) of crude **1,1,1-trimethyltriphenyldisiloxane**,[10] m.p. 48–50°, containing some higher melting material. Distillation afforded 15.2 g. of a pure fraction, b.p. 215–218° (13 mm.), m.p. 48°, n^{25}D 1.560 (supercooled).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis of Fluorine-containing Organosilanes

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Fluorinated organosilanes in which the perfluoroalkyl group is separated from the silicon atom by an ethylene group have been prepared by reaction of the Grignard reagent of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane and silicon tetrachloride or ethyl silicate. The bromide was prepared by dehydration of 3,3,4,4,5,5,5-heptafluoro-2-pentanol followed by addition of hydrogen bromide to the olefin in the presence of activated carbon. A silanol, silanediol and disiloxane were prepared from the fluorinated silanes as well as silicone oils.

The most convenient method for the synthesis of organosilanes is the reaction of silicon tetrachloride or ethyl silicate with a Grignard reagent. For the preparation of fluorinated organosilanes this investigation has made use of the readily available 3,3,4,4,5,5,5-heptafluoro-1-bromopentane in which the bromine atom is separated from the perfluoroalkyl group by an ethylene group which would be expected to completely mask the powerful electron attracting effect of the fluorinated portion of the carbon chain. Therefore, this bromide, as contrasted to a more fully fluorinated alkyl bromide, would be expected to form a normal Grignard reagent.

The starting material, 3,3,4,4,5,5,5-heptafluoro-2-pentanol, was prepared by reaction of ethyl heptafluorobutyrate with a mixture of methyl and isopropyl Grignard reagents.[2] The secondary alcohol

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[1] Presented before the Division of Organic Chemistry, 123rd National Meeting of the American Chemical Society, 1953.

[2] O. R. Pierce, E. T. McBee and J. C. Siegle, unpublished results.

was heated with phosphorus pentoxide to give a good yield of the corresponding olefin. Hydrogen bromide was found to add to this olefin to give yields up to 85% of the reverse Markownikoff addition product, 3,3,4,4,5,5,5-heptafluoro-1-bromopentane, in the presence of activated carbon at 120–140° using a simple apparatus permitting recycling of the unreacted olefin. Activated carbon was found previously by Park, Sharrah and Lacher[3] to be the best of many catalysts used in their technique of adding hydrogen bromide to completely halogenated olefins. Experiments using calcium sulfate as promoter gave higher conversions than those performed in the absence of promoter; but a more important means of increasing catalyst activity was found to be the technique of allowing the catalyst to cool after a short period of activity.

The reaction of heptafluoropentylmagnesium bromide with silicon tetrachloride gave the solid trisubstituted chlorosilane as the principal product using several different techniques. About the same ratio of products was obtained, using either the simplest procedure of quickly adding silicon tetrachloride solution to the cooled Grignard solution and letting the mixture warm up and stand at room temperature, or the more elaborate techniques of dropping the Grignard solution into silicon tetrachloride solution in ether, dropping a benzene-ether solution of the Grignard reagent into refluxing benzene solution of silicon tetrachloride, or of adding the bromide slowly to a mixture of ether, magnesium and silicon tetrachloride.

The reaction of 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide with ethyl silicate gave the mono- and disubstituted ethoxysilane in good yield with only small amounts of higher substituted products obtained. Several different techniques were employed as in the silicon tetrachloride experiments, but the simplest technique proved to be the most satisfactory, giving up to 25% of the disubstituted ethoxysilane and up to 20% of the monosubstituted ethoxysilane. This method consisted of adding the Grignard reagent slowly to a mixture of ether and ethyl silicate.

Hydrolysis of the trisubstituted chlorosilane gave a silanol which upon treatment with hydrochloric acid in acetic acid gave a crystalline disiloxane. Mild hydrolysis of the disubstituted diethoxysilane gave a crystalline silanediol. A silicone oil was obtained by vigorous hydrolysis of the disubstituted diethoxysilane and a very viscous silicone oil was obtained by hydrolysis of the monosubstituted ethoxysilane.

Experimental

3,3,4,4,5,5,5-Heptafluoro-1-pentene.—In a 500-ml. round-bottom flask equipped with thermometer well was placed 200 g. (0.93 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol. The flask was cooled in an ice-bath and 176 g. (1.24 moles) of phosphorus pentoxide added in 50-g. portions with shaking and cooling to give a homogeneous mixture. The mixture was allowed to warm up and stand overnight. The flask was attached to a 7-inch Vigreux column connected to a water-cooled condenser leading into a Dry Ice-cooled receiver. The flask was heated by means of a heating mantle at a temperature affording a steady rate of evolution of olefin. The heating was carried on for 2 hours at 32–189°, 2.7 hours at 185–197°, 2.5 hours at 197–245°, and finally for 3.5 hours at 245–341°. The colorless distillate of olefin weighed 173.5 g. (0.88 mole), a yield of 95%. Analyzed samples were specially purified by shaking with aqueous bicarbonate followed by drying over Drierite and distillation from phosphorus pentoxide through a Todd column packed with glass helices (b.p..31°). The olefin has a refractive index below 1.30, is oxidized by 2% aqueous permanganate–acetone mixture, and has an infrared spectrum which indicates the presence of a double bond.

Anal. Calcd. for $C_5H_3F_7$: C, 30.62; H, 1.54. Found: C, 30.61; H, 1.65.

3,3,4,4,5,5,5-Heptafluoro-1-bromopentane.—Hydrogen bromide gas was treated with 3,3,4,4,5,5,5-heptafluoro-1-pentene in the presence of activated carbon at 120–140°, using a simple apparatus which permitted continuous recycling of unreacted olefin.

a. Apparatus.—The olefin was vaporized from a round-bottomed flask, A, by means of a heating mantle, the vapors passing upward into a Y-tube assembly, B, where they were mixed with hydrogen bromide gas. The mixture of gases then passed upward into the reaction chamber, C, which contained the catalyst. The reaction chamber consisted of three tubes positioned concentrically by means of grooved asbestos plates (Transite) fastened to iron rings. The innermost tube containing the catalyst was 400 mm. long and 32 mm. in diameter. The gases passed from the reaction tube to a connecting tube, D, which was joined at one end to the reaction tube and at the other end to the reservoir of the Y-tube assembly, B. The hot gases not condensing in the reservoir passed upward through a water-cooled condenser and thence to a Dry Ice-cooled condenser which was vented to the atmosphere, thus allowing some of the hydrogen bromide gas to escape from the system. The capillary U tube functioned as a valve permitting liquid to flow into the flask, A, but blocking the passage of vapors the opposite way. Hydrogen bromide gas from a cylinder was passed first through a drying tube containing calcium chloride and phosphorus pentoxide, then through a washing bottle containing tetralin, then through a tube packed with glass wool and silica gel, and thence to the tube assembly, B.

b. Procedure.—A catalyst consisting of 25% of 20–30 mesh calcium sulfate and 75% 20–48 mesh Columbia activated carbon was activated just prior to the experiment by heating at 200° for three hours under reduced pressure and then allowing the catalyst mass to cool. The activated catalyst (158 g.) was placed in the reaction chamber and 454.1 g. (2.31 moles) of 3,3,4,4,5,5,5-heptafluoro-1-pentene in the flask, A. After allowing hydrogen bromide to pass into the catalyst for about 30 minutes while bringing the temperature of the reaction chamber to about 120°, the heating mantle under flask A was turned on. For the next 13.5 hours hydrogen bromide and olefin were passed through the catalyst maintained at 125–135°, the hydrogen bromide passing through the tetralin at the rate of 120–170 bubbles per minute.

The experiment was then continued for 12 hours at a reaction tube temperature of 134–143°. The rate of hydrogen bromide uptake was observed to be much greater than previously. The addition reaction was then completed in 6 hours at reaction tube temperature of 128–138°. In order to remove adsorbed product from the catalyst the heater under flask A was turned off, and for 2 hours hydrogen bromide was passed in rapidly with the reaction tube temperature being brought to 315°. The crude product in flask A was washed with aqueous bicarbonate, added to phosphorus pentoxide, and fractionated through a Todd column. The yield of bromide, boiling at 97–98°, was 546.4 g. (1.97 moles, 85%). Pure 3,3,4,4,5,5,5-heptafluoro-1-bromopentane is a colorless liquid boiling at 97.8° at 747 mm., $n^{20}D$ 1.3378, and forms a trace of precipitate when heated with alcoholic silver nitrate for five minutes.

Anal. Calcd. for $C_5H_4F_7Br$: C, 21.67; H, 1.46; Br, 28.85. Found: C, 21.50; H, 2.02; Br, 28.72.

3,3,4,4,5,5,5-Heptafluoro-1,2-dibromopentane.—Bromine was added to 3,3,4,4,5,5,5-heptafluoro-1-pentene in the presence of activated carbon using a smaller model of the apparatus described previously for the preparation of heptafluoropentyl bromide. The gas inlet of tube assembly B was closed off and 53.8 g. (0.27 mole) of olefin and 33.5 g. of bromine placed in flask A. Over a period of 3.5 hours the reaction tube temperature gradually increased from 114 to

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[3] J. C. Park, M. L. Sharrah and J. R. Lacher, THIS JOURNAL, **71**, 2339 (1949).

143°. At intervals more bromine was added until a total of 51.5 g. (0.32 mole) had been added. The catalyst was 58 g. of 20–48 mesh Columbia activated carbon, freshly activated by heating to 200° for 3 hours under vacuum. The crude product was shaken with aqueous sodium bisulfite and added to ether extracts of the water layer. The ether solution was dried over Drierite and distilled to remove ether. Fractionation of the residue through a Todd column gave 45.9 g. (0.13 mole, 48%) boiling at 140–141°, n^{20}D 1.3874.

Anal. Calcd. for $C_5H_3F_7Br_2$: C, 16.87; H, 0.85; Br, 44.90. Found: C, 16.83; H, 1.00; Br, 44.74.

Preparation of the Grignard Reagent.—The apparatus comprised a one-liter, three-necked flask fitted with a dropping funnel, a sealed Hershberg stirrer and a condenser protected with a drying tube. Magnesium (16 g., 0.66 mole) was placed in the flask and the assembly dried by heating in a nitrogen atmosphere. Anhydrous ether (250 ml.) was then added to the flask followed by a few crystals of iodine and several milliliters of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane. The reaction mixture was then heated to reflux and maintained at this temperature until reaction began. A solution of the bromide (165 g., 0.60 mole) in 250 ml. of ether was then added dropwise at a rate sufficient to maintain reflux. The addition required two hours and the solution was refluxed for two additional hours.

Preparation of Silanes.—The apparatus comprised a one-liter, three-necked flask fitted with a dropping funnel, stirrer and reflux condenser protected with a drying tube. An ether solution of either silicon tetrachloride or ethyl silicate was placed in the flask and the Grignard reagent was added dropwise to the reaction mixture which was maintained at reflux temperature in an atmosphere of dry nitrogen. Generally, a mole ratio of Grignard reagent to the silicon-containing reactant of 2:1 was found to be satisfactory.

After the addition was complete, the reaction mixture was refluxed for eight hours, the ether solvent replaced by benzene, and the mixture cooled to room temperature. The magnesium salts present were separated by centrifugation and the benzene solution distilled at atmospheric pressure to remove the solvent followed by rectification at reduced pressure in a Todd distillation assembly to separate the reaction products. The products obtained are listed as follows:

Pure tris-(3,3,4,4,5,5,5-heptafluoropentyl)-chlorosilane boils at 133–134° at 15 mm. and melts at 34–35° (yield 47%). *Anal.* Calcd. for $C_{15}H_{12}F_{21}ClSi$: C, 27.51; H, 1.84; Cl, 5.42. Found: C, 27.14; H, 1.87; Cl, 5.28.

Pure tetrakis-(3,3,4,4,5,5,5-heptafluoropentyl)-silane boils at 71–72° at 25 mm. (yield 10%). *Anal.* Calcd. for $C_{20}H_{16}H_{28}Si$: C, 29.42; H, 1.97; F, 65.2. Found: C, 29.21; H, 2.14; F, 65.0.

Pure (3,3,4,4,5,5,5-heptafluoropentyl)-triethoxysilane boils at 92.5–93° at 25 mm. (yield 20%). *Anal.* Calcd. for $C_{11}H_{19}F_7O_3Si$: C, 36.66; H, 5.31. Found: C, 36.81; H, 5.25.

Pure bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane boils at 117.5–118.0° at 25 mm. (yield 25%). *Anal.* Calcd. for $C_{14}H_{18}F_{14}O_2Si$: C, 32.82; H, 3.54. Found: C, 32.84; H, 3.58.

By varying the mode of addition of the reactants and reaction temperatures it was possible to change the ratio of products. However, the procedure described above was found to be the most suitable for laboratory preparations. It is emphasized, also, that the reaction product must be completely free of salts before distillation is attempted or considerable decomposition will occur.

Tris-(3,3,4,4,5,5,5-heptafluoropentyl)-silanol.—To 46.8 g. (0.071 mole) of tris-(3,3,4,4,5,5,5-heptafluoropentyl)-chlorosilane boiling at 141–146° at 25 mm. was added 50 ml. of water. The mixture was refluxed for seven hours and the oily product extracted with ether. After drying over Drierite the ether was removed by distillation and the residue fractionated through a Todd column. There was obtained at 25 mm., 19.3 g. (0.030 mole, 42%) of tris-(3,3,4,4,5,5,5-heptafluoropentyl)-silanol boiling at 151–153° (n^{20}D 1.3378).

Anal. Calcd. for $C_{15}H_{13}F_{21}OSi$: C, 28.31; H, 2.05; F, 62.70. Found: C, 28.33; H, 2.15; F, 62.42.

Hexakis-(3,3,4,4,5,5,5-heptafluoropentyl)-disiloxane.—Heating 8.7 g. (0.014 mole) of tris-(3,3,4,4,5,5,5-heptafluoropentyl)-silanol with methanol and hydrochloric acid followed by fractionation at 22 mm. gave a distillate of starting material and a solid pot residue. The residue and distillate were then added to 20 ml. of glacial acetic acid and 5 ml. of hydrochloric acid. This mixture was refluxed for 64 hours. The crystalline deposit was recrystallized from chloroform, giving 2.9 g. (0.0023 mole, 33%) of white crystals melting at 65–66°. Two more recrystallizations from ligroin, and then from methanol, raised the melting point to 66.5–67°.

Anal. Calcd. for $C_{30}H_{24}F_{42}OSi_2$: C, 28.72; H, 1.93; F, 63.8. Found: C, 28.62; H, 1.89; F, 64.0.

Bis-(3,3,4,4,5,5,5-heptafluoropentyl)-silanediol.—To 60 ml. of methanol and 10 ml. of water was added 13.4 g. (0.026 mole) of bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane and the two-layer mixture stirred for 30 minutes to give a homogeneous solution. After standing for 22 hours the solvent was removed by distillation and the semi-solid residue added to about 50 ml. of chloroform. The mixture was allowed to stand several days in the refrigerator and the oily crystals removed by filtration. Recrystallization from chloroform gave 7.6 g. (0.017 mole, 65%) of large crystals melting at 61–63°. Another recrystallization from chloroform gave 6.7 g. of long needles melting at 64.5–65°.

Anal. Calcd. for $C_{10}H_{10}F_{14}O_2Si$: C, 26.32; H, 2.21. Found: C, 26.24; H, 2.22.

3,3,4,4,5,5,5-Heptafluoropentyl Acetate.—A mixture consisting of 94.7 g. (0.34 mole) of 3,3,4,4,5,5,5-heptafluoropentyl bromide, 69.9 g. (0.85 mole) of sodium acetate and 200 ml. of glacial acetic acid was refluxed 86 hours, after which it was poured into 1 liter of water and neutralized with 280 g. of sodium bicarbonate. Some product separated as a bottom oily layer. The oil was combined with several ether extracts of the water layer and the ether solution dried over Drierite. Distillation to remove ether followed by fractionation of the residue through a small Todd column packed with helices yielded 31.2 g. (0.12 mole, 35%) of ester boiling at 137–137.5°, n^{20}D 1.3276.

Anal. Calcd. for $C_7H_7F_7O_2$: C, 32.82; H, 2.75. Found: C, 32.96; H, 2.81.

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