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Study of the alkylation of chlorosilanes. Part III. Synthesis and reactivity of new fluorinated organolithium reagents

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Abstract

The effect of the structure of the fluoroalkyl group $R_FC_2H_4$, where $R_F=CF_3$, C_6F_{13} and $(CF_3)_2CF$, on the synthesis and reactivity of organolithium reagents $R_FC_2H_4Li$ towards trimethylchlorosilane, $(CH_3)_3SiCl$, and tris(fluoroalkyl)silanes, $R_1R_2R_3SiF$, where $R = R_FC_2H_4$, has been studied. As a result, new fluorinated organolithium reagents have been synthesized, as well as new silanes such as a tris(fluoroalkyl)fluorosilane, $[(CF_3)_2CFC_2H_4]_2SiF(C_2H_4C_6F_{13})$, and fluorinated tetraalkylsilanes such as $C_6F_{13}C_2H_4Si(CH_3)_3$ and $[(CF_3)_2CFC_2H_4]_2Si(C_2H_4C_6F_{13})(C_2H_4C_6F_{13})$. All the products have been characterized by ¹H, ¹⁹F and ²⁹Si NMR spectroscopy.

Keywords: Synthesis; Reactivity; Alkylation; Fluorinated organolithium reagents; NMR spectroscopy

1. Introduction

The synthesis of non-fluorinated tetraalkylsilanes using organomagnesium or organolithium reagents has been reported previously [1–6]. Few examples of the synthesis of tetra(fluoroalkyl)silanes are known and they were obtained using mainly organomagnesium reagents [7,8].

In a previous publication [9], we described the synthesis of new tetra(fluoroalkyl)silanes via organometallic reagents (magnesium and lithium) and we showed that with fluoroalkyl Grignard reagents $R_FC_2H_4MgX$ (where R_F is a perfluorinated chain) it was possible to introduce only three $R_FC_2H_4$ chains on a silane. The introduction of the fourth fluoroalkyl chain was achieved either by using a fluoroalkyllithium reagent $CF_3C_2H_4Li$, or by hydrosilylation [9,10].

In this paper, we deal only with the use of fluoroalkyllithium reagents $R_FC_2H_4Li$. We have been interested in the influence of the structure of the R_F chain, $R_F = CF_3$, C_6F_{13} and $(CF_3)_2CF$, on the synthesis of organolithium reagents in ether (Et₂O), dibutyl ether ("Bu₂O) and tetrahydrofuran (THF), and on the reactivity of these reagents towards $(CH_3)_3SiCl$ and $(CF_3C_2H_4)_3SiF$. The purpose of this study was the synthesis of new tetra(fluoroalkyl)silanes, $R_1R_2R_3R_4Si$, via the reaction of R_4Li with $R_1R_2R_3SiX$ (where $R_i = R_FC_2H_4$ and X = Cl, F).

Because of their physical and thermal properties, the liquid tetra(fluoroalkyl)silanes are potentially interesting for high technology applications, such as aerospace or electronics [9].

2. Results and discussion

2.1. Synthesis of the lithium reagent $R_F C_2 H_4 Li$ (1)

Following the general method reported by Gilman et al. [11] for the synthesis of non-fluorinated n-alkyllithium reagents, we reacted a 1.5 M solution of 2perfluoroalkyl 1-halogenoethane, $R_FC_2H_4X$ (X = Cl, Br, I), with an excess lithium in an aprotic solvent [diethyl ether (Et₂O), dibutyl ether ("Bu₂O) or tetrahydrofuran (THF)] (see Table 1).

The reaction was followed by gas chromatography after hydrolysis (with 20% HCl) of an aliquot of the reaction mixture (Scheme 1). Generally, the extent of conversion and the selectivity of the synthesis depended on the nature of the R_F chain and of the halogen atom

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Table 1 Summary of the results obtained for the synthesis of $R_F C_2 H_4 Li$ in $Et_2 O$ or "Bu_2 O

$R_F C_2 H_4 X$	Solvent	Temp.	Time	Yield (%)	
		(°C)	(n)	R _F C ₂ H ₅ (3)	$(R_FC_2H_4)_2$ (2)
CF ₃ C ₂ H ₄ Cl	Et ₂ O	-33	19	100	0
$C_6F_{13}C_2H_4Cl$	Et ₂ O	20	19	0	0
	ⁿ Bu ₂ O	80	38	0	0
C ₆ F ₁₃ C ₂ H ₄ Br	Et ₂ O	20	19	0	0
	"Bu ₂ O	80	38	50	50
$C_6F_{13}C_2H_4I$	Et ₂ O	20	19	50	50
	"Bu ₂ O	20	19	50	50
(CF ₃) ₂ CFC ₂ H ₄ I	Et ₂ O	20	19	24	76
$C_4F_9CF_2CF(CF_3)C_2H_4I$	Et ₂ O	20	48	0	0

$$\begin{array}{cccc} R_FC_2H_4X + Li & \longrightarrow & R_FC_2H_4Li + (R_FC_2H_4)_2 \\ (X=Cl, Br, I) & (1) & (2) \\ & & \downarrow & 20\% \ HCl \\ & & R_FC_2H_5 + 2 \\ & & (3) \end{array}$$

Scheme 1.

X, on the solvent and on the temperature. Dimerization can occur during the synthesis [12], especially when X=I. The results of the reactions carried out in Et₂O or ⁿBu₂O are summarized in Table 1.

These results show that when R_F is a linear chain, the yield of $R_FC_2H_4Li$ decreased as the length of R_F increased. The formation of $R_FC_2H_4Li$ was even more difficult with branched R_F and here, also, the yield of $R_FC_2H_4Li$ decreased as the steric hindrance of R_F increased. For the same perfluorinated chain, $R_F = C_6F_{13}$, for $R_FC_2H_4X$, it was found that the organolithium reagent formed more readily for the iodide (X=I) than for the bromide (X=Br) and was not possible when starting from the chloride (X=CI).

Hence, we decided to explore the use of the solvent THF, to see if it would be possible to obtain $C_6F_{13}C_2H_4Li$ from $C_6F_{13}C_2H_4Cl$ or from $C_6F_{13}C_2H_4Br$ under milder conditions and with a better yield than in "Bu₂O. However, in THF, we observed the formation of mainly 1H, 1H, 2H-tridecafluoro-octene (4) and no lithium reagent (Scheme 2). The reaction was started at 0 °C and left for one day at 0 °C, and for two more days at 20 °C.

$$C_{6}F_{13}C_{2}H_{4}X + Li \xrightarrow[(0-20 \circ C, 2-3 d)]{} C_{6}F_{13}CH = CH_{2}$$

$$(X = Cl, Br) \qquad (4)$$

Scheme 2.

The ¹H and ¹⁹F NMR spectra of olefin 4 confirmed the structure as all the expected signals were exhibited, i.e. a complex system centred at δ 5.8 ppm for the vinyl protons and the six signals for the CF₃CF₂CF₂CF₂CF₂CF₂ chain, respectively.

A study of the stability of n-butyllithium ("BuLi) in THF [13] at various temperatures has shown that "BuLi begins to decompose slowly at low temperature (6% decomposition after 12 h at -30 °C, 38% decomposition after 22 h at 0 °C) and is totally decomposed after 47 h at 0 °C or after 2 h at 27 °C. Two mechanisms have been proposed [14,15] to explain the decomposition (Scheme 3).



Scheme 3.

The presence of the entities α or β could possibly induce the dehydrohalogenation of the remaining RX in the reaction mixture, leading to olefin 4 in our case. However, after hydrolysis of an aliquot of the reaction mixture, we could only identify $R_FCH=CH_2$ (4) with neither RH nor R(CH₂)₄OH being observed.

Having obtained the new organolithium reagents, the reactivities of $CF_3C_2H_4Li$ and $C_6F_{13}C_2H_4Li$ were compared.

2.2. Study of the reactivity of $R_F C_2 H_4 Li$

2.2.1. Reactivity towards (CH₃)₃SiCl

An excess of trimethylchlorosilane was added to an ethereal solution of $R_F C_2 H_4 Li$ and the corresponding (fluoroalkyl)trimethylsilane (5) was obtained (Scheme 4).

It was noted that the yield of compound 5 decreased as the length of the R_F chain increased.

Compounds 5 were isolated after treatment of the reaction mixture with ethanol to eliminate the excess lithium reagent and then with 40% HF, according to Ref. [16], to convert the unreacted $(CH_3)_3SiCl$ into the corresponding volatile fluorosilane $(CH_3)_3SiF$ (b.p. 16–18 °C).

$$R_{F}C_{2}H_{4}Li + (CH_{3})_{3}SiCl \longrightarrow R_{F}C_{2}H_{4}Si(CH_{3})_{3} + LiCl$$
(5)

(a)
$$R_F = CF_3$$
 5a 40%
(b) $R_F = C_6F_{13}$ 5b 20%

Scheme 4.

The (trifluoropropyl)trimethylsilane (5a) which was obtained in 40% yield has been described previously [9]; the (tridecafluoro-octyl)trimethylsilane (5b) was obtained in 20% yield after distillation (b.p. 130 °C). Its structure was confirmed from its ¹H and ¹⁹F NMR spectra (see Table 2).

In order to study the effect of the nature of the halogen atom X in the reaction of R₁R₂R₃SiX with $R_FC_2H_4Li$, we decided to explore the addition of $R_FC_2H_4Li$ [where $R_F = CF_3$, C_6F_{13} and $(CF_3)_2CF$] to $(CF_3C_2H_4)_3SiF.$

2.2.2. Reactivity towards $(CF_3C_2H_4)_3$ SiF

The tris(trifluoropropyl)fluorosilane $(CF_3C_2H_4)_3SiF$ was added to an excess of R_FC₂H₄Li diluted in Et₂O at -33 °C. After 8 h at -33 °C, the mixture was left at 20 °C for 24 h (Scheme 5).

$$(CF_{3}C_{2}H_{4})_{3}SiF + R_{F}C_{2}H_{4}Li \xrightarrow{-LiF} R_{F}C_{2}H_{4}Si(C_{2}H_{4}CF_{3})_{3}$$
(6)
(a) $R_{F}=CF_{3}$
(b) $R_{F}=C_{6}F_{13}$
(c) $R_{F}=(CF_{3})_{2}CF$
(6)

0%

Scheme 5.

Under these conditions, only CF₃C₂H₄Li reacted with $(CF_3C_2H_4)_3SiF$ (which is more hindered than (CH₃)₃SiCl) to give the tetrakis(trifluoropropyl)silane (6a) [9]. Considering that $CF_3C_2H_4Li$ was prepared in quantitative yield and was more reactive than $C_6F_{13}C_2H_4Li$ and $(CF_3)_2CFC_2H_4Li$ towards \geq SiCl or SiF, we decided to select this lithium reagent and study its reactions with $R_1R_2R_3SiF$, since this appeared to be more reactive than $R_1R_2R_3SiCl$ [17–19]. Since R_1 , R_2 and R_3 are fluoroalkyl chains, we should thus be able to prepare tetra(fluoroalkyl)silanes.

2.2.3. Synthesis of tetra(fluoroalkyl)silanes (9)

Trifluoropropyl lithium was reacted with three different fluorosilanes 8a, 8b and 8c to yield the corresponding tetra(fluoroalkyl)silanes 9a, 9b and 9c (Scheme 6).

 $R_1R_2R_3SiF + CF_3C_2H_4Li \longrightarrow (CF_3C_2H_4)SiR_1R_2R_3$ (8) (9)

(a)
$$R_1 = R_2 = C_2 H_4 C_6 F_{13}$$

 $R_3 = C_2 H_4 C F_3$ 9a 50%(b) $R_1 = R_2 = R_3 = C_2 H_4 C_6 F_{13}$ 9b 58%(c) $R_1 = R_2 = C_2 H_4 C F(CF_3)_2$
 $R_3 = C_2 H_4 C_6 F_{13}$ 9c 50%

We have reported the synthesis and spectroscopic data for compounds 8a, 8b, 9a and 9b in a previous paper [9].

To synthesize the tetra(fluoroalkyl)silane 9c, we first prepared the monofluorosilane 8c according to the following route (Scheme 7):

$$C_{6}F_{13}C_{2}H_{4}SiCl_{3} \xrightarrow{HF} C_{6}F_{13}C_{2}H_{4}SiF_{3}$$
(7)
(CF_{3})_{2}CFC_{2}H_{4}MgI + 7 \longrightarrow
(excess)
$$[(CF_{3})_{2}CFC_{2}H_{4}]_{2}SiF(C_{2}H_{4}C_{6}F_{13})$$
(8c) (56%)

Scheme 7.

In the first step, (tridecafluoro-octyl)trichlorosilane was converted quantitatively to the corresponding trifluorosilane 7 by the addition of 48% aqueous HF in ethanol [20]. Then, compound 7 was reacted with an excess of Grignard reagent, (CF₃)₂CFC₂H₄MgI, to give the monofluorosilane 8c in 56% yield. The ¹H, ¹⁹F and ²⁹Si NMR data for compounds 7, 8c and 9c are summarized in Table 2.

The ¹⁹F NMR spectrum of compound 9c exhibits a triplet at -69.2 ppm for the CF₃C₂H₄ group just introduced into the molecule, with no signal at -172.5ppm characteristic of the initial Si-F group in 8c being present. The fluorosilane 8c exhibited a doublet at +28.8 ppm in the ²⁹Si NMR spectrum, with $^{1}J(\text{Si-F}) = 290 \text{ Hz}$, and compound **9c** exhibited a singlet at +7.53 ppm which is consistent with a tetraalkyl Si atom [9,21].

3. Experimental details

NMR spectra were recorded on Bruker WP 200 or WH 250 spectrometers with TMS as reference for ¹H and ²⁹Si NMR and CFCl₃ as reference for ¹⁹F NMR. Chemical shifts are reported in ppm: s=singlet, d = doublet, t = triplet, q = quadruplet and m = multiplet. All spectra were recorded for CDCl₃ solutions, the data obtained being reported in Table 2.

3.1. General procedure for the synthesis of $R_F C_2 H_4 Li$ in Et_2O or nBu_2O

Lithium (9 g) dispersed in mineral oil (containing 25 wt.% of pure Li) was introduced into a two-necked flask, equipped with a condenser, and a dropping funnel, and placed under a stream of argon. The lithium was washed with 2×60 ml of anhydrous pentane and then

and ¹H NMR spectra of silanes 5b, 7, 8c and 9c

Table 2

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the pentane was replaced by 20 ml of Et₂O or ⁿBu₂O. The reaction was started by the addition of five drops of 1,2-dibromoethane and then a solution consisting of 9×10^{-2} mol of halide $R_FC_2H_4X$ in 40 ml of Et₂O was added dropwise.

All the reactions were followed by gas chromatography after hydrolysis of an aliquot with 20% HCl. The aliquot was successively co-injected with previously synthesized $R_FC_2H_5$, $(R_FC_2H_4)_2$ and $R_FCH=CH_2$ to establish whether or not the organolithium reagent had been formed.

3.2. Synthesis of $C_6F_{13}C_2H_4Li$ in Et_2O/THF or THF

Using the general procedure described above, after washing the lithium the pentane was replaced by 20 ml of anhydrous THF or by a mixture of 20 ml Et₂O and 20 ml THF. After 8 h at 0 °C and 2 d at 20 °C, the crude reaction mixture was cautiously treated with 20% HCl/EtOH. The organic layer was dried and after distillation gave 1H, 1H, 2H-tridecafluoro-octene, C₆F₁₃CH=CH₂ (b.p. 102 °C).

3.3. (Tridecafluoro-octyl)trimethylsilane (5b)

Trimethylchlorosilane (32.9 g, 0.3 mol) in 30 ml of Et₂O was added dropwise to a solution of $C_6F_{13}C_2H_4Li$ in 250 ml of Et₂O. After 2 d at 20 °C, the unreacted $C_6F_{13}C_2H_4Li$ was eliminated with EtOH and the reaction mixture treated with 12 ml of 40% HF, washed with water, dried and distilled, to yield 12 g (20%) of silane **5b** (b.p. 130 °C). ²⁹Si NMR δ : +2.5 (s) ppm.

3.4. (3,3,3-Trifluoropropyl)(tridecafluoro-octyl) bis(2-perfluoro-isopropylethyl)silane (9c)

C₆F₁₃C₂H₄SiCl₃ (31 g, 0.0642 mol) was treated at 0 °C with 47 ml of EtOH and 30 ml of 48% HF [20] to give 27.5 g of (tridecafluoro-octyl)trifluorosilane, C₆F₁₃C₂H₄SiF₃ (7). Yield, 99%; b.p. 39 °C/20 mmHg. ²⁹Si NMR δ: -60.41 (q, ¹*J*(Si–F)=278 Hz) ppm.

The Grignard reagent $(CF_3)_2CFC_2H_4MgI$ was prepared in Et₂O from the corresponding iodide according to the procedure previously described [9] giving 70% yield of the Grignard reagent together with 30% yield of dimer [(CF₃)₂CFC₂H₄]₂. Compound 7 (12.4 g, 0.029 mol) dissolved in 6 ml of Et₂O was added dropwise to a solution of 0.09 mol of Grignard reagent in 306 ml of Et₂O. After 19 h reflux, the mixture was cooled and treated with EtOH/40% HF. The organic layer was washed with water, dried over Na₂SO₄ and distilled to give 12.6 g of pure [(CF₃)₂CFC₂H₄]₂SiF(C₂H₄C₆F₁₃) (8c). Yield, 56%; b.p.141 °C/20 mmHg. ²⁹Si NMR δ : +28.8 (d, ¹J(Si-F) = 290 Hz) ppm.

C ₆ F ₁₃ C ₂ H4 = CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ CH ₂	(CF3)2CI	FCH2CH2	(CF _a)	cFCH2CH3	CF.3C	h ₂ ch ₂	$\operatorname{SiF}_{g,n}(n=)$	1, 3)					
Silanes	¹⁹ F NMI	R (CFCI ₃)	(mqq) õ								ίν Η _τ	AR (TN	(S) 8
											(mqq)		
	a,	a″	æ	q	J	q	υ	f	හ	ັໝ	CH3	CH_2	CH2
$C_6F_{13}C_2H_4Si(CH_3)_3$ (5b)			- 81.5	- 116.7	- 122.5	- 123.5	- 124	- 126.8			0.05	0.75	2.10
			(3F)	(2F)	(2F)	(2F)	(2F)				(H6)	(2H)	(2H)
$C_6F_{13}C_2H_4SiF_3$ (7)			- 82	- 117.6	- 122.7	- 123.6	- 124.2	- 127		- 138.2		1.27	2.26
			(3F)	(2F)	(2F)	(2F)	(2F)	(2F)		(3F)		(2H)	(2H)
$[(CF_3)_2CFC_2H_4]_2SiF(C_2H_4C_6F_{13}$ (8c)		- 76.5	-81.2	- 116.5	- 122.3	- 123.4	- 123.8	- 126.6	- 185	-172.5		1.10	2.20
		(12F)	(3F)	(2F)	(2F)	(2F)	(2F)	(2F)	(2F)	(2F)		(H9)	(H9)
$[(CF_3)_2CFC_2H_4]_2Si(C_2H_4C_6F_{13})(C_2H_4CF_3)$ (9c)	- 69.2	- 76	- 81.3	- 116.6	- 122.3	- 123.3	- 123.7	- 126.6	-184.3			0.9	2.10
	(3F)	(12F)	(3F)	(2F)	(2F)	(2F)	(2F)	(2F)	(2F)			(H8)	(H8)

Finally, 12 g (0.0154 mol) of fluorosilane **8c** diluted in 6 ml of Et₂O was added dropwise to a solution of 0.054 mol of CF₃C₂H₄Li in 36 ml of Et₂O. The mixture was stirred for 6 h at -33 °C, then 3 d at room temperature. The excess lithium reagent was cautiously eliminated with EtOH and then the mixture was treated with 40% HF. The organic layer was washed with water, dried over Na₂SO₄ and distilled to yield 6.75 g (50%) of silane **9c**; b.p. 84 °C/2×10⁻² mmHg. ²⁹Si NMR δ : +7.53 (s) ppm.

4. Conclusions

A study of the influence of the structure of the R_F chain on the synthesis of fluoroalkyllithium reagents, $R_FC_2H_4Li$, has shown that the greater the length and steric hindrance of R_F , the lower was the conversion of the organolithium reagents.

Three new $R_FC_2H_4Li$ compounds have been synthesized with $R_F = CF_3$, C_6F_{13} and $(CF_3)_2CF$. Their reactivities towards $(CH_3)_3SiCl$ or $(CF_3C_2H_4)_3SiF$ have been studied and it was again noted that yields during the addition of $R_FC_2H_4Li$ to SiX decreased when the length and steric hindrance of R_F increased. Tris(trimethyl)tridecafluoro-octyl silane, $C_6F_{13}C_2H_4Si(CH_3)_3$, and tetrakis(trifluoropropyl)silane, $(CF_3C_2H_4)_4Si$ (already known [7,9], have been prepared.

Finally, the reaction of $CF_3C_2H_4Li$ with different tris(fluoroalkyl)silane fluorides, $R_1R_2R_3SiF$, led to the corresponding tetra(fluoroalkyl)silanes.

References

- C. Tamborski and C.E. Snyder, Jr (to US Dept. of the Air Force), US Patent Application 336 474, 1982; [*Chem. Abs.*, 97 (1982) 198 373t].
- [2] G. Baum and C. Tamborski, J. Chem. Eng. Data, 6 (1961) 142.
- [3] H. Rosenberg, J.D. Groves and C. Tamborski, J. Org. Chem., 25 (1960) 243.
- [4] R.H. Meen and H. Gilman, J. Org. Chem., 23 (1958) 314.
- [5] H. Gilman and R.K. Ingham, J. Am. Chem. Soc., 77 (1955) 1680.
- [6] A.D. Petrov and E.A. Chernyshev, Dokl. Akad. Nauk. SSSR, 86 (1952) 737.
- [7] R.N. Haszeldine, M.J. Newlands and B.R. Iles, British Patent 1 075 101, 1967; [*Chem. Abs.*, 67 (1967) 100 240].
- [8] O.R. Pierce, E.T. McBee and R.E. Cline, J. Am. Chem. Soc. 75 (1953) 5618.
- [9] B. Boutevin, F. Guida-Pietrasanta, A. Ratsimihety, G. Caporiccio and G. Gornowicz, J. Fluorine Chem., 60 (1993) 211.
- [10] B. Boutevin, F. Guida-Pietrasanta, A. Ratsimihety and G. Caporiccio, J. Fluorine Chem., 68 (1994) 71.
- [11] H. Gilman, J.A. Bell, C.G. Brannen, M.W. Bullock, G.E. Dunn and L.S. Miller, J. Am. Chem. Soc., 71 (1949) 1499.
- [12] P. Powell, Principles of Organometallic Chemistry, 2nd edn., 1988, pp. 39-40.
- [13] H. Gilman and B.J. Gaj, J. Org. Chem., 22 (1957) 1165.
- [14] A. Rembaum, S.P. Siao and N. Indictor, J. Polym. Sci., 56 (1962) S17.
- [15] A. Maercker and W. Theysohn, *Liebigs Ann. Chem.*, 746 (1971) 70.
- [16] C. Eaborn, J. Chem. Soc., (1952) 2846.
- [17] W.H. Nebergall and O.H. Johnson, J. Am. Chem. Soc., 71 (1949) 4022.
- [18] M. Takakusa, Bull. Chem. Soc. Jpn., 36 (1963) 31.
- [19] A.D. Petrov and T.I. Chernysheva, J. Gen. Chem. USSR, 24 (1954) 1179, 1189; [Chem. Abs., 49 (1955) 12276c].
- [20] N.S. Marans, L.H. Sommer and F.C. Whitmore, J. Am. Chem. Soc., 73 (1951) 5127.
- [21] H. Marsmann, in P. Diehl, E. Fluck and R. Kosfeld (eds.), NMR Spectroscopy; Basic Principles and Progress, Springer Verlag, Berlin, 1981, Vol. 17, pp. 65–235.