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Reactions of cesium perfluorotertiary alkoxides and perfluorotertiary alcohols with reactive halides ☆

Grace J. Chen, Loomis S. Chen *

University of Dayton Research Institute, Dayton, OH 45469-0168, USA

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Abstract

Reactions of cesium perfluorotertiary alkoxides and perfluorotertiary alcohols with chlorotrimethylsilane, benzoyl chloride, perfluoroacyl halides and 3-phenoxybenzoyl chloride gave the compounds $Me_3SiOR_f^1$ (**3**), $C_6H_5C(O)OR_f^1$ (**4a**), $C_6H_5C(O)OR_f^2$ (**4b**), $R_f'C(O)OR_f^1$ (**5a**), $R_f'C(O)OR_f^2$ **5b**), $R_f''C(O)OR_f^3$ (**6**), $n\text{-}C_3F_7C(O)OR_f^1$ (**7**) and $(3\text{-}C_6H_5O)C_6H_4C(O)OR_f^2$ (**8**), where $R_f^1 = (CF_3)(n\text{-}C_6F_{13})(n\text{-}C_8F_{17})C–$, $R_f^2 = [(CF_3)_2CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C–$, $R_f^3 = (CF_3)(n\text{-}C_6F_{13})[(CF_3)_2CFO(CF_2)_4]C–$, $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$ and $R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)–$. The relative thermal and hydrolytic stabilities of some of these compounds **3**, **5a** and **8** were determined.

Keywords: Reactions; Cesium perfluorotertiary alkoxides; Perfluorotertiary alcohols; Halides; NMR spectroscopy; Syntheses; Thermal stability; Mass spectrometry

1. Introduction

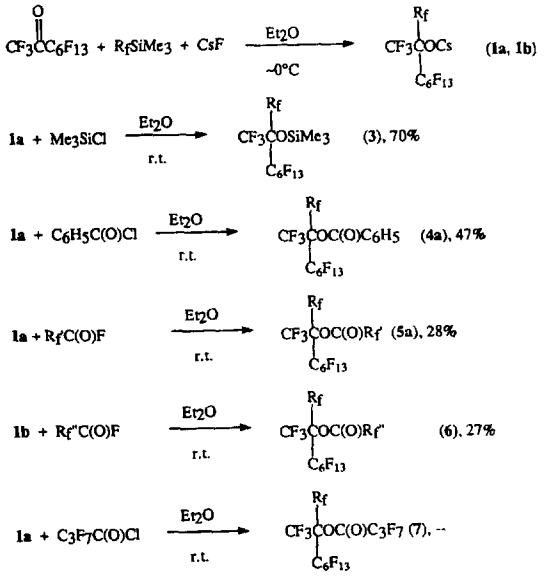
Partially, or completely fluorinated esters have been prepared by various routes [1–12]. Two of the more common methods are: (a) the reaction of metal (Li, Na, K or Cs) salts of fluorinated alcohols with acid halides or anhydrides [1–9]; (b) the reactions of fluorinated alcohols directly with acid halides or anhydrides in the presence of bases such as Et_3N and 2-methylpyridine [3,10]. The lithium [1,2,13], sodium [3,4] and potassium [5,6,14] salts of perfluorotertiary alcohols and cesium salts of perfluoro primary and secondary alcohols [7,15,16] have been reported.

In a previous communication [17], we have described the preparation of a number of high-molecular weight perfluorinated tertiary alcohols by the reaction of perfluoroalkyl trimethylsilanes with perfluoroketones. In this report, we have utilized the alcohols as well as cesium perfluorotertiary alkoxides to prepare both partially and completely fluorinated esters.

2. Results and discussion

2.1. Synthesis

The reactions of cesium perfluorotertiary alkoxides with reactive halides are outlined in Scheme 1. All results and reaction conditions are listed in Table 1. Cesium salt **1a** reacted with chlorotrimethylsilane to afford **3** in high yield (70% – see Table 1, Exp. 1). The partially and completely



1a, 3, 4a, 5a, 7: $R_f = C_8F_{17}$-.
1b, 6: $R_f = (CF_3)_2CFO(CF_2)_4$-.
$R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$-.
$R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-.

Scheme 1. Reactions of cesium perfluorotertiary alkoxides and reactive halides.

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* Corresponding author.

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Table 1
Reactions of cesium salts with halides at room temperature in Et_2O

Exp. No.	$CF_3C(O)C_6F_{13}$ (mmol)	Silane (mmol)	CsF (mmol)	Halide (mmol)	Time (h)	Product, esters Isolated/GC area %
1	12.1	$C_8F_{17}SiMe_3$ 12.7	14.0	Me_3SiCl 20.3	47	**3** [d], 70/93
2	6.68	$C_8F_{17}SiMe_3$ 7.00	7.96	$C_6H_5C(O)Cl$ 11.2	48	**4a** [a], 47/82
3	6.68	$C_8F_{17}SiMe_3$ 7.11	7.89	$R_f'C(O)F$ [c]	89	**5a** [a], 28/70
4	2.76	$(CF_3)_2CFO(CF_2)_4SiMe_3$ 2.97	3.42	$R_f''C(O)F$ [c]	41	**6** [a], 27/64
5	4.80	$C_8F_{17}SiMe_3$ 4.67	4.70	$C_3F_7C(O)Cl$ 5.00	5	**7** [b], –/48

[a] Compounds isolated by preparative GC.
[b] Not isolated as the boiling points of ester and alcohol are too close for effective separation.
[c] $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$; $R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)–$.
[d] Product was the trimethylsilyl derivative.

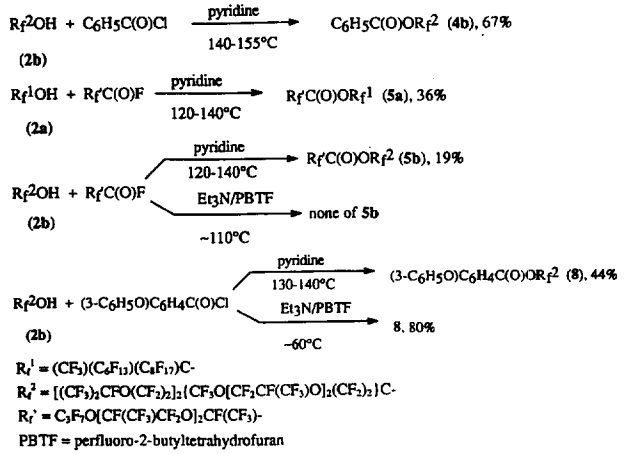
Table 2
Reactions of perfluorotertiary alcohols with halides

Exp. No.	Alcohol [a] (mmol)	Halide [b] (mmol)	Base (mmol)	Temperature (°C)	Time (h)	Product, esters Isolated/GC area %
1	R_f^2OH 9.90	$C_6H_5C(O)Cl$ 22.1	C_5H_5N 10.0	140–155	71	**4b**, 67/80
2	R_f^1OH 2.63	$R_f'C(O)F$ 3.58	C_5H_5N 2.65	120–140	68	**5a**, 36/63
3	R_f^2OH 2.82	$R_f'C(O)F$ 3.21	Et_3N 2.80	110 [c]	53	**5b**, –/0
4	R_f^2OH 4.43	$R_f'C(O)F$ 6.17	C_5H_5N 4.42	120–140	120	**5b**, 19/35
5	R_f^2OH 4.30	$(3\text{-}C_6H_5O)C_6H_4C(O)Cl$ 4.30	C_5H_5N 4.35	130–140	75	**8**, 44/68
6	R_f^2OH 4.70	$(3\text{-}C_6H_5O)C_6H_4C(O)Cl$ 5.12	Et_3N 4.73	~60 [c]	24	**8**, 80/93

[a] $R_f^1 = (CF_3)(C_6F_{13})(C_8F_{17})C–$; $R_f^2 = [(CF_3)_2CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C–$.
[b] $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$.
[c] Solvent: perfluoro-2-butyltetrahydrofuran (PBTF).

fluorinated esters (**4a, 5a, 6** and **7**) were prepared readily in medium to low yield by the reactions of cesium perfluorotertiary alkoxides with reactive acyl halides according to Scheme 1 (Exp. 2–5, Table 1). Hydrolytic stability studies (Section 2.2) showed that the fluorinated ester **5a** was rapidly cleaved under basic conditions. Hence, the reaction mixtures of esters were washed with water before purification in order to remove the cesium fluoride byproduct which could cause decomposition of the esters [7]. Compound **7** was not isolated since the boiling points of ester **7** and alcohol **2a** are too close to each other to allow effective separation.

In order to increase the yield of esters, the reactions of perfluorotertiary alcohols with acyl halides in the presence of bases such as pyridine and triethylamine were investigated by varying experimental conditions such as temperature, reaction stoichiometry, the use of different bases and the



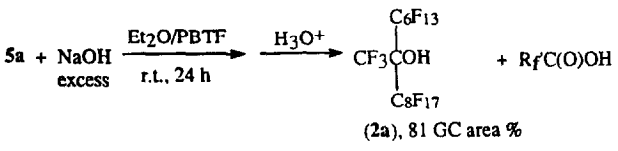
Scheme 2. Reactions of perfluorotertiary alcohols and reactive acyl halides.

presence or absence of solvent. The results are listed in Table 2 and outlined in Scheme 2. Perfluorotertiary alcohol **2b** reacted with two molar proportions of benzoyl chloride at 140–155 °C in the presence of pyridine to give ester **4b** in good yield (67%) (Table 2, Exp. 1). The optimum experimental conditions for the preparation of ester **8** in high yield (80%) were perfluoro-2-butyltetrahydrofuran (PBTF) as solvent at ~60 °C for ~1 d using Et_3N as the base (Table, 2, Exp. 6). However, the reactions of perfluorotertiary alcohols with a perfluoroacyl fluoride gave low yields (36%, 0% and 19%; Exp. 2, 3 and 4, Table 2), possibly because of the instability of the perfluoroesters in the basic solution – see Section 2.2.

The MS, IR, ^1H NMR and ^{19}F NMR spectra, and elemental analysis data for all the new fluorinated compounds, **3, 4a, 4b, 5a, 5b, 6** and **8**, were consistent with the assigned structures. The results are presented in Tables 3 and 4.

2.2. Hydrolytic stability studies

The hydrolytic stabilities of compounds **3, 5a** and **8** towards water, acid and base in solvent (Et_2O or Et_2O/PBTF) were examined. The relative stability of the compounds was inferred from the GC area % of the unhydrolyzed starting materials, after partial hydrolysis under identical conditions – see Table 5. No attempt was made to determine accurately the amounts of starting materials. The relative hydrolytic stability was found to be in the order **8** > **5a** > **3**. Perfluoro-aryl ester **8** was stable under all experimental conditions. Perfluoro-alkyl ester **5a** was slowly hydrolyzed in Et_2O/PBTF/H_2O and Et_2O/PBTF/2 N HCl at room temperature but rapidly cleaved under basic conditions, i.e. Et_2O/PBTF/2N NaOH. The hydrolysis product was neutralized to yield compound **2a** and $R_f'C(O)OH$ which were identified by GC–MS only.



(2a), 81 GC area %

Trimethylsilyl perfluoroether **3** is hydrolytically unstable. In an Et_2O/H_2O mixture at room temperature for 3 h, **3** was completely cleaved to form trimethylsilanol and alcohol **2a**. These hydrolysis products were also identified by GC–MS only.

2.3. Thermal stability studies

The relative thermal stabilities of several derivatives of fluorinated compounds were determined using a flow pyrolyzer attached to a gas chromatograph. As with the hydrolytic stability studies (Section 2.2), the GC area % was used to estimate the percentage of undegraded starting materials under identical experimental conditions. The results of the pyrolysis of compounds **3, 5a, 5b** and **8** are presented in Fig. 1 and indicate that derivatives with the same perfluorotertiary group ($R_f = R_f^1$ for **3** and **5a**; $R_f = R_f^2$ for **5b** and **8**) have similar thermal stabilities except that the completely fluorinated compounds (**5a** and **5b**) start to decompose at a lower temperature than the partially fluorinated compounds (**3** and **8**). The results also show that R_f^1, $(CF_3)(C_6F_{13})(C_8F_{17})C$–, derivatives are more stable than R_f^2, $[(CF_3)_2CFO(CF_2)_2]_2$-$\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C$–, derivatives.

3. Experimental details

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. Benzoyl chloride, 3-phenoxybenzoic acid, pyridine and thionyl chloride (Aldrich Chemical Co.), cesium fluoride, chlorotrimethylsilane, $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F$ ($n = 1, 2$), C_3F_7-$C(O)Cl$ and perfluoro-2-butyltetrahydrofuran (PBTF) (PCR, Inc., FL), $CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2C(O)$-$OCH_3$ (Exfluor Research Corporation) and $(CF_3)_2CFO$-$(CF_2)_nI$ ($n = 2, 4$) (Allied Chemical Co.) were commercial materials. Perfluorotertiary alcohols were prepared by reported procedures [17,18] and 3-phenoxybenzoyl chloride by the action of thionyl chloride upon the acid. Gas chromatographic analyses were performed on a HP 5890 series II GC, using a 25 m HP-1 fused silica capillary column. The GC–MS analyses were performed on a Finnigan 4021 mass spectrometer in the electron impact mode. Infrared spectra (IR) were recorded on an Analect AQS-20M FT-IR spectrometer. NMR spectra were obtained on a Unity 500 instrument. All temperatures are uncorrected. All the major products obtained were characterized by a combination of analytical techniques, e.g., IR, GC–MS, NMR and elemental analyses except for $C_3F_7C(O)OC(CF_3)(C_6F_{13})(C_8F_{17})$ (see Tables 3 and 4). The minor products were identified only by GC–MS methods.

3.1. Synthesis of $(CF_3)(C_6F_{13})(C_8F_{17})COCs$ (1a)

To a diethyl ether solution (20 ml) of n-$C_8F_{17}SiMe_3$ (6.96 g, 14.0 mmol) and $CF_3C(O)C_6F_{13}$ (5.97 g, 14.4 mmol) was slowly added CsF (2.15 g, 14.1 mmol) at 0 °C. After stirring at 0 °C for 8 h, the excess solvent was removed under vacuum and a viscous white residue was obtained (attempts to precipitate the cesium salt with solvents such as Et_2O, C_6F_6 and pentane were unsuccessful). The white residue was then dried under vacuum at room temperature for 24 h. IR (cm^{-1}): 1661 (s) (C–O–Cs); MS (m/z): 797 $(M - CsF - F)^+$; 133 $(Cs)^+$; and ^{19}F NMR (Table 4) spectra were consistent with the proposed structure. The material failed to give satisfactory elemental analyses. It was hydrolyzed to a mixture of $(CF_3)(C_6F_{13})(C_8F_{17})C(OH)$ (**2a**) (96% GC area) and $(CF_3)(C_6F_{13})_2C(OH)$ (3% GC area), distillation of which yielded pure alcohol **2a** (b.p. 104–108 °C/3 mmHg (75% yield) [17].

Table 3
Physical properties and analysis for trimethylsilyl derivative and fluorinated esters

Compounds [a]	MS/EI (m/z)	B.p. (°C/mmHg)	Elemental analysis (calc./found) (%)			IR, >C=O (cm^{-1})
			C	H	F	
$R_f^1OSiMe_3$ (**3**) (nc)	893 $[M-CH_3]^+$	100/0.2	25.12 24.61	1.00 0.92	69.02 69.73	1065 (SiO); 855, 764 ($SiCH_3$)
$R_f^1OC(O)C_6H_5$ (**4a**) (nc)	940 $[M^+]$	[c]	29.38 29.00	0.54 0.49	66.68 65.98	1794
$R_f^2OC(O)C_6H_5$ (**4b**) (nc)	803 $[M-CF_3OC_3F_6OC_3F_6O]^+$ [b]	114/0.005	26.58 26.13	0.41 0.20	63.83 63.41	1792
$R_f^1OC(O)R_f'$ (**5a**) (nc)	963 $[M-C_3F_7OC_3F_6OC_3F_6]^+$ [b]	117/0.01	22.71 22.87	–	71.88 71.25	1836
$R_f^2OC(O)R_f'$ (**5b**) (nc)	679 $[(C_3F_7OC_2F_4)_2C(C_2F_3)O]^+$ [b]; 501 $[C_3F_7OC_3F_6OC_3F_6]^+$ [b]	~115/0.005	21.84 21.42	–	69.08 68.64	1839
$R_f^3OC(O)R_f''$ (**6**) (nc)	829 $[M-R_f'']^+$ [b]; 785 $[M-R_f''-CO_2]^+$ [b]	[c]	22.52 21.99	–	71.23 70.55	1836
$R_f^1OC(O)C_3F_7$ (**7**) (nc)	763 $[M-C_5F_{11}]^+$ [b]; 663 $[M-C_7F_{15}]^+$ [b]	[d]	–	–	–	1842
$R_f^2OC(O)C_6H_4(3\text{-}C_6H_5O)$ (**8**) (nc)	998 $[M-CF_3OC_3F_6O-CO_2F]^+$ [b]	151/0.005	30.20 30.09	0.69 0.53	59.35 59.28	1791

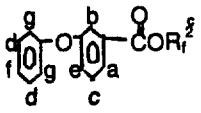
[a] $R_f^1=(CF_3)(C_6F_{13})(C_8F_{17})C-$; $R_f^2=[(CF_3)_2CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C-$; $R_f^3=(CF_3)(C_6F_{13})[(CF_3)_2CFO(CF_2)_4]C-$; $R_f'=C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)-$; $R_f''=C_3F_7OCF(CF_3)CF_2OCF(CF_3)-$.

[b] The parent ion peak (> 1000) was beyond the limit of the spectrometer used. However, the fragmentation peaks were consistent with the structure.

[c] Isolated by preparative GC.

[d] Not isolated as the boiling points of ester and alcohol are too close to each other for effective separation.

Table 4
NMR spectra of fluorinated compounds [a]

Compounds [b]	^{1}H NMR δ (ppm)	^{19}F NMR δ (ppm)
R_f^1OCs [c] (**1a**)	–	−71.4 (m, CF_3 on C–O); −81.7 (tt, $2CF_3$); −112.4 (ab, $2CF_2$ on C–O); −119.0 (br, $2CF_2$); −121.6 to −123.2 (sbrr, $6CF_2$); −126.8 (br, $2CF_2$ next to CF_3)
$R_f^1OSiMe_3$ [d] (**3**)	0.3 (s, $OSiMe_3$)	−68.2 (m, CF_3 on C–O); −81.4 (t, $2CF_3$); −111.2 (ab, br, $2CF_2$ next to C–O); −118.8 (ab, br, $2CF_2$); −121.8 (ab, br, CF_2); −122.0 (ab, br, $2CF_2$); −122.3 (ab, br, CF_2); −123.0 (ab, br, CF_2); −123.1 (ab, br, CF_2); −126.6 (ab, br, $2CF_2$ next to CF_3)
$R_f^1OCC_6H_5$ [c] (**4a**)	8.06 (d, *ortho* H's); 7.67 (t, *para* H's); 7.52 (t, *meta* H's)	−60.5 (nm, CF_3); −81.6 (ut, $2CF_3$); −109.2 (ab, br, $2CF_2$ nearest to C–O); −119.7 (br, um, $2CF_2$); −121.2 (br, um, CF_2); −121.5 (br, um, CF_2); −122.0 (br, um, CF_2); −122.3 (br, um, CF_2); −123.0 (br, um, CF_2); −123.2 (br, um, CF_2); −126.7 (uab, $2CF_2$ next to CF_3)
$R_f^2OCC_6H_5$ [c] (**4b**)	8.03 (d, *ortho* H's); 7.66 (t, *para* H's); 7.49 (t, *meta* H's)	−56.1 (q, CF_3O); −75 to −76 (om, CF_3+2CF_2O); −80 to −82 (om, $5CF_3+2CF_2O$); −85.8 (ab, CF_2O); −104.4 to −105.2 (om, $3CF_2$ on quat. carbon); −145 to −146 (thm, 4CFO)
$R_f^1OCR_f'$ [c] (**5a**)	–	−61.1 (um, CF_3 on C–O); −80 to −83 (om, $6CF_3+3CF_2O$); −109.0 (br, $2CF_2$ on C–O); −119.9 (ab, $2CF_2$ beta to C–O); +121 to −123.5 (ssbrp, $6CF_2$, midchain); −126.8 (um, $2CF_2$ next to CF_3); −130.4 (um, CF_2 in propyl); −131.7 (m, CFO next to carbonyl); −145.5 (om, 2CFO)
$R_f^2OCR_f'$ [c] (**5b**)	–	−56.4 (om, OCF_3); −76 to −77 (om, CF_3+2CF_2O); −78 to −87 (om, $9CF_3+6CF_2$); −105.9 (br, $3CF_2$); −130.4 to −131.1 (om, CF_2); −132.3 (om, OCF); −145 to −146 (om, 6OCF)
$R_f^3OCR_f''$ [c] (**6**)	–	−61.1 (um, CF_3 on C–O); −80 to −81.5 (om, $6CF_3+3CF_2O$); −109.1 ($2CF_2$ on C–O); −120.0 (ab, $2CF_2$ beta to C–O); −120.5 to −125 (sbrp, $3CF_2$ in chain); −126.7 (m, CF_2 next to CF_3); −130.3 (s, CF_2 next to CF_3); −132.0 (tp, OCF); −146.5 (thm, 2OCF)
	7.66 (d, H [a]); 7.54 (s, H [b]); 7.42 (t, H [c]); 7.36 (t, 2H [d]); 7.30 (dd, h [e]); 7.16 (t, H [f]); 7.01 (d, 2 H [g])	−56.1 (tt, OCF_3); −75 to −76.2 (om, CF_3+2CF_2O); −80 to −82 (om, $5CF_3+2CF_2O$); −85.8 (ab, CF_2O); −104 to −106 (om, $3CF_2$); −145.5 to −146.2 (thm, 4CFO)

[a] ^{1}H NMR (499.8 MHz); ^{19}F NMR (470.2 MHz); ab = ab pattern, br = broad, d = doublet, dd = doubled doublet, m = multiplet, nm = ninefold multiplet; om = overlapping multiplets, q = quartet, s = singlet, sbrp = series of broad peaks, sbrr = series of broad resonances, ssbrp = series of six broad peaks, t = triplet, thm = three multiplets, tp = two peaks, uab = unresolved ab pattern, um = unresolved multiplet, ut = unresolved triplet.
[b] $R_f^1 = (CF_3)(n\text{-}C_6F_{13})(n\text{-}C_8F_{17})C$; $R_f^2 = [(CF_3)_2CFOCF_2CF_2]_2\{CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2\}C$; $R_f^3 = (CF_3)(n\text{-}C_6F_{13})[(CF_3)_2CFO(CF_2)_4]C$; $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)-$; $R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)-$.
[c] Solvent: $CDCl_3$ plus Freon-113; Reference: ^{1}H NMR, TMS; ^{19}F NMR, Freon-113.
[d] Solvent: $CDCl_3$; Reference: ^{1}H NMR, TMS; ^{19}F NMR, $CFCl_3$.

3.2. Synthesis of $(CF_3)(C_6F_{13})[(CF_3)_2CFO(CF_2)_4]COCs$ (1b)

Cesium salt **1b** was synthesized by a similar procedure to that described above and was used for subsequent reaction with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ without isolation.

3.3. Typical procedure for the reactions of cesium salts and halides – synthesis of $(CF_3)(C_6F_{13})(C_8F_{17})COSiMe_3$ (3)

To a diethyl ether solution (20 ml) of n-$C_8F_{17}SiMe_3$ (6.26 g, 12.7 mmol) and $CF_3C(O)C_6F_{13}$ (5.05 g, 12.1 mmol) was added CsF (2.13 g, 14.0 mmol) at ~0 °C. The reaction mixture was stirred at ~0 °C for 20 h. To this solution at 0 °C was added Me_3SiCl (2.20 g, 20.3 mmol). Reaction started immediately as evidenced by an exotherm and salt formation. The reaction mixture was warmed up to room temperature and stirred for an additional 47 h or until the yield of the expected product was maximized, and then centrifuged. The liquid was decanted from the solid and the residual solid was extracted with additional Et_2O (2 × 15 ml). The organic solutions were combined and concentrated to obtain the crude product (9.0 g, 93 GC area % of **3** and 4 GC area % of alcohol **2a**) which was fractionally distilled to yield **3** (7.69 g, 70% yield, b.p. 100 °C/0.2 mmHg).

Compounds, $R_f^1OC(O)C_6H_5$ (**4a**), $R_f^1OC(O)R_f'$ (**5a**), $R_f^3OC(O)R_f''$ (**6**) and $R_f^1OC(O)C_3F_7$ (**7**) {$R_f^1 = (CF_3)$-

Table 5
Hydrolysis of fluorinated compounds [a] at room temperature

Reagents (time, h)	GC area % of hydrolysis products from:		
	$(3\text{-}C_6H_5O)C_6H_4C(O)OR_f^2$ (8) [b]	$R_f'C(O)OR_f^1$ (5a) [c]	$Me_3SiOR_f^1$ (3) [b,d]
H_2O			
0.5	0	0	76
1	0	0	93
3	0	0	100
24	0	3	–
2 N HCl			
24	0	3	–
2 N NaOH			
3	0	45	–
24	0	81	–

[a] $R_f^1 = (CF_3)(C_6F_{13})(C_8F_{17})C–$; $R_f^2 = [(CF_3)_2CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C–$; $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$.
[b] Solvent: Et_2O.
[c] A mixture of Et_2O/PBTF (1:1) was used as solvent. The hydrolysis product from **5a** was R_f^1OH (**2a**) and $R_f'C(O)OH$.
[d] The hydrolysis product from **3** was Me_3SiOH and R_f^1OH (**2a**).

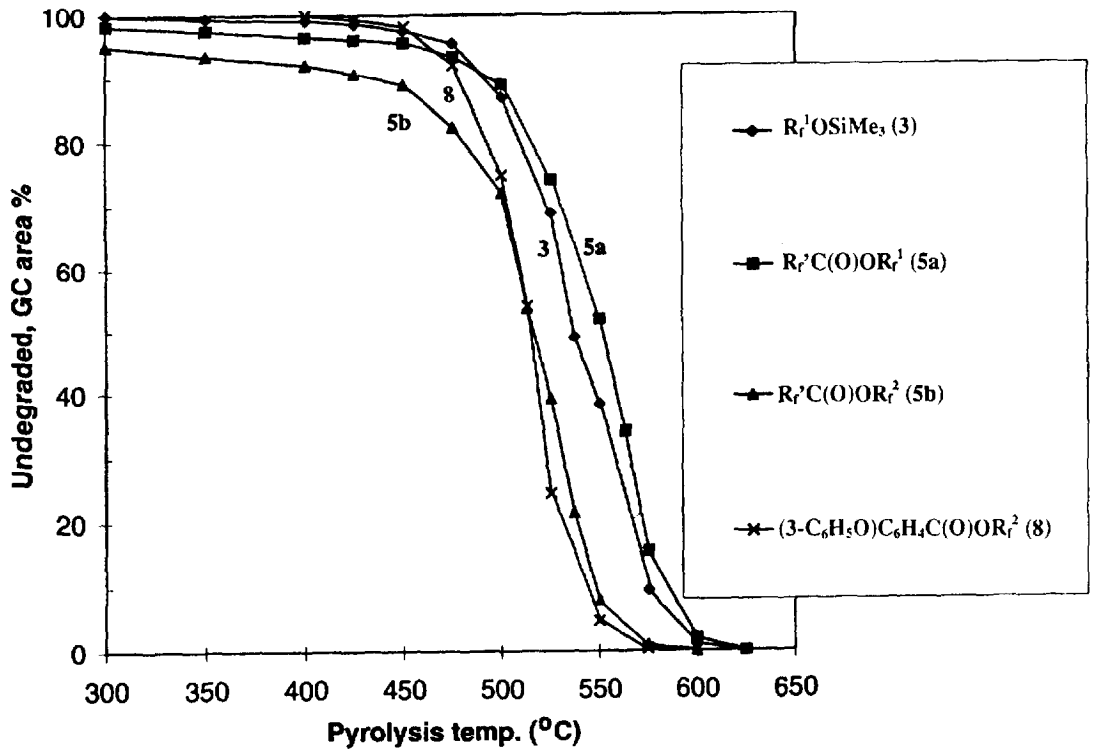


Fig. 1. Thermal stability of fluorinated compounds on pyrolysis as estimated by chromatography. All experimental conditions were the same. $R_f^1 = (CF_3)(C_6F_{13})(C_8F_{17})C–$; $R_f^2 = [(CF_3)CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C–$; $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$.

$(C_6F_{13})(C_8F_{17})C–$; $R_f^3 = (CF_3)(C_6F_{13})[(CF_3)_2CFO(CF_2)_4]C–$; $R_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)–$, $R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)–$} were prepared by a procedure similar to that described above except that the reactants, their concentrations and the reaction times were varied (Table 1). All the crude products (esters) were washed with water before purification. The physical properties and analyses of all isolated compounds are summarized in Tables 3 and 4.

3.4. Typical procedure for the reactions of perfluorotertiary alcohols with halides – synthesis of $(3\text{-}C_6H_5O)C_6H_4C(O)OR_f^2$ (8), $R_f^2 = [(CF_3)_2CFO(CF_2)_2]_2\{CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2\}C–$

A mixture of R_f^2OH (**2b**) (5.25 g, 4.70 mmol), $(3\text{-}C_6H_5O)C_6H_4C(O)Cl$ (1.19 g, 5.12 mmol) and Et_3N (0.48 g, 4.73 mmol) in perfluoro-2-butyltetrahydrofuran (PBTF) (6.0 ml) was heated to ~60 °C. Aliquot samples were

removed periodically and analyzed by GC. After heating at ~60 °C for 5.5 and 24 h, GC results showed 91% and 93% of **8**, respectively. The reaction mixture was hydrolyzed with water at room temperature and the layers were separated. The water layer was extracted with the additional PBTF (2×5 ml). The organic solutions were combined and distilled to yield compound **8** (4.0 g, 80%, b.p. 151 °C/0.005 mmHg). An unsuccessful attempt was made to prepare **8** by the reaction of 3-phenoxybenzoic acid with perfluorotertiary alcohol **2b** in hexafluorobenzene in the presence of a small proportion of concentrated sulfuric acid.

Compound **4b, 5a** and **5b** were prepared by a similar procedure except that pyridine was used instead of triethylamine and no solvent was used. The reactions studied are summarized in Table 2 and analytical data of all isolated esters are presented in Tables 3 and 4.

3.5. Hydrolysis studies of compounds 3, 5a and 8

Samples (0.20 g) of compounds **3** and **8** were individually dissolved in diethyl ether (4.0 ml). Due to its low solubility, compound **5a** (0.20 g) was dissolved in a mixture of Et_2O (2.0 ml) and PBTF (2.0 ml). The solutions of compounds **3, 5a** and **8** were then treated with 100 μl of the reagents H_2O, 2 N HCl or 2 N NaOH, and stirred at room temperature. Aliquots of the organic solutions were periodically removed, washed with H_2O and analyzed by GC at 0.5, 1, 3 and 24 h. The GC area % of the hydrolysis products are listed in Table 5.

3.6. Thermal stability studies of compounds 3, 5a, 5b and 8

The relative thermal stabilities of compounds **3, 5a, 5b** and **8** were determined by means of pyrolysis/gas chromatographic analysis using a Scientific Glass Engineering International Pty.Ltd. pyrojector II unit attached to a HP 5890 series II GC. Experiments were conducted under the following conditions: pyrojector pressure/column pressure: 20/10 psi; pyrolysis temperature: 300–625 °C; column: DB-1, 30 m (length), 0.32 mm (i.d.), crosslinked methylsilicon 0.2 μm (film thickness); sample size: 0.1 μl; initial temperature: 60 °C; program rate: 15 °C min^{-1}; final temperature: 275 °C; injection temperature: 285 °C; detector temperature: 300 °C; detector: flame ionization. Plots of GC area % of undegraded compounds **3, 5a, 5b** and **8** against the pyrolysis temperature (°C) are presented in Fig. 1. All experimental conditions were the same.

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