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Perfluoro tertiary alcohols. III. (Perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes in the synthesis of perfluorinated tertiary alcohols*

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Abstract

High-molecular weight perfluorinated tertiary alcohols, $R_f^1R_f^2R_f^3C(OH)$ $\{R_f^1=n\text{-}C_8F_{17}$, $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$; $R_f^1=(CF_3)_2CFO(CF_2)_4$, $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$; $R_f^1=C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$, $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$; $R_f^1=n\text{-}C_8F_{17}$, $R_f^2=CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$, $R_f^3=(CF_3)_2CFO(CF_2)_2\}$ (**IIIa–d**), have been prepared by the reactions of (perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes (**Ia–d**) with fluoroketones (**IIa–c**). Ketones containing a trifluoromethyl group as well as higher molecular weight perfluorinated substituents have been studied under different experimental conditions. The yield of tertiary alcohol is influenced by the solvents, reaction temperatures, type and concentration of metal fluorides, and structures of the fluoroalkyltrimethylsilanes and fluoroketones. The reaction has been extended to carbonyl compounds other than ketones. While a perfluorinated secondary acid fluoride gave good yield of the ketone, no reaction was observed with esters.

1. Introduction

We have reported previously [1, 2] a convenient and high-yield synthesis procedure for the preparation of perfluoro tertiary alcohols via perfluorooxaalkyl-lithium intermediates, R_fLi. The relatively stable type of R_fLi, containing an oxygen atom β to the carbon atom attached to lithium, is required to convert ketones to tertiary alcohols.

Recently, DesMarteau et al. [3] have reported the preparation of fluorinated tertiary alcohols from carbonyl compounds, CF_3SiMe_3, and KF in CH_3CN at −40 °C. The isolated yields of $(CF_3)_3C(OH)$, $CF_3CF_2C(CF_3)_2OH$, $[(CF_3)_2CF]C(CF_3)_2(OH)$ and $CF_3(CF_2)_6C(CF_3)_2OH$ were 91.3%, 85.0%, 21.2% and ~10%, respectively. The CF_3SiMe_3 compound was prepared by reported methods [4].

We have investigated this approach utilizing silicon reagents as an alternative to our earlier method [1, 2] in preparing high-molecular weight perfluorinated tertiary alcohols from carbonyl compounds. Our results are presented here along with procedures for the preparation of (perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes, and some fluoroketones.

2. Results and discussion

2.1. Synthesis of (perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes, $R_f^1SiMe_3$ (I)

The silanes, $R_f^1SiMe_3$ (**I**), were prepared by two different methods as follows.

Method A: *Grignard reagent route* [5] – (*see Eq.* (1))

$$R_f^1I + RMgBr + ClSiMe_3 \xrightarrow[-60\ ^\circ C\ to\ -50\ ^\circ C]{THF/Et_2O} \underset{(\mathbf{I})}{R_f^1SiMe_3} \quad (1)$$

($R=CH_3$ or C_2H_5; **Ia**: $R_f^1=(CF_3)_2CFO(CF_2)_4$; **Ib**: $R_f^1=n\text{-}C_8F_{17}$)

Compounds **Ia** and **Ib** were synthesized by the metal–halogen exchange reactions [5] between the corresponding R_f^1I and methyl or ethyl magnesium bromide in the presence of trimethylchlorosilane in an in-situ manner in a THF/Et_2O mixture (2:1 by volume). This method is preferable for the preparation of primary $R_f^1SiMe_3$.

Method B: *modified procedure of Ruppert et al.* [4] – (*see Eq.* (2))

$$R_f^1I + ClSiMe_3 + (Et_2N)_3P \xrightarrow[\sim 0\ ^\circ C]{C_6H_5CN} \underset{(\mathbf{I})}{R_f^1SiMe_3} \quad (2)$$

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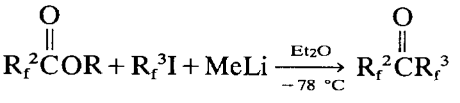
(**Ia**: $R_f^1 = (CF_3)_2CFO(CF_2)_4$:
Ic: $R_f^1 = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$;
Id: $R_f^1 = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$)

Compounds **Ia**, **Ic** and **Id** were prepared by reaction of the corresponding R_f^1I, trimethylchlorosilane and hexaethylphosphorus triamide in benzonitrile at ~0 °C. For secondary perfluorooxaalkyltrimethylsilanes (**Ic**, **d**), method B is preferable since much better yields were obtained compared to primary perfluorooxaalkyltrimethylsilane (**Ia**). The characterization data and NMR spectral data of compounds **Ia–d** are listed in Tables 1 and 2, respectively.

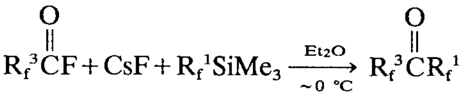
2.2. *Synthesis of perfluoroalkyl and perfluorooxaalkyl ketones*

The ketones $CF_3C(O)C_6F_{13}$ (**IIa**) and $CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2C(O)(CF_2)_2OCF(CF_3)_2$ (**IIb**) were synthesized by methods which we have previously reported [6], starting from perfluoroalkyl and perfluorooxaalkyl esters (Eq. (3)). Ketone **IIc** was prepared from perfluorooxaalkyl acid fluoride, CsF, and perfluorooxaalkyltrimethylsilane. This is a modified procedure of Farnham [5(b)] – Eq. (4). No reaction occurred when the reagents were mixed in the ratio of $R_f^3C(O)F/R_f^1SiMe_3/CsF = 1:1.1:1.1$. However, the reaction started when an additional amount of CsF (40% molar excess) was added to the reaction mixture. The products of the reaction are described in the Experimental section, and contained traces of perfluorinated tertiary alcohol (**IIIe**) and some decomposition products of $(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**).



$$R_f^2\overset{\overset{O}{\|}}{C}OR + R_f^3I + MeLi \xrightarrow[-78\ ^\circ C]{Et_2O} R_f^2\overset{\overset{O}{\|}}{C}R_f^3 \qquad (3)$$

(**IIa, b**)



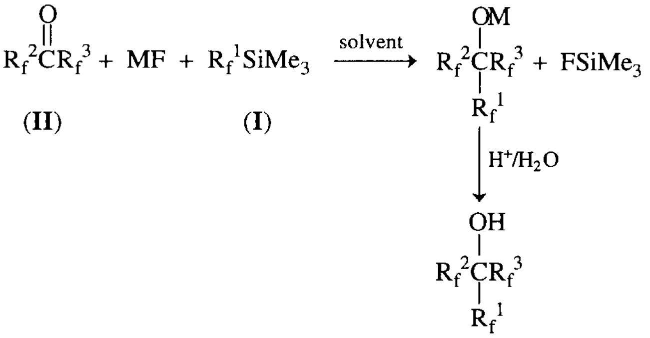
$$R_f^3\overset{\overset{O}{\|}}{C}F + CsF + R_f^1SiMe_3 \xrightarrow[\sim 0\ ^\circ C]{Et_2O} R_f^3\overset{\overset{O}{\|}}{C}R_f^1 \qquad (4)$$

(**IIc**)

(**IIc**:$R_f^1 = (CF_3)_2CFO(CF_2)_4$,
$R_f^3 = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$)

2.3. *Synthesis of perfluorinated tertiary alcohols*

The high molecular weight perfluoroalkyl and perfluorooxaalkyl tertiary alcohols (**IIIa–e**) were prepared by the reaction of perfluoroketones **IIa–c**, metal fluorides (MF), and (perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes according to Eq. (5).



$$R_f^2\overset{\overset{O}{\|}}{C}R_f^3 + MF + R_f^1SiMe_3 \xrightarrow{solvent} R_f^2\overset{OM}{\underset{R_f^1}{C}}R_f^3 + FSiMe_3 \xrightarrow{H^+/H_2O} R_f^2\overset{OH}{\underset{R_f^1}{C}}R_f^3$$

(**II**) (**I**) (**III**) (5)

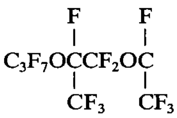
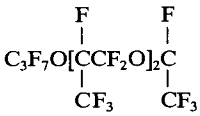
(M = K, Cs; solvent: THF, CH_3CN, Et_2O; **IIIa**: $R_f^1 = n\text{-}C_8F_{17}$, $R_f^2 = CF_3$, $R_f^3 = n\text{-}C_6F_{13}$; **IIIb**: $R_f^1 = (CF_3)_2CFO(CF_2)_4$, $R_f^2 = CF_3$, $R_f^3 = n\text{-}C_6F_{13}$; **IIIc**: $R_f^1 = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$, $R_f^2 = CF_3$,

TABLE 1. Preparation and characterization of (perfluoroalkyl)- and (perfluorooxaalkyl)-trimethylsilanes

Compound	Method[a]	Isolated yield (%)	Boiling point (°C mmHg^{-1})	MS (EI)	Combustion data (calc./found)	
					%C	%H
$(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**)	A	75[b]	71/52	366 $(M - Me_3SiF)^+$	26.21 25.81	1.98 1.89
$n\text{-}C_8F_{17}SiMe_3$ (**Ib**)[c]	A	76	88/40	400 $(M - Me_3SiF)^+$	–	–
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)SiMe_3$ (**Ic**)	B	69	63/18	432 $(M - Me_3SiF)^+$	25.20 25.47	1.73 1.67
$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)SiMe_3$ (**Id**)	B	89	33/0.01	598 $(M - Me_3SiF)^+$	24.36 24.18	1.31 1.20

[a] Method A: Grignard reagent route. Method B: modified procedure of Ruppert et al.
[b] Isolated yield was 52% by Method B.
[c] Known compound, b.p. 70 °C/9.6 mmHg, see Ref. [5(a)].

TABLE 2. NMR spectra of perfluorooxaalkyltrimethylsilanes[a]

Compound	R_f^1 ($R_f^1SiMe_3$)	^1H NMR	^{19}F NMR
Ia	$(CF_3)_2CFO(CF_2)_4$	0.29 (s)	−81.2 (ut, $2CF_3$); −81.5 (b, CF_2 next to O); −119.8 (s, CF_2); −125.5 (t, CF_2); −129.0 (t, CF_2); −145.8 (t, CF)
Ic	 $C_3F_7O\underset{CF_3}{\overset{F}{C}}CF_2O\underset{CF_3}{\overset{F}{C}}$	0.28 (s)	−78.7 (t, CF_3); −80.1 (m, CF_3); −82.1 (dt, CF_3); −77.5 to −83 (AB, CF_2O); −130.2 (d, CF_2 next to CF_3); −145.4 (t, CF in chain); −149.9 (q, CF on Si)
Id	 $C_3F_7O[\underset{CF_3}{\overset{F}{C}}CF_2O]_2\underset{CF_3}{\overset{F}{C}}$	0.27 (s)	−78.6 (td, CF_3); −80.6 (tm, $2CF_3$); −82.2 (m, CF_3); −77 to −83 (AB, CF_2O); −130.4 (tm, CF_2 next to CF_3); −145.5 (tm, 2F in chain); −149.5 (tm, CF on Si)

[a] ^1H NMR (300 MHz), chemical shifts (ppm/TMS); ^{19}F NMR (282.3 MHz), chemical shifts [ppm/$CFCl_3$ (**Ia** and **Id**) or $CF_2ClCFCl_2$ (**Ic**)/$CDCl_3$], s = singlet, b = broad, m = multiplet, q = quartet, t = triplet, AB — broad AB patterns, dt = doublet — each triplet, td = two doublets, tm = two overlapping multiplets, ut = unsymmetrical triplet.

$R_f^3 = n\text{-}C_6F_{13}$; **IIId**: $R_f^1 = n\text{-}C_8F_{17}$, $R_f^2 = CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$, $R_f^3 = (CF_3)_2CFO(CF_2)_2$; **IIIe**: $R_f^1 = R_f^2 = (CF_3)_2CFO(CF_2)_4$, $R_f^3 = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$).

In our present study we have examined in detail the reaction of $n\text{-}C_6F_{13}C(O)CF_3$ (**IIa**) and $n\text{-}C_8F_{17}SiMe_3$ (**Ib**). The reactions were carried out under various experimental conditions using different metal fluorides (MF), different molar ratios of MF/ketone, and different solvents and temperatures, as listed in Table 3. Table 4 lists the yield of the reaction product, $R_f^1R_f^2R_f^3C(OH)$, obtained. The characterization data for the perfluoro tertiary alcohols are presented in Table 5.

From the results in Table 3, it can be seen that the experimental conditions are critical, and substantially affect the yield of alcohol formed. The optimum experimental conditions are as follows: MF = CsF, molar ratio of CsF to ketone ≥ 1:1, Et_2O as solvent, and reaction temperature, ~0 °C.

Reactions of the same fluoroketone, $n\text{-}C_6F_{13}C(O)CF_3$ (**IIa**), with the secondary $R_f^1SiMe_3$ (**Id**), $R_f^1 = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$, required a much longer reaction time (7 h) than with the primary $R_f^1SiMe_3$ (**Ia,b**) $R_f^1 = n\text{-}C_8F_{17}$ and $(CF_3)_2CFO(CF_2)_4$, (3 h) (see Table 4, Exp. 1, 2 and 3). Reaction of the same silane, $n\text{-}C_8F_{17}SiMe_3$ (**Ib**), with a higher molecular weight ketone (**IIb**) ($R_f^2 = CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$, $R_f^3 = (CF_3)_2CFO(CF_2)_2$) was much slower than with one containing a trifluoromethyl group, e.g. ketone **IIa** ($R_f^2 = CF_3$, $R_f^3 = n\text{-}C_6F_{13}$) (see Table 4, Exp. 1 and 4). The rate of reaction between the secondary ketone $(CF_3)_2CFO(CF_2)_4C(O)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (**IIc**) and $(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**) was very slow compared to the rate of decomposition of **Ia** (see Table 4, Exp. 5). These structural effects of R_f^1, R_f^2 and R_f^3 groups on the rate of reaction may be due to steric factors as well as to the solubility of the reagents and substrates in the solvent. We found that in one reaction the addition of some perfluoro-2-butyltetrahydrofuran

TABLE 3. Reaction of $n\text{-}C_6F_{13}C(O)CF_3$ (**IIa**) and $n\text{-}C_8F_{17}SiMe_3$ (**Ib**) at ~0 °C in the presence of MF

Exp.	MF	Molar ratio of MF/ketone	Solvent	Time (h)	Product **IIIa**[a] yield (GC area %)
1	KF	1.25	THF	3	0
2	KF	1.13	Et_2O	3	0
3	CsF	1.07	CH_3CN	3	33
4	CsF	1.21	THF	6	41
5	CsF	1.10	Et_2O	3	91[b]
6	CsF	1.10	Et_2O	3[c]	60
7	CsF	0.06	Et_2O	6	~5

[a] All of the reactions yielded some by-products, i.e. C_8F_{16}, $C_8F_{17}H$, $C_{16}F_{32}$ and $FSiMe_3$.
[b] Alcohol was isolated in 69% yield by preparative GC.
[c] Reaction temperature ~23 °C; the decomposition products of $n\text{-}C_8F_{17}SiMe_3$ increased with time.

TABLE 4. Reaction of $R_f^2C(O)R_f^3$, CsF and $R_f^1SiMe_3$ at ~0 °C in Et_2O[a]

Exp.	Substrate $R_f^2C(O)R_f^3$ (II)	Reagent $R_f^1SiMe_3$ (I)	Time (h)	Product $R_f^1R_f^2R_f^3C(OH)$, yield, % (GC area %)
1	**IIa**: $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$	**Ib**: $R_f^1=n\text{-}C_8F_{17}$	3	**IIIa**, 69 (91)
2	**IIa**: $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$	**Ia**: $R_f^1=(CF_3)_2CFO(CF_2)_4$	3	**IIIb**, 73 (99)
3	**IIa**: $R_f^2=CF_3$, $R_f^3=n\text{-}C_6F_{13}$	**Id**: $R_f^1=C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$	7	**IIIc**[b], 67 (93)
4	**IIb**: $R_f^2=CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$ $R_f^3=(CF_3)_2CFO(CF_2)_2$	**Ib**: $R_f^1=n\text{-}C_8F_{17}$	3 8 10 16[c]	**IIId**,-(5) **IIId**,-(30) **IIId**,-(33) **IIId**, 30 (67)[d]
5	**IIc**: $R_f^2=(CF_3)_2CFO(CF_2)_4$ $R_f^3=C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	**Ia**: $R_f^1=(CF_3)_2CFO(CF_2)_4$	3 19[c]	**IIIe**,-(trace) **IIIe**,-(2)[e]

[a] Molar ratio of $R_f^2C(O)R_f^3/R_f^1SiMe_3/CsF=1:1.1:1.1$.
[b] Compound is unstable under GC conditions; c. 10% decomposition was observed when the GC injection temperature was 280 °C and the detector temperature was 300 °C.
[c] Reaction mixture was allowed to warm to room temperature.
[d] A mixed solvent, Et_2O (75%)/perfluoro-2-butyltetrahydrofuran (25%), was required for a better yield.
[e] $R_f^2C(O)R_f^3$ was recovered and $R_f^1SiMe_3$ decomposed.

TABLE 5. Characterization of perfluoro tertiary alcohols

Compound	Boiling point (°C mmHg^{-1})	IR:(OH) (cm^{-1})	Combustion data (calc./found)		MS (electron impact mode)
			%C	%H	
IIIa (nc)	190[a]	3618	22.98 22.77	0.12 0.13	817 $(M-F)^+$
IIIb (nc)	105/5	3620	22.46 22.21	0.13 0.11	763 $(M-F-HF)^+$
IIIc (nc)	199[a]	3619	22.07 21.89	0.10 0.08	995 $(M-F-HF)^+$
IIId (nc)	124/0.2	3615	22.10 21.92	0.08 0.06	829[b] $(M-HF-CF_3OC_3F_6OC_3F_6)^+$

[a] Boiling point determined by differential scanning calorimetry. Compounds were isolated by preparative GC.
[b] Molecular ion peaks > 1000 amu were beyond the limit of the spectrometer. Fragmentation was consistent with structure.

(~25% by volume) improved the yield of the alcohol **IIId** from 33 to 67 GC area %.

The reaction has been extended to carbonyl compounds other than ketones. Two $R_f^1SiMe_3$ (**Ia,b**) were reacted with CsF and esters, MeOC(O)OMe and $R_fC(O)OC_2H_5$ ($R_f=CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$), at ~0 °C and ~23 °C in Et_2O and CH_3CN. Only decomposition products of $R_f^1SiMe_3$ were observed. However, **Ia** reacted with CsF and with the secondary acid fluoride $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ to yield mainly ketone **IIc** (68 GC area %), traces of tertiary alcohol **IIIe** and decomposition products of **Ia**. The condition used for this experiment were molar ratio of acid fluoride/silane/CsF = 1:2:2, Et_2O for solvent, and at ~0 °C for 4 h and ~23 °C for 3 d. This procedure was used to obtain ketone **IIc** from the acid fluoride (see above).

3. Experimental details

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. The solvents used were obtained from Aldrich Chemical Co. and were anhydrous. Chemicals CH_3Li, RMgBr (R = Me, Et), KF, $(Et_2N)_3P$ and MeOC(O)OMe were also purchased from Aldrich Chemical Co.; CsF, $ClSiMe_3$,

R_f^1I (R_f^1 = n-C_8F_{17}) and $R_f^2C(O)OC_2H_5$ (R_f^2 = CF_3, n-C_6F_{13}, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$) were from PCR, Inc., $CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2C(O)OCH_3$ was obtained from Exfluor Research Corporation; and $(CF_3)_2CFO(CF_2)_nI$ ($n = 2, 4$) was received from Allied Chemical Co. The secondary perfluorooxaalkyl iodides, $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)I$ ($n = 1,2$), were prepared by modification of reported procedures [7]. GC analyses were performed on a Perkin-Elmer Sigma I or IIB chromatograph using either a 2 ft stainless-steel column (1/4 in o.d.) packed with 5% Dexsil 400 on 100–200 mesh Supelcoport or a 6 ft stainless steel column (1/4 in o.d.) packed with 10% SP-2100 on 80–100 mesh Supelcoport. The GC–MS analyses were performed on a Finnigan 4021 mass spectrometer in the electron impact mode. IR spectra were recorded on a Perkin-Elmer 683 spectrometer. NMR spectra were obtained on a NT-300 spectrometer. All boiling points are uncorrected.

3.1. Preparation of $(CF_3)_2CFO(CF_2)_4SiMe_3$ (Ia) by method A

A diethyl ether (300 ml) and tetrahydrofuran (600 ml) solution of $(CF_3)_2CFO(CF_2)_4I$ (101.4 g, 0.198 mol) and $ClSiMe_3$ (26.1 g, 0.241 mol) was cooled to c. −70 °C. To this solution was added MeMgBr solution (87 ml of a 2.85 M in Et_2O solution, 0.248 mol) dropwise during 15 min while stirring at −60 °C to −50 °C. The progress of the reaction was monitored by withdrawing and hydrolyzing aliquot samples for GC analyses. After stirring for 5 h, the reaction mixture was hydrolyzed at −50 °C with conc. HCl (10 ml). The reaction mixture was then poured into 2 N HCl (100 ml) and Et_2O (300 ml), phase-separated, dried over $MgSO_4$ and concentrated by distillation to yield the crude product. Distillation of the crude product on a spinning band column gave $(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**) (67.3 g, 75% yield).

Compound n-$C_8F_{17}SiMe_3$ (**Ib**) was synthesized by the same procedure. The results are shown in Table 1.

3.2. Preparation of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$-$SiMe_3$ (Id)by method B

A benzonitrile (20 ml) solution of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)I$ (19.7 g, 26.5 mmol) and $ClSiMe_3$ (2.94 g, 27.1 mmol) was cooled to c. −5 °C. To this solution was added $(Et_2N)_3P$ (6.74 g in 10 ml C_6H_5CN, 27.2 mmol) dropwise during a 20 min period. After stirring at ~0 °C for an additional 1 h, the bottom layer (18.5 g) was separated and subsequently distilled at reduced pressure to yield **Id** (16.3 g, 89% yield).

Compounds $(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)SiMe_3$ (**Ic**) were also synthesized by the same procedure, except that the reaction time required for **Ia** was longer. The results are listed in Table 1.

3.3. Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)$-$(CF_2)_4OCF(CF_3)_2$ (IIc)

To a diethyl ether (13 ml) solution of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ (4.84 g, 9.72 mmol) and $(CF_3)_2CFO(CF_2)_4SiMe_3$ (**Ia**) (4.79 g, 10.5 mmol) at ~0 °C was added CsF (1.68 g, 11.1 mmol). After stirring the mixture at ~0 °C for 2.5 h, an aliquot sample was removed, hydrolyzed with 2 N HCl and analyzed by GC. The ketone did not appear in the reaction mixture. Therefore, more CsF (0.60 g, 4.0 mmol) was added to the above mixture at ~0 °C. The reaction appeared to start immediately on addition of this excess CsF. After the reaction mixture had been stirred for 3 h at ~0 °C, it was allowed to warm to room temperature and was hydrolyzed with 2 N HCl (10 ml). The organic layer was separated, washed with H_2O (2×5 ml) and dried over $MgSO_4$. A GC–MS analysis of the solution indicated the presence of the ketone **IIc** in 83 GC area %, and some by-products, i.e. $(CF_3)_2CFO(CF_2)_2CF{=}CF_2$, $C_3F_7OCF(CF_3)CF_2$-$OCF{=}CF_2$, $C_3F_7OCF(CF_3)CF_2OCFH(CF_3)$, $(CF_3)_2$-$CFOCF_2CF_2CF_2CF{=}CFCF_2CF_2CF_2OCF(CF_3)_2$ and a trace of alcohol **IIIc**. The ketone **IIc** was characterized by its IR spectrum $\nu(CO) = 1790\ cm^{-1}$; MS (EI) *m/e*: 845 $(M-F)^+$; 679 $(M-C_3F_7O)^+$; 513 $(M-C_3F_7OC_2F_4)^+$; 385 $(C_3F_7OC_4F_8)^+$; 335 $(C_3F_7OC_3F_6)^+$; 169 $(C_3F_7)^+$; and elemental analysis: Calc. for $C_{16}F_{32}O_4$: C, 22.24%. Found: C, 22.00%.

Compounds **IIa** and **IIb** were synthesized from $R_f^2C(O)OR$, R_f^3I and MeLi according to the procedure which we have previously reported [6].

3.4. Typical procedure for the synthesis of the perfluoro tertiary alcohol $R_f^1R_f^2R_f^3C(OH)$ {IIIc, $R_f^1 = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$, $R_f^2 = CF_3$, $R_f^3 =$ n-C_6F_{13}}

To a diethyl ether solution (2.0 ml) of $R_f^1SiMe_3$ (1.46 g, 2.11 mmol) and $R_f^2C(O)R_f^3$ (0.79 g, 1.90 mmol) was slowly added CsF (0.34 g, 2.24 mmol) at 0 °C. The progress of the reaction was monitored by GC. After stirring at 0 °C for 7 h, the reaction was hydrolyzed with 2 N HCl (10 ml). The bottom layer was separated, washed with H_2O (2×4 ml) and yielded the crude product (2.02 g). The desired product **IIIc** was isolated in 67% yield by preparative GC.

Compounds **IIIa**, **IIIb** and **IIId** were prepared by a similar procedure except that **IIId** was prepared using a mixture of Et_2O (75% by volume) and perfluoro-2-butyltetrahydrofuran (25% by volume) as solvent, and the reaction temperature was allowed to warm to ~23 °C for 16 h after stirring at 0 °C for 10 h.

The yield, boiling points, IR, MS and elemental analysis data of all the alcohols are listed in Tables 4 and 5. The NMR spectrum of one alcohol (**IIIb**) has been obtained and is given below: $(CF_3^A)[(CF_3^C)_2CF^LOCF_2^BCF_2^HCF_2^FCF_2^E](CF_3^DCF_2^K$-$CF_2^JCF_2^ICF_2^GCF_2^E)C(OH^M)$ (**IIIb**) ($CDCl_3$) δ:A − 71.2 (m); B − 81.1 (br s); C − 81.5 (m); D − 81.8 (t, t); E − 112.0 (AB pattern); F − 119.4 (br s): G − 119.9 (br s); H − 122.0 (br s); I − 123.2 (br s); J − 125.2 (m); K − 126.8 (m); L − 145.8 (t); M 2.15 (br s) ppm; ^1H NMR (300 MHz, $CHCl_3$); ^{19}F NMR (282.3 MHz, Freon-113).

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