

## Reactions Leading to Heptafluoropropyl Silanes

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In a recent communication (1) we described the synthesis of heptafluoropropyllithium and its reaction with diethyldichlorosilane to give diethylbis-(heptafluoropropyl) silane and diethylheptafluoropropylchlorosilane. Subsequently (2) Haszeldine reported the synthesis of bis(trifluoromethyl)dichlorosilane and trifluoromethyltrichlorosilane.

There have been other reports of the synthesis of perfluoroalkyl-substituted silanes (3, 4) from the reaction of trifluoromethyl iodide with a silicon-copper couple. This report is on the synthesis of heptafluoropropyl-substituted silanes from the reaction of heptafluoropropyllithium with several polyfunctional silanes. Perfluoropropyl-substituted silanes were obtained in yields ranging up to 46 per cent. Either butyl ether or an ethyl ether-pentane mixture is a suitable solvent.

One of the interesting observations was that neither heptafluoropropyllithium nor methylolithium replace an ethoxy group from ethyl silicate, methyltriethoxysilane, ethoxytrichlorosilane, diethoxydichlorosilane, or methyl-diethoxychlorosilane. In the case of methyltrichlorosilane, only a low yield of perfluoropropyltrimethylsilane was obtained.

Methylolithium competes with heptafluoropropyllithium for the silanes thus methylation occurs also. The relative insolubility of methylolithium in the reaction mixture, however, minimizes this reaction.

Perfluoropropyl-substituted silanes of non-, mono- and di-functionality can be prepared. The non-functional silanes are stable to water and hot concentrated sulfuric acid, but decompose in base with differing degrees of ease, depending on the particular silane. The mono- and di-functional compounds react in a characteristic manner. Fluorosilanes were formed from a side reaction of the chlorosilanes with lithium fluoride, resulting from the decomposition of heptafluoropropyllithium. The higher the functionality of the chlorosilane, the lower was the yield of the desired perfluoropropyl-substituted silane and the higher the yield of fluorosilane, the latter reaching maximum with silicon tetrachloride. Methyltrichlorosilane gave only methylbis-(heptafluoropropyl)chlorosilane. The latter two results indicate that where there is high functionality in the perfluoroalkyl substituted chlorosilane, the probability of substitution of chlorine atoms by fluorine is very high.

### Experimental<sup>1</sup>

#### Intermediates:

**Preparation of Methyl-diethoxychlorosilane.** A mixture of 184 g. (4 moles) of anhydrous ethanol and 316 g. (4 moles) of anhydrous pyridine was added over a period of 4 hrs. to 300 g. (2 moles) of

1. Fluorine analyses were made by Clark Microanalytic Laboratories, Urbana, Illinois. Carbon, hydrogen and chlorine were determined by Mrs. Yeh and Mrs. Portney, Purdue University Microanalysts.

methyltrichlorosilane dissolved in 3.4 l. of anhydrous benzene. The product was filtered with a Buchner funnel and the filter cake washed with five 200 ml. portions of anhydrous benzene. The benzene was then removed by distillation through an 18" glass helices-packed column as the pot temperature rose to 92°. The residual mixture was cooled in ice to precipitate the pyridine hydrochloride; the liquid was decanted and rectified. There was obtained 220.5 g. (65.6%) of methyldiethoxychlorosilane, b.p. 75-85°/139 mm. Re-rectification gave 179.5 g. of material, b.p. 81.8°/153 mm.,  $n_D^{20}$  1.3912,  $d_4^{20}$  0.989. Anal. Calcid. for  $C_5H_{13}ClO_2$  Si:C, 35.6; H, 7.7; Cl, 21.1 Found: C, 35.6; H, 7.7; Cl, 21.4. From a one mole run there was also obtained 21.5 g. (12%) of methyltriethoxysilane, b.p. 95° at 158 mm.,  $n_D^{20}$  1.3828.

**Ethoxytrichlorosilane, Diethoxydichlorosilane and Triethoxychlorosilane.** The ethoxysilanes were produced by adding a mixture of pyridine and ethanol to silicon tetrachloride at 0° in a benzene or pentane solvent during 1 hr. (5).

**Methylithium.** An ethyl ether solution of methylithium was prepared from 86.1 g. (12.34 g. atoms) of lithium according to the published procedure (6).

**Heptafluoro-1-iodopropane.** A total of 21.7 pounds of silver heptafluorobutyrate and 19 pounds of iodine was converted to heptafluoro-1-iodopropane, (63.7%) according to the published procedure (7).

#### Reactions of Heptafluoropropylithium

**With Methyltriethoxysilane.** Methylithium (326 ml., 1.125 N, 0.366 mole) was added simultaneously with 65 g. (0.366 mole) of methyltriethoxysilane during 1 hr. to 108.2 g. (0.366 mole) of heptafluoro-1-iodopropane dissolved in 200 ml. of anhydrous ether at -42°. The solution was maintained between -40 and -55° for 5 hrs., -38 to -26° for 4 hrs. and -26 to 10° for 15 hrs. Raising the temperature to 35° gave 9.7 g. (17.6%) of hexafluoropropene. The ether solution was distilled and the residue transferred with dry benzene to two 250 ml. centrifuge tubes and the solid was removed by centrifugation.

The benzene solution was rectified to give 47.4g. (73%) of recovered methyltriethoxysilane and no perfluoropropyl-substituted silane.

**With Trimethylchlorosilane; (A) In Ethyl Ether:** Chlorotrimethylsilane (b.p. 57.3°,  $n_D^{20}$  1.3890) (27 g., 0.25 mole) was dissolved in 50 ml. of anhydrous ether and added during ½ hr. along with 165 ml. of 1.52 N methylithium (0.25 mole) to 74 g. (0.25 mole) of heptafluoro-1-iodopropane dissolved in 200 ml. of ether and maintained at  $-30 \pm 3^\circ$ . The chlorosilane was kept in excess, and the addition of methylithium was completed 15 mins. later than the addition of the silane. The temperature was raised to -18° during 45 mins., to -10° during the next 15 mins. and to 6° during the next 45 mins. Hexafluoropropene (27 g., 72%) was collected and the solution was refluxed to distill off the majority of an azeotrope, b.p. 32-35°, and the residue (about 14 ml.) was rectified. The remainder of the ether heptafluoro-1-iodopropane azeotrope was

removed (35-45°) and 3.9 g. (6.3%) of trimethyl(heptafluoropropyl)silane was obtained, b.p. 88°;  $n_D^{20}$  1.3222.

**In Butyl Ether.** A few crystals of ferrous sulfate hexahydrate was added to 600 ml. of butyl ether which was then distilled, discarding the forerun; b.p. to 72° at 72 mm., and approx. 20 ml. of brown residue. The product which boiled constantly at 72° at 72 mm. was dried over calcium hydride for 24 hrs.

Five hundred ml. of an ethyl ether solution of methyllithium (1.25 N, 0.76 mole) was added to the butyl ether and the ethyl ether was removed by gradually reducing the pressure and elevating the pot temperature. The resulting slurry was added slowly during 1 hr. to 65 g. (0.596 mole) of trimethylchlorosilane and 177 g. (0.597 mole) of heptafluoro-1-iodopropane dissolved in 50 ml. of anhydrous, peroxide-free butyl ether, maintained between -40 and -45°. The solution was then maintained between -38 and -4° for 64 hrs. and was then allowed to reach room temperature during 8 hrs. The solution was heated to 85° and the gaseous products were collected in a Dry Ice trap. These consisted of 50 g. (56%) of hexafluoropropane, b.p. -30°, 15 g. of a material, b.p. 12.4°, which was crude trimethylfluorosilane.

Rectification of the residue remaining after distilling of the butyl ether gave 46.7 g. (27%) of heptafluoro-1-iodopropane, and 1.1 g. (2.7%) trimethyl(heptafluoropropyl)silane b.p. 84-86°,  $n_D^{20}$  1.3508.

**Preparation of Trimethylfluorosilane.** Trimethylchlorosilane (54.2 g., 0.5 mole) was dissolved in 200 ml. of butyl ether (free of peroxides) and stirred with 13 g. (0.5 mole) of anhydrous lithium fluoride. The temperature was raised to reflux, and after several hours, 1 g. of low boiling material with a pungent odor distilled over with 1 g. of trimethylchlorosilane. The low boiling material was distilled from trap to trap and an infrared absorption curve made. The principal peaks were at 3.48, 7.98, 11.00, 11.80, 13.00, and 13.25  $\mu$ . Smaller peaks were found at 4.56, 6.87, 8.75, 10.25 and 10.60  $\mu$ , with shoulders at 7.92 and 11.15  $\mu$ . Peaks not found in trimethylchlorosilane are those at 4.56, 8.75, 11.0 and 13.25  $\mu$ . The peak at 10.60  $\mu$  is apparently shifted from 10.34.

The molecular weight of this low boiling gas was 92 ( $(\text{CH}_3)_3\text{SiF} = 92$ ).

Eight grams of an azeotrope of trimethylchlorosilane, b.p. 42°,  $n_D^{20}$  1.3707, was obtained from the butyl ether after heating at reflux three days. This was separated by hydrolysis to give 0.3 g. of n-butyl fluoride, b.p. 26°,  $n_D^{20}$  1.3450 (lit. 32°/745,  $n_D^{20}$  1.3419) and trimethylsiloxane, b.p. 96°. There was also recovered 27 g. of trimethylchlorosilane, b.p. 58°,  $n_D^{20}$  1.3842.

**With Dimethyldichlorosilane.** One liter of a methyllithium solution (2.15 moles) was added to a mixture of 278 g. (2.15 moles) of dimethyldichlorosilane, 637 g. (2.15 moles) of heptafluoro-1-iodopropane and 400 ml. of pentane at -70° during one hour. The solution was warmed to -40° in one hour and then cooled to -78°; an additional liter of methyllithium was quickly added and the solution warmed to 27°. On refluxing 76 g. (24%) of hexafluoropropene was evolved. The solution was filtered,

the low boiling mixture of pentane, ether, heptafluoropropyl-1-iodopropane and methyl iodide removed, and the residue rectified.

There was obtained 42 g. (8.1%) of trimethyl(heptafluoropropyl)silane b.p. 89.9°,  $n_D^{20}$  1.3222,  $d_4^{20}$  1.18, and 160.5 g. (38%) of dimethylbis(heptafluoropropyl)silane, b.p. 133.5°,  $n_D^{20}$  1.3110,  $d_4^{20}$  1.57.

**With Ethylvinylchlorosilane.** Methylithium (1.05 l., 0.935 mole) was added during 30 mins. to a mixture of 277 g. (0.935 mole) of heptafluoro-1-iodopropane, 145 g. (0.935 mole) of ethylvinylchlorosilane and 500 ml. of pentane maintained below -64°. The solution was warmed to -43° during 1 hr., cooled to -78° and 0.5 liter (0.935 mole) additional methylithium added. Refluxing the solution for one hour gave 40 g. (28.5%) of hexafluoropropene. After removal of the pentane-heptafluoro-1-iodopropane-ether-methyl-iodide azeotrope, the residue was washed three times with distilled water to give 185 g. of a light yellow solution, which was rectified to give 78 g. (31%) of ethylmethyl(heptafluoropropyl)vinylsilane, b.p. 82-83°/2 mm.,  $n_D^{20}$  1.3568,  $d_4^{20}$  1.27.

Anal. Calcd. for  $C_8H_{11}F_7Si$ : MR 45.75. Found: MR 47.20.

**With Diethoxydichlorosilane.** A methylithium solution (650 ml., 2.09 N, 1.36 moles) was added simultaneously with 128.5 g. (0.68 mole) of diethoxydichlorosilane to 403 g. (1.36 moles) of heptafluoro-1-iodopropane cooled to -78° and maintained between -43 and -45° during the addition, which required 1.5 hrs. After the solution was maintained at -43° for 2 days, it was warmed to room temperature and 75 g. (37%) of hexafluoropropene was obtained.

**With Methyltrichlorosilane.** (A) Methylithium (440 ml., 1.125 N., 0.495 mole) and methyltrichlorosilane (74 g., 0.495 mole) in 50 ml. of ether were added simultaneously to heptafluoro-1-iodopropane (146 g., 0.495 mole) in 200 ml. of ether at -40° during 1.5 hrs. The solution temperature which was -5° after 4 hrs. was lowered to -30°, and then allowed to rise to -12° during 28 hrs. The solution was refluxed, and 18 g. (24%) of hexafluoropropene was collected in the Dry Ice trap. All material boiling below 45° was removed. The residual liquid was distilled from the solid into a trap at -74°, by reducing the pressure in stages to 0.5 mm. and raising the mantle temperature at 100°. The liquid was distilled and the fraction, b.p. 48-65°/158 mm.,  $n_D^{20}$  1.3230-1.3152, was fractionated to give 14.5 g. (14%) of methylbis(heptafluoropropyl)chlorosilane, b.p. 64.5-65°/158 mm.,  $n_D^{20}$  1.3168-1.3145.

Anal. Calcd. for  $C_7H_{13}F_{14}Cl$ : C, 20.1; H, 0.72; Cl, 8.53; F, 63.90, MR 51.37. Found: C, 23.61; H, 1.59; Cl, 7.66; F, 63.48, MR 51.30.

(B) Methylithium (500 ml., 1.52 N, 0.75 mole) was added during 2 hrs. to a mixture of 224 g. (1.5 mole) of methyltrichlorosilane, 223 g. (0.75 mole, 112 ml.) of heptafluoro-1-iodopropane and 50 ml. of ether contained in a one liter 3-necked flask and maintained at -24 to -58° for 24 hrs. and then allowed to warm to room temperature. The isolation of the product was similar to that for (A) and gave 21.5 g. (10.3%) of product.

**With Ethyltrichlorosilane.** Methyl lithium (500 ml., of 1.52 N, 0.76 mole) was added dropwise to a mixture of 245 g. (1.5 mole) of ethyltrichlorosilane, 223 g. (0.75 mole) of heptafluoro-1-iodopropane and 50 ml. of ether maintained at  $-40^{\circ}$  during 1.5 hrs. The temperature was then maintained for 20 hrs. at  $-30^{\circ}$ .

Five hundred grams of heptafluoro-1-iodopropane-ether azeotrope boiling at  $31^{\circ}$  was removed through a 2' glass helices-filled column. Pentane (150 ml.) was then added, the solution treated with 5 g. of activated carbon, and filtered with suction into a chilled flask. The pentane was removed through the 2' glass-helices-filled column, and the resulting residual solution was rectified through a 3' glass helices-filled Todd column (18 plates) to give the following fluorine-containing fractions: (a) 41.5 g. (10.6%), b.p.  $83.5^{\circ}/92$  mm.,  $n_D^{20}$  1.3871  $d_4^{20}$  1.6755  $C_3F_7Si(C_2H_5)Cl_2$  MR Calcd. 43.29. Found: 41.95. (b) 18 g. (11.6%) b.p.  $61^{\circ}/4$  mm.,  $n_D^{20}$  1.3344,  $d_4^{20}$  1.5500.  $(C_3F_7)_2Si-(C_2H_5)CH_3$  MR Calcd. 53.83 found 55.1.

**With Methyl diethoxychlorosilane.** Methyl lithium (500 ml., 1.52 N, 0.76 mole) and methyl diethoxychlorosilane (84 g., 0.5 mole) dissolved in 100 ml. of ether were added simultaneously during two hours to heptafluoro-1-iodopropane (296 g., 1.0 mole) maintained at  $-40^{\circ}$ . The temperature was then allowed to rise to  $27^{\circ}$  during 66 hrs. The solution was then refluxed and the hexafluoropropene distilled through a 2 ft. stainless steel Heligrid-packed column into a trap cooled to  $-74^{\circ}$ ; this was followed by the ethermethyl iodide-heptafluoro-1-iodopropane azeotrope, b.p.  $30-38^{\circ}$ . Rectification gave 46 g. (40.4%) of hexafluoropropene, b.p.  $-30$  to  $-28^{\circ}$ . Pentane (125 ml.) was added to the residue, the solid removed by centrifugation, and the supernatant rectified. There was obtained 19 g. of methyl diethoxyfluorosilane, b.p.  $100.5^{\circ}$   $n_D^{20}$  1.3558.

Anal. Calcd. for  $C_5H_{13}FSiO_2$ : C, 39.50; H, 8.50; F, 12.31. Found: C, 39.37; H, 8.60; F, 13.12.

**With Ethoxytrichlorosilane.** (A) Methyl lithium (1,100 ml., 2.03 N) (2.29 moles) was added simultaneously with 207 g. (1 mole) of ethoxytrichlorosilane to 680 g. (2.29 moles) of heptafluoro-1-iodopropane maintained between  $-55$  and  $-60^{\circ}$  during the addition period of two hours. The solution was kept below  $-48^{\circ}$  for 48 hrs. and then slowly warmed to room temperature during 24 hrs. One hundred and twenty grams (4.8 mole, 35%) of hexafluoropropene was collected and redistilled. The ether-heptafluoroiodopropane azeotrope was distilled through a  $1\frac{1}{2}'$  column, pentane was added until the distillation temperature was  $37^{\circ}$ , and the residue was filtered. The filtrate was rectified through an 18 plate column to give 2.9 g. of methylheptafluoropropylethoxychlorosilane b.p.  $117.5^{\circ}/135$  mms.,  $n_D^{20}$  1.3208. This reaction was repeated several times and equimolar quantities of ethoxytrichlorosilane and heptafluoro-1-iodopropane were added to pentane and cooled to  $-78^{\circ}$ . An equimolar amount of a solution of methyl lithium in ether was added during  $\frac{1}{2}$  hr., maintaining the temperature between  $-50$  and  $-60^{\circ}$ . The temperature was raised to  $-40^{\circ}$  for one hour and then cooled to  $-78^{\circ}$ , where an additional equimolar amount of methyl lithium was added over twenty minutes. The

solution was then rapidly warmed to room temperature, filtered and rectified. Three separate runs were made using a total of 803 g. (4.4 moles) of ethoxytrichlorosilane, 1294 g. (4.03) heptafluoro-1-iodopropane and 8.2 moles of methylolithium.

The runs were combined after removal of the hexofluoropropene and rectified. The crude fractions (214 g.) b.p. 47-72°/8 to 0.5 mm. were combined and refractionated to give 49.5 g. (9.2%) of crude methylheptafluoropropylethoxychlorosilane, b.p. 49-54°/18 mm.  $n_D^{20}$  1.3329 and 87.2 g. (9.6%) of bis(heptafluoropropyl)ethoxychlorosilane, b.p. 54-55°/4 mm.  $n_D^{20}$  1.3144.

**Silicon Tetrachloride.** Methylolithium (2.09 N, 1.05 moles) was added simultaneously with 34 g. (0.2 mole) of silicon tetrachloride dissolved in 100 ml. of ether to 310 g. (1.05 moles) of heptafluoro-1-iodopropane maintained between -55 and -65° during 1.5 hrs. The temperature was then maintained between -42 and -45° for six hours and below 25° for two hours. Distillation through the 18" glass helices-packed column gave 72 g. (47%) of hexafluoropropene and a fuming silane. The solid (210 grams) was filtered and the low boiling solvents was removed. The residue (18 g.) was then rectified through a 3' glass helices-packed Todd column to give crude tris(heptafluoropropyl)methylsilane b.p. 130-133° (1.9 g.),  $n_D^{20}$  1.3078,  $d_4^{20}$  1.65.

**Anal.** Calc'd for  $C_{10}H_3F_{21}Si$ : C, 21.80; H, 0.54; F, 72.6. Found: C, 25.2; H, 0.95; F, 71.7.

### Summary

The reaction of heptafluoropropylolithium with functional silanes has given compounds having a perfluoropropyl group attached directly to the silicon atom.

### Literature Cited

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