Study of the alkylation of chlorosilanes. Part I. Synthesis of tetra(1H, 1H, 2H, 2H-polyfluoroalkyl)silanes

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Abstract

The synthesis and structural characterization of tetra(1H,1H,2H,2H-polyfluoroalkyl)silanes with the same or different chain lengths C_nF_{2n+1} linked to Si ($1 \leqslant n \leqslant 6$) is reported.

When the synthesis was effected from chlorosilanes and fluorinated organomagnesium or organolithium reagents, the trialkylsilanes were obtained. The last fluorinated chain was introduced either via a fluoroalkyllithium reagent or by hydrosilylation of the trialkylsilanes.

Some properties and characterization by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy of the 1H,1H,2H,2H-polyfluoroalkylsilanes are described.

Introduction

The synthesis of tetra-alkylsilanes by organometallic routes, using an alkylmagnesium halide, or an alkyllithium compound on silicon halides or alkoxysilanes, has been described in the literature [1–6]. More recently, other routes via dialkylmagnesium [7] or aluminium alkyl compounds [8] have been reported and tetra–alkylsilanes of different molecular weights have been obtained.

Interesting characteristics of tetra–alkylsilanes, particularly those bearing different carbon number alkyl groups linked to the silicon, have been pointed out, such as their high flash point and favourable viscosity index. They have been proposed, therefore, as candidates for hydraulic and lubricant fluids for aerospace requirements, and also for high technology applications.

Moreover, tetra(1H,1H,2H,2H-polyfluoroalkyl)silanes have been known for some time [9, 10] and some of their properties have been shown to be interesting because of their thermal resistance and fluid compatibility. We have focused our interest on reconsidering the feasibility of the synthesis of fluoroalkylsilanes of higher molecular weight, following conventional reaction schemes based on magnesium and lithium organometallic compounds.

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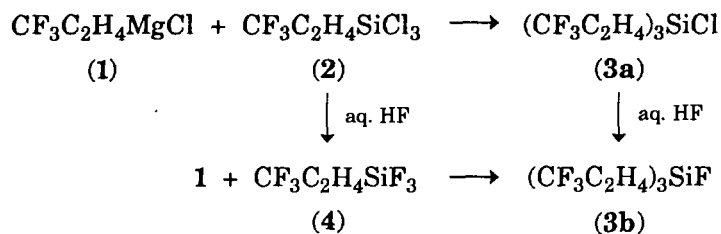
Results and discussion

The synthesis of tetra($1H,1H,2H,2H$-polyfluoroalkyl)silanes has been reported in the literature by Pierce *et al.* [9] and Haszeldine [10]. In addition, after describing the synthesis of $C_3F_7C_2H_4Br$, Pierce and his coworkers obtained the corresponding Grignard reagent and studied its reaction with $SiCl_4$ and $Si(OEt)_4$. With $SiCl_4$, the main product obtained was the trialkyl-chlorosilane (47%) along with the tetra-alkylsilane (10%), whilst with $Si(OEt)_4$ they showed that the mono- and di-alkylsilanes were the main products. In this work, characterization was by elemental analysis (C, H, F).

Haszeldine *et al.* reported the preparation of tetrakis(3,3,3-trifluoro-propyl)silane by reacting $SiCl_4$ with the Grignard reagent of $CF_3C_2H_4I$ (conversion 14%); a better yield was obtained by alkylation of trichlorosilane to give tris(3,3,3-trifluoropropyl)silane followed by its hydrosilylation with 3,3,3-trifluoropropene.

Apparently, no exhaustive alkylation of silicon halides with $1H,1H,2H,2H$-polyfluoroalkyl compounds has been reported for perfluoroalkyl groups longer than CF_3 and C_3F_7.

Synthesis of $(CF_3C_2H_4)_4Si$

First, we explored the addition of 3,3,3-trifluoropropylmagnesium chloride (1) to 3,3,3-trifluoropropyltrichlorosilane (2) in ether. Although an excess of Grignard reagent was used, we only obtained the trialkylsilane $(CF_3C_2H_4)_3SiCl$ (3a) (Scheme 1). Compound 3a was identified after transformation into the corresponding tris(trifluoropropyl)fluorosilane, $(CF_3C_2H_4)_3SiF$ (3b), by reaction with aqueous HF and subsequent distillation. Identification was achieved by ^{29}Si NMR spectroscopy; substitution of Cl by F on the Si atom facilitates the interpretation. The coupling between Si and F ($J_{Si-F} = 289$ Hz) is very important; it is consistent with the literature value [11], the presence of a doublet indicating substitution at Si by three alkyl groups. The ^{19}F NMR spectrum also confirmed the structure, a classical triplet for CF_3 (relative intensity, 9F) and a singlet for Si–F (1F) being present in the correct ratio.

$$CF_3C_2H_4MgCl + CF_3C_2H_4SiCl_3 \longrightarrow (CF_3C_2H_4)_3SiCl$$
$$(1) \qquad\qquad (2) \qquad\qquad\qquad (3a)$$

$$\downarrow \text{aq. HF} \qquad\qquad \downarrow \text{aq. HF}$$

$$1 + CF_3C_2H_4SiF_3 \longrightarrow (CF_3C_2H_4)_3SiF$$
$$(4) \qquad\qquad\qquad (3b)$$

Scheme 1.

We have also carried out the alkylation of 3,3,3-trifluoropropyltrifluo-rosilane (4) via the Grignard reagent 1 (compound 4 was prepared from the corresponding trichlorosilane 2). In that case, as well, we were able to obtain and isolate only the tris(3,3,3-trifluoropropyl)fluorosilane (3b). This

last route gave higher yields of the trialkylsilane relative to the previous one.

Even when a large excess of Grignard reagent was used, it was not possible to obtain the tetrasubstituted compound, at least in a noticeable quantity. These results are in disagreement with those reported in the literature [9, 10].

Faced with the difficulty of optimizing exhaustive silane alkylation using a Grignard reagent, we have concentrated on exploring the feasibility of this alkylation via alkyllithium reagents (Scheme 2).

$$CF_3C_2H_4Cl + Li \longrightarrow CF_3C_2H_4Li \xrightarrow{Me_3SiCl} CF_3C_2H_4SiMe_3$$

(5)
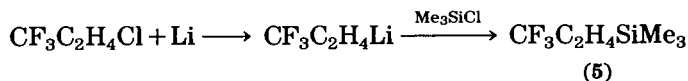
Scheme 2.

As a result of such a reaction compound **5** was isolated in 40% yield, its structure being confirmed by ^1H, ^{19}F and ^{29}Si NMR spectroscopy.

We have successfully repeated the alkylation of tris(trifluoropropyl)fluorosilane (**3b**) by $CF_3C_2H_4Li$ according to Scheme 3 and obtained tetrakis(trifluoropropyl)silane (**6**).

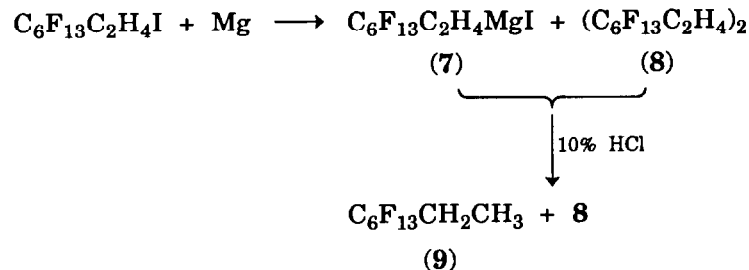$$CF_3C_2H_4Li + (CF_3C_2H_4)_3SiF \xrightarrow[-LiF]{} (CF_3C_2H_4)_4Si$$

(3b) (6)
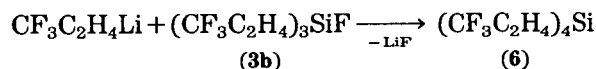
Scheme 3.

The structure of **6** was also confirmed by ^1H, ^{19}F and ^{29}Si NMR spectroscopy. The results showed that it was relatively easy to achieve exhaustive alkylation of trialkylhalosilanes by means of an organolithium reagent. For this reason, we have explored the same type of reaction on compounds involving longer perfluorinated groups.

Synthesis of $(C_6F_{13}C_2H_4)_3SiC_2H_4CF_3$

Tridecafluoro-octylmagnesium iodide (**7**) was prepared in ether solution. Grignard formation was followed by GC analysis on samples taken from the reaction mixture hydrolyzed with aqueous hydrochloric acid (Scheme 4).

$$C_6F_{13}C_2H_4I + Mg \longrightarrow C_6F_{13}C_2H_4MgI + (C_6F_{13}C_2H_4)_2$$

(7) (8)

$$\downarrow 10\% \ HCl$$

$$C_6F_{13}CH_2CH_3 + 8$$

(9)

Scheme 4.

Besides the expected alkane $C_6F_{13}CH_2CH_3$ (**9**), we observed the formation of compound **8** having the structure $C_6F_{13}C_2H_4-C_2H_4C_6F_{13}$. Although the
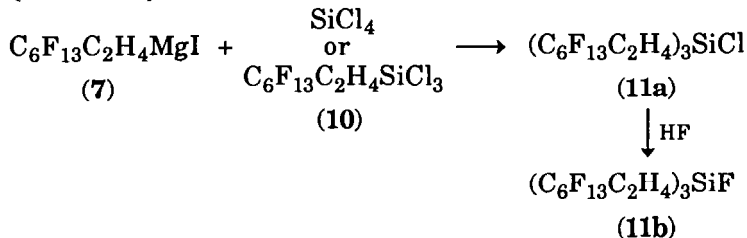
proportion of this dimer depended on the reaction conditions, even in very dilute solution (0.3 M) we obtained at least 20% of **8**. This result is in full agreement with those of von Werner *et al.* [12] who described the formation of compound **8** during the synthesis of carboxylic acids using the same Grignard reagent. Moreover, they demonstrated the influence of temperature on the reaction since the proportions of dimer and alkane changed from 37% and 45%, respectively, at 5 °C, to 48% and 26% at 35 °C. In contrast, they obtained only the alkane in 87% yield with an organozinc reagent. The ^{19}F NMR spectra of compounds **8** and **9** are identical to those described in the literature [12].

Compound **7** was capable of reaction with either tetrachlorosilane or the monosubstituted trichlorosilane **10** prepared by hydrosilylation [13] according to Scheme 5:

$$C_6F_{13}CH=CH_2 + HSiCl_3 \xrightarrow{H_2PtCl_6} C_6F_{13}C_2H_4SiCl_3$$
$$(10)$$
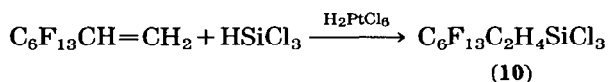
Scheme 5.

Alkylation of $SiCl_4$ or compound **10** with a large excess of Grignard reagent **7** led to the formation of the trialkylsilane $(C_6F_{13}C_2H_4)_3SiCl$ (**11a**) as the main product, isolation in the pure state being possible by distillation. Compound **11a** was then converted to the monofluoride $(C_6F_{13}C_2H_4)_3SiF$ (**11b**) (Scheme 6).

$$
\begin{array}{ccc}
 & SiCl_4 & \\
C_6F_{13}C_2H_4MgI \; + & or & \longrightarrow \quad (C_6F_{13}C_2H_4)_3SiCl \\
(7) & C_6F_{13}C_2H_4SiCl_3 & (11a) \\
 & (10) & \\
\end{array}
$$

$$\downarrow HF$$

$$(C_6F_{13}C_2H_4)_3SiF$$
$$(11b)$$

Scheme 6.

The trialkylfluorosilane **11b** was then alkylated with $CF_3C_2H_4Li$ to give tris($1H,1H,2H,2H$-tridecafluoro-octyl)trifluoropropylsilane (**12**) (Scheme 7).

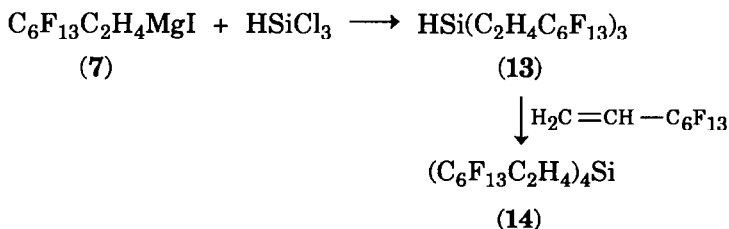$$11b + CF_3C_2H_4Li \xrightarrow[-LiF]{} (C_6F_{13}C_2H_4)_3SiC_2H_4CF_3$$
$$(12)$$
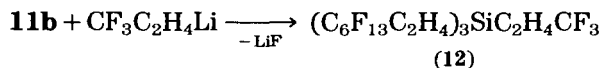
Scheme 7.

Compounds **11b** and **12** were characterized, as before, by NMR spectroscopy. The ^{29}Si NMR spectra showed a doublet ($J_{Si-F} = 289$ Hz) for **11b** and a singlet for **12** respectively, while in the ^{19}F NMR spectra compound **11b** exhibited resonances due to the C_6F_{13} group with a theoretical ratio of 39F relative to the signal of Si–F (1F), and compound **12** showed two different CF_3 resonances with theoretical ratios 9F and 3F corresponding to the terminal groups of the $C_6F_{13}C_2H_4$ and $CF_3C_2H_4$ chains.

This result demonstrates that the steric hindrance associated with the three $C_6F_{13}C_2H_4$ chains does not prevent exhaustive alkylation via the lithium alkyl.

Synthesis of $(C_6F_{13}C_2H_4)_4Si$

Tetrakis($1H,1H,2H,2H$-tridecafluoro-octyl)silane (**14**) was obtained by the route already employed by Haszeldine *et al.* [10] for the preparation of $(CF_3C_2H_4)_4Si$ (Scheme 8).
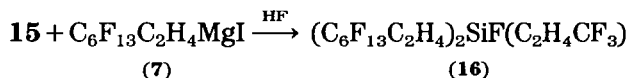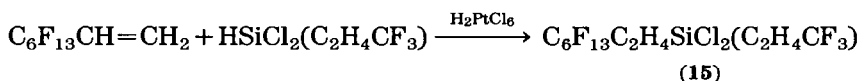
$$C_6F_{13}C_2H_4MgI \ + \ HSiCl_3 \ \longrightarrow \ HSi(C_2H_4C_6F_{13})_3$$

$$\text{(7)} \hspace{5cm} \text{(13)}$$

$$\Big\downarrow H_2C = CH - C_6F_{13}$$
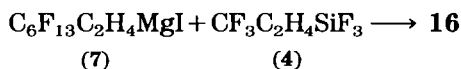
$$(C_6F_{13}C_2H_4)_4Si$$

$$\text{(14)}$$

Scheme 8.

The trialkylsilane **13** was obtained in high yield (88%). Its IR spectrum showed the characteristic absorption at 2150 cm^{-1} attributed to the Si−H bond. Its ^{1}H, ^{19}F and ^{29}Si NMR spectra confirmed the structure (singlet in the ^{29}Si NMR spectrum). Hydrosilylation of **13** with $C_6F_{13}-CH=CH_2$, using H_2PtCl_6 in 2-propanol as a catalyst, was successfully carried out in a sealed tube and the tetrafluoroalkylsilane **14** was obtained in 80% yield. It was identified by means of IR, ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy. The IR spectrum showed the absence of an absorption peak corresponding to the Si−H group while the ^{29}Si NMR spectrum exhibited a singlet.
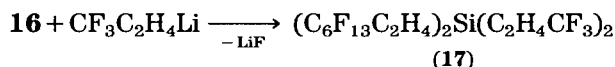
Synthesis of $(C_6F_{13}C_2H_4)_2Si(C_2H_4CF_3)_2$

Silane **17** was prepared by two alternative routes, Schemes 9 and 11, and Schemes 10 and 11:

$$C_6F_{13}CH=CH_2 + HSiCl_2(C_2H_4CF_3) \xrightarrow{H_2PtCl_6} C_6F_{13}C_2H_4SiCl_2(C_2H_4CF_3)$$

$$\text{(15)}$$

$$\mathbf{15} + C_6F_{13}C_2H_4MgI \xrightarrow{HF} (C_6F_{13}C_2H_4)_2SiF(C_2H_4CF_3)$$

$$\text{(7)} \hspace{4cm} \text{(16)}$$

Scheme 9.

$$C_6F_{13}C_2H_4MgI + CF_3C_2H_4SiF_3 \longrightarrow \mathbf{16}$$

$$\text{(7)} \hspace{3cm} \text{(4)}$$

Scheme 10.

$$\mathbf{16} + CF_3C_2H_4Li \xrightarrow[-LiF]{} (C_6F_{13}C_2H_4)_2Si(C_2H_4CF_3)_2$$

$$\text{(17)}$$

Scheme 11.

$1H,1H,2H,2H$-Tridecafluoro-octyl(trifluoropropyl)dichlorosilane (**15**) was prepared by hydrosilylation of $C_6F_{13}CH=CH_2$ with $HSiCl_2(C_2H_4CF_3)$. The structure of **15** was confirmed by ^1H, ^{19}F and ^{29}Si NMR spectroscopy. The ^{19}F NMR spectrum showed two different types of CF_3 with the same relative intensity, while the ^{29}Si NMR spectrum exhibited a singlet.

Dichlorosilane **15** was reacted with the Grignard compound according to Scheme 9: after treatment with HF, the bis(tridecafluoro-octyl)trifluoropropylmonofluorosilane (**16**) was isolated. Its ^{29}Si NMR spectrum showed a doublet ($J_{Si-F} = 289$ Hz).

Compound **16** was also obtained by reaction of the Grignard reagent with trifluoropropyltrifluorosilane (**4**) (Scheme 10).

Finally, the reaction of trifluoropropyllithium with the monofluorosilane **16** allowed bis($1H,1H,2H,2H$-tridecafluoro-octyl)bis(3,3,3-trifluoropropyl)-silane (**17**) to be obtained; this was also characterized by ^1H, ^{19}F and ^{29}Si NMR spectroscopy. The ^{29}Si NMR spectrum showed a singlet at $+7.15$ ppm in good agreement with a tetra-alkylsilane structure.

Experimental

IR spectra were recorded on a Perkin-Elmer 398 spectrophotometer. ^1H and ^{19}F NMR spectra were recorded on a Bruker CW60 or WH250 spectrometer, with TMS and $CFCl_3$ as references. ^{29}Si NMR spectra were recorded on a Bruker WP 80 spectrometer with TMS as a reference. Chemical shifts are reported in ppm units being denoted as follows: s = singlet, d = doublet, t = triplet and m = multiplet. All spectra were recorded for $CDCl_3$ solutions, the data obtained being reported in Tables 1, 2 and 3.. The boiling points of the $1H,1H,2H,2H$-polyfluoroalkylsilanes obtained are listed in Table 4. All Grignard syntheses and subsequent silylations were conducted under dry nitrogen.

General procedure for the synthesis of the Grignard reagent $R_F \cdot C_2H_4MgX$

In a 1 l flask equipped with a condenser, magnetic stirrer and dropping funnel containing 0.1 mol $R_FC_2H_4X$ diluted with 300 ml anhydrous ether, were placed 0.12 mol of magnesium turnings and 10 ml anhydrous ether. The magnesium was activated by adding two drops of dibromoethane. The ethereal solution of $R_FC_2H_4X$ was added slowly in order to maintain the ether at reflux. When the addition was complete, the mixture was left at reflux for 2 h. An aliquot of the solution was hydrolyzed with 20% aq. HCl solution and examined by gas chromatography (SE 30 column, 2 m) to determine the extent of the reaction.

General procedure for hydrosilylation

A solution consisting of 1.2 mol hydridosilane, 1 mol fluorinated olefin and 200 ppm of H_2PtCl_6 relative to the amount of olefin (10% solution of

TABLE 1

^{1}H NMR chemical shifts relative to TMS (multiplicity, relative intensity) for the different silane products

Silane	δ_H (ppm)		
	a (a')	b (b')	c
(CF$_3$CH$_2$CH$_2$)$_3$SiF (**3b**) a b	2.17 (m, 2H)	1.0 (t, 2H)	
CF$_3$CH$_2$CH$_2$SiF$_3$ (**4**) a b	2.3 (m, 2H)	1,2 (t, 2H)	
CF$_3$CH$_2$CH$_2$Si(CH$_3$)$_3$ (**5**) a b c	2.0 (m, 2H)	0.75 (m, 2H)	0.05 (s, 9H)
(CF$_3$CH$_2$CH$_2$)$_4$Si (**6**) a b	2.05 (m, 2H)	0.9 (m, 2H)	
C$_6$F$_{13}$CH$_2$CH$_3$ (**9**) a' b'	2.0 (m, 2H)	1.1 (t, 3H)	
(C$_6$F$_{13}$CH$_2$CH$_2$)$_3$SiCH$_2$CH$_2$CF$_3$ (**12**) a' b' b a	2.1 (m, 2H)	0.95 (m, 2H)	
(C$_6$F$_{13}$CH$_2$CH$_2$)$_3$SiH (**13**) a' b' c	2.1 (m, 6H)	1.0 (m, 6H)	3.95 (s, 1H)
(C$_6$F$_{13}$CH$_2$CH$_2$)$_4$Si (**14**) a' b'	2.1 (m, 2H)	1.0 (m, 2H)	
C$_6$F$_{13}$CH$_2$CH$_2$SiCl$_2$(CH$_2$CH$_2$CF$_3$) (**15**) a' b' b a	2.3 (m, 2H)	1.4 (m, 2H)	
(C$_6$F$_{13}$CH$_2$CH$_2$)$_2$SiF(CH$_2$CH$_2$CF$_3$) (**16**) a' b' b a	2.2 (m, 2H)	1.05 (m, 2H)	
(C$_6$F$_{13}$CH$_2$CH$_2$)$_2$Si(CH$_2$CH$_2$CF$_3$)$_2$ (**17**) a' b' b a	2.05 (m, 2H)	0.9 (m, 2H)	

H$_2$PtCl$_6$·6H$_2$O in 2-propanol) was placed in a glass tube which was sealed and heated overnight at 100 °C. After cooling and opening the tube, the black reaction mixture obtained was filtered and distilled.

General procedure for converting chlorosilanes to fluorosilanes [14]
    The ethereal solution of the chlorosilane obtained in the Grignard reaction was added to an equal volume of ethanol or acetone and treated with an excess of 40% HF at 0 °C. The resulting mixture was stirred at room temperature for a few hours (1–4 h) and then poured into a large excess

TABLE 2

^{19}F NMR chemical shifts relative to CFCl$_3$ (multiplicity, relative intensity) for the different silanes

$$C_6F_{13}C_2H_4 = CF_3CF_2CF_2CF_2CF_2CF_2C_2H_4, \quad CF_3C_2H_4, \quad SiF_n \ (n=1, 2, 3)$$

a f e d c b a' g

Silane	δ_F (ppm) a'	a	b	c	d	e	f	g
(CF$_3$C$_2$H$_4$)$_3$SiF (**3b**)	−69.7 (t, 9F)							−172.35 (1F)
CF$_3$C$_2$H$_4$SiF$_3$ (**4**)	−70 (t, 3F)							−138 (3F)
CF$_3$C$_2$H$_4$Si(CH$_3$)$_3$ (**5**)	−69 (t)							
(CF$_3$C$_2$H$_4$)$_4$Si (**6**)	−69.3 (t)							
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiF (**11b**)		−81.5 (9F)	−114 (6F)	−122.4 (6F)	−123.4 (6F)	−123.5 (6F)	−126.7 (6F)	−171.5 (1F)
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiC$_2$H$_4$CF$_3$ (**12**)	−70.3 (3F)	−82.4 (9F)	−117.5 (6F)	−123.3 (6F)	−124.3 (6F)	−124.8 (6F)	−127.7 (6F)	
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiH (**13**)		−82 (3F)	−117 (2F)	−122.8 (2F)	−123.7 (2F)	−124.2 (2F)	−127.1 (2F)	
(C$_6$F$_{13}$C$_2$H$_4$)$_4$Si (**14**)		−82 (3F)	−117 (2F)	−122.7 (2F)	−123.7 (2F)	−124 (2F)	−127 (2F)	
C$_6$F$_{13}$C$_2$H$_4$SiCl$_2$(C$_2$H$_4$CF$_3$) (**15**)	−69.5 (3F)	−81.9 (3F)	−116.8 (2F)	−122.8 (2F)	−123.5 (2F)	−124 (2F)	−127 (2F)	
(C$_6$F$_{13}$C$_2$H$_4$)$_2$SiF(C$_2$H$_4$CF$_3$) (**16**)	−69.5 (3F)	−81.5 (6F)	−117 (4F)	−122.5 (4F)	−123.5 (4F)	−124.5 (4F)	−127 (4F)	−172 (1F)
(C$_6$F$_{13}$C$_2$H$_4$)$_2$Si(C$_2$H$_4$CF$_3$)$_2$ (**17**)	−69.5 (3F)	−81.5 (3F)	−116.8 (2F)	−122.5 (2F)	−123.5 (2F)	−124 (2F)	−126.7 (2F)	

TABLE 3

^{29}Si NMR chemical shifts relative to TMS (multiplicity) and coupling constants for the different silanes

Silane	δ_{Si} (ppm)
(CF$_3$C$_2$H$_4$)$_3$SiF (3b)	+29.0 (d), J_{Si-F} = 289 Hz
CF$_3$C$_2$H$_4$SiF$_3$ (4)	−60.4 (q), J_{Si-F} = 278 Hz
CF$_3$C$_2$H$_4$Si(CH$_3$)$_3$ (5)	+2.49 (s)
(CF$_3$C$_2$H$_4$)$_4$Si (6)	+6.34 (s)
C$_6$F$_{13}$C$_2$H$_4$SiCl$_3$ (10)	+11.5 (s)
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiCl (11a)	+31.6 (s)
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiF (11b)	+29.5 (d), J_{Si-F} = 289 Hz
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiC$_2$H$_4$CF$_3$ (12)	+7.91 (s)
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiH (13)	+2.0 (s)
(C$_6$F$_{13}$C$_2$H$_4$)$_4$Si (14)	+8.35 (s)
C$_6$F$_{13}$C$_2$H$_4$SiCl$_2$(C$_2$H$_4$CF$_3$) (15)	+31.02 (s)
(C$_6$F$_{13}$C$_2$H$_4$)$_2$SiF(C$_2$H$_4$CF$_3$) (16)	+29.36 (d), J_{Si-F} = 289 Hz
(C$_6$F$_{13}$C$_2$H$_4$)$_2$Si(C$_2$H$_4$CF$_3$)$_2$ (17)	+7.15 (s)

TABLE 4

Boiling points (°C/mmHg) for 1H,1H,2H,2H-polyfluoroalkylsilanes

Silane	Boiling point
(CF$_3$C$_2$H$_4$)$_3$SiF (3b)	93/20
CF$_3$C$_2$H$_4$SiF$_3$ (4)	43/760 (≡Lit. [15])
CF$_3$C$_2$H$_4$Si(CH$_3$)$_3$ (5)	40/20
(CF$_3$C$_2$H$_4$)$_4$Si (6)	135–140/20
C$_6$F$_{13}$C$_2$H$_4$SiCl$_3$ (10)	85/20 [PETRARCH b.p., 192]
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiCl (11a)	130/0.5
(C$_6$F$_{13}$C$_2$H$_4$)$_3$Si(C$_2$H$_4$CF$_3$) (12)	114/10^{-4}
(C$_6$F$_{13}$C$_2$H$_4$)$_3$SiH (13)	150/10^{-3}
C$_6$F$_{13}$C$_2$H$_4$SiCl$_2$(C$_2$H$_4$CF$_3$) (15)	112/20
(C$_6$F$_{13}$C$_2$H$_4$)$_2$SiF(C$_2$H$_4$CF$_3$) (16)	160–165/20
(C$_6$F$_{13}$C$_2$H$_4$)$_2$Si(C$_2$H$_4$CF$_3$)$_2$ (17)	96/7×10^{-2}

of water and extracted with ether. The ether solution was dried with Na$_2$SO$_4$ and concentrated, and the product distilled.

3,3,3-Trifluoropropylmagnesium chloride (1)

A solution of trifluoropropyl chloride in ether was reacted with Mg as described above. Hydrolysis of an aliquot of the solution only led to the corresponding hydrocarbon CF$_3$CH$_2$CH$_3$ with no dimer being formed.

Tris(3,3,3-trifluoropropyl)fluorosilane (3b)

From CF$_3$C$_2$H$_4$SiCl$_3$

A solution consisting of 0.055 mol (12.8 g) of 3,3,3-trifluoropropyl-trichlorosilane (2) in 120 ml dry ether was slowly added to a solution of

0.165 mol of the previously prepared Grignard reagent **1** in 550 ml dry ether. The mixture was refluxed for 24 h. After cooling, the mixture was treated with 10 ml acetone to destroy the unreacted Grignard reagent, filtered and distilled. A first fraction (b.p., 45–50 °C/20 mmHg) was isolated and shown to be $CF_3C_2H_4C(OH)(CH_3)_2$ (yield 74%). IR (film) (cm^{-1}): 3600–3200 (OH). ^{1}H NMR δ: 1.0 (s, 6H, $-C(CH_3)_2$); 1.6 (m, 2H, $CH_2C(CH_3)_2$); 1.9 (m, 2H, CF_3CH_2); 3.4 (s, 1H, OH)* ppm. ^{19}F NMR δ: -69 [t, CF_3CH_2 ($J = 10$ Hz)] ppm.

The residue containing the tris(trifluoropropyl)monochlorosilane (**3a**) was treated with 40% HF. After extraction and distillation, the corresponding monofluoride **3b** was obtained in 12% yield (based on $CF_3C_2H_4SiCl_3$); b.p., 93 °C/20 mmHg.

From $CF_3C_2H_4SiF_3$ (4)

The trifluorosilane **4** was prepared from 35 g (0.15 mol) $CF_3C_2H_4SiCl_3$ in 140 ml ethanol and treated with an excess (50 ml) of 40% HF at room temperature during 3 h. After distillation, 15.65 g (57% yield) of $CF_3C_2H_4SiF_3$ (**4**) was isolated; b.p., 43 °C/760 mmHg [15].

In the second step, 9.15 g (0.05 mol) of compound **4**, dissolved in 10 ml dry ether, was added to a solution of 0.165 mol of Grignard reagent **1** in 550 ml dry ether. The mixture was refluxed for 8 h. The resulting mixture was extracted and distilled to give 15.2 g (90% yield) of $(CF_3C_2H_4)_3SiF$ (**3b**); b.p., 93 °C/20 mmHg.

3,3,3-Trifluoroprolyltrimethylsilane (5)

First, 3,3,3-trifluoropropyllithium under argon was prepared. Thus 9 g of Li dispersed in mineral oil was washed with pentane and placed in 20 ml dry ether. This suspension was cooled to -33 °C and 11.94 g (9×10^{-2} mol) of $CF_3C_2H_4Cl$, dissolved in 40 ml dry ether, was added slowly through a dropping funnel. The mixture was then stirred overnight at -33 °C. GC analysis of an aliquot hydrolyzed by 20% HCl showed the formation of the corresponding alkane and no unreacted $CF_3C_2H_4Cl$.

To a freshly prepared solution of $CF_3C_2H_4Li$ in ether at -33 °C was slowly added 21.6 g (0.2 mol) of trimethylchlorosilane, $(CH_3)_3SiCl$, in 20 ml ether. The resulting mixture was then stirred for 8 h at -33 °C and for 24 h at room temperature. After filtration, it was treated with acetone/40% HF according to the general procedure $Si-Cl \rightarrow Si-F$, washed with water, dried over Na_2SO_4 and distilled to give 13.6 g (40% yield) of 3,3,3-trifluoropropyltrimethylsilane (**5**); b.p., 40 °C/20 mmHg.

Tetrakis(3,3,3-trifluoropropyl)silane (6)

The synthesis was conducted in an argon atmosphere. A solution consisting of 15 g (4.5×10^{-2} mol) of tris(3,3,3-trifluoropropyl)fluorosilane (**3b**) in 10 ml dry ether was added dropwise to 45 ml of a solution of $CF_3C_2H_4Li$ in

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*Peak position varied with dilution of solution.

ether at -33 °C (prepared from 11.94 g (9×10^{-2} mol) of $CF_3C_2H_4Cl$ and an excess of Li). The excess lithium and the unreacted organolithium reagent were cautiously treated with ethanol. Then the mixture was treated with 40% HF and worked-up previously described to yield, after distillation, 60% of tetrakis(3,3,3-trifluoropropyl)silane (**6**); b.p., 135–140 °C/20 mmHg.

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Using the general procedure described above, tridecafluoro-octyl magnesium iodide (**7**) was prepared from 47.4 g (0.1 mol) of $C_6F_{13}C_2H_4I$ and 3.65 g (0.15 mol) of Mg in 350 ml dry ether (0.3 M solution). After 2 h at reflux, the mixture was hydrolyzed with 50 ml of 20% aq. HCl and the ether distilled to give 13.9 g (20% yield) of dimer $(C_6F_{13}C_2H_4)_2$ (**8**); b.p., 95 °C/0.5 mmHg (lit. [12] m.p., 49 °C) and 27.8 g (80% yield) of tridecafluoro-octane $C_6F_{13}C_2H_5$ (**9**); b.p., 125 °C/760 mmHg.

(Tridecafluoro-octyl)trichlorosilane (10)

Following the general procedure for hydrosilylation described above, the trichlorosilane **10** was obtained in 83% yield from tridecafluoro-octene $C_6F_{13}CH=CH_2$ and trichlorosilane $HSiCl_3$; b.p., 85 °C/20 mmHg.

Tris(tridecafluoro-octyl)chlorosilane (11a) and tris(tridecafluoro-octyl)fluorosilane (11b)

From $C_6F_{13}C_2H_4SiCl_3$

(Tridecafluoro-octyl)trichlorosilane (**10**) (4.815 g, 0.01 mol) dissolved in 5 ml dry ether was added to a solution containing 0.04 mol of $C_6F_{13}C_2H_4MgI$ (**7**) [prepared from 23.7 g (0.05 mol) of $C_6F_{13}C_2H_4I$ in 150 ml ether]. After 18 h at reflux, the mixture was hydrolyzed with 20% aq. HCl to decompose the unreacted Grignard reagent and the ether layer was separated, concentrated and distilled *in vacuo* to give 27% of tris(tridecafluoro-octyl)chlorosilane (**11a**); b.p., *c.* 130 °C/0.5 mmHg.

Treatment of **11a** with 40% HF using the general procedure led to tris(tridecafluoro-octyl)fluorosilane (**11b**).

From $SiCl_4$

Tetrachlorosilane (3.4 g, 0.02 mol) in 10 ml anhydrous ether was added to a solution containing 0.16 mol of $C_6F_{13}C_2H_4MgI$ (**7**) in 600 ml ether. After 4 h at reflux, the ether was distilled off and replaced by 150 ml dibutyl ether. The mixture was heated at 90 °C for 2 h. The ether layer was then separated and treated with ethanol/40% HF to give 46% of tris(tridecafluoro-octyl)fluorosilane (**11b**).

Tris(tridecafluoro-octyl)trifluoropropylsilane (12)

A solution consisting of 5.44 g (5×10^{-3} mol) of $(C_6F_{13}C_2H_4)_3SiF$ (**11b**) in 10 ml anhydrous ether was added, under argon, to a solution of 0.15 mol of $CF_3C_2H_4Li$ in 100 ml ether, cooled at -33 °C. The mixture was stirred at -33 °C for 5 h, then left for 3 d at room temperature. The ether

solution was filtered and distilled to give 3.38 g (58% yield) of tris(tridecafluoro-octyl)trifluoropropylsilane (**12**); b.p., 114 °C/10^{-4} mmHg.

Tris(tridecafluoro-octyl)hydrogenosilane (13)

Trichlorosilane, HSiCl$_3$ (2.71 g, 0.02 mol), in 5 ml anhydrous ether was added under nitrogen to a solution of 0.09 mol of C$_6$F$_{13}$C$_2$H$_4$MgI (**7**) in 225 ml ether. The mixture was refluxed for 18 h when two phases were formed. The ether solution was separated and distilled to give 18.83 g (88% yield) of tris(tridecafluoro-octyl)silane (**13**); b.p., 150 °C/10^{-3} mmHg. IR (film between KBr plates) (cm^{-1}): 2150 (Si—H).

Tetrakis(tridecafluoro-octyl)silane (14)

Silane **13** (6.42 g, 6×10^{-3} mol) was reacted with 2.49 g (7.2×10^{-3} mol) of C$_6$F$_{13}$CH=CH$_2$ and 20 μl of 10% H$_2$PtCl$_6$ solution in 2-propanol. After filtration of the crude product, an oily liquid was obtained which was GC analysed and contained no **13**. The new product which was formed quantitatively was tetrakis(tridecafluoro-octyl)silane (**14**). IR (film between KBr plates) (cm^{-1}): 1400–1100 (fluorinated chain) (no Si—H absorption at 2150 cm^{-1}).

Tridecafluoro-octyl(trifluoropropyl)dichlorosilane (15)

From 11.82 g (0.06 mol) of trifluoropropyldichlorosilane, CF$_3$C$_2$H$_4$-Si(H)Cl$_2$, reacted with tridecafluoro-octene, C$_6$F$_{13}$CH=CH$_2$, according to the general procedure for hydrosilylation, was obtained 27.69 g (85% yield) of compound **15**; b.p., 112 °C/20 mmHg.

Bis(tridecafluoro-octyl)trifluoropropylfluorosilane (16)

A solution consisting of CF$_3$C$_2$H$_4$SiF$_3$ (**4**) (0.025 mol) diluted in 10 ml anhydrous ether was added dropwise to a solution of 0.08 mol of C$_6$F$_{13}$C$_2$H$_4$MgI (**7**) in 300 ml anhydrous ether (made from 0.1 mol of C$_6$F$_{13}$C$_2$H$_4$I). The mixture was held for 8 h at reflux and 24 h at room temperature, then reacted with ethanol/40% HF, as usual, and extracted to yield 11.1 g (53% yield) of bis(tridecafluoro-octyl)trifluoropropylfluorosilane (**16**); b.p., 160–165 °C/20 mmHg.

Bis(tridecafluoro-octyl)bis(trifluoropropyl)silane (17)

Fluorosilane **16** (8.39 g, 0.01 mol) in 10 ml anhydrous ether was added, under argon, to a freshly prepared solution of 0.09 mol of CF$_3$C$_2$H$_4$Li in 60 ml anhydrous ether at −33 °C. The mixture was left for 5 h at −33 °C, then for 18 h at room temperature. The excess lithium reagent was cautiously decomposed with ethanol. The resulting mixture was treated with 5 ml of 40% HF and extracted to yield after distillation 4.58 g (50% yield) of bis(tridecafluoro-octyl)bis(trifluoropropyl)silane (**17**); b.p., 96 °C/7×10^{-2} mmHg.

Conclusion

Several tetra(1*H*,1*H*,2*H*,2*H*-polyfluoroalkyl)silanes have been obtained by alkylation of halosilanes with fluoroalkyl organometallic reagents (Mg, Li). Generally, Grignard reagents led to the formation of a trialkylhalosilane as the main product, while 3,3,3-trifluoropropyllithium gave rise to exhaustive alkylation.

In one case, the tetraalkylsilane was also obtained by hydrosilylation of a trialkylsilane, prepared using a Grignard reagent.

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