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Perfluoro tertiary alcohols
I. Synthesis of high molecular weight perfluorinated monoketones and tertiary alcohols

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Abstract

A series of high molecular weight perfluoro ketones, $R_f^1C(O)R_f^2$ (II) and alcohols, $R_f^1R_f^2R_f^3COH$ (III) [R_f^1, R_f^2: n-C_6F_{13}, $(CF_3)_2CFO(CF_2CF_2)_x$ ($x=1$ and 2), $C_2F_5O(C_2F_4O)_yCF_2$ ($y=4$ and 5), $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$ and $C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$; R_f^3: $(CF_3)_2CFOCF_2CF_2$ and $C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$ where R_f^1, R_f^2 and R_f^3 may be the same or different, has been prepared in good to excellent yields. This was accomplished by the reaction of the appropriate perfluoroorganometallic reagent and diethyl carbonate or perfluoroalkylether ester under suitable conditions to yield symmetric or asymmetric ketones (II). These ketones (II) were then reacted with perfluoroalkylether lithium, containing an oxygen atom β to the carbon atom attached to lithium, to produce tertiary alcohols (III). The yield of alcohol is influenced by the type of perfluoroorganometallic reagents, the mode of addition and the solvents.

Introduction

The preparation of tertiary alcohols having three perfluoroalkylether substituents has not yet been reported. However, t-alcohols with one perfluoroalkylether substituent, such as $(CF_3)_2CFOCF_2CF_2C(CF_3)_2OH$, have been prepared by the organometallic route [1, 2]. A large number of low molecular weight non-ether-containing perfluoro tertiary alcohols have been synthesized by various routes [3–13]. Tarrant *et al.* [3], Tamborski *et al.* [4–6] and Chang *et al.* [7] have reported the synthesis of specific perfluoro tertiary alcohols, $R_fC(CF_3)_2OH$, $R_f=CF_2=CF$, n-C_8F_{17} or 4-C_6F_4X ($X=F$ or CF_3), by the reaction of hexafluoroacetone and the corresponding organometallic reagent. Tarrant *et al.* [3] and Chang *et al.* [7] have also reported the synthesis of perfluoro tertiary alcohols by the reaction of $CF_2=CFLi$ and C_6F_5Li with $CF_3C(O)Cl$ and $C_6F_5C(O)Cl$. According to Wiley [8], perfluoro tertiary alcohols can be formed by the reaction of an alkyl ester of a perfluoro carboxylic acid or a perfluoro ketone with an alkali metal alkoxide. Perfluoroalkyl tertiary alcohols, $R_fR_f^1C(C_2F_5)OH$ ($R_f=CF_3$, C_2F_5, C_3F_7 or n-C_7F_{15}; $R_f^1=CF_3$ or C_2F_5) have been prepared by the condensation of an alkali metal salt of perfluoro alcohols with tetrafluoroethylene [9, 10]. Perfluoro-t-butyl alcohols have also been prepared by heating $(CF_3)_3CNO$ with dinitrogen

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tetraoxide followed by hydrolysis [11], by fluorination of $(CF_3)_2C(CCl_3)OH$ [12], and by treating perfluoroisobutene oxide with HF/SbF_5 [13].

The thermal stability and reactivity of a number of perfluoroorganometallic reagents and also the synthesis of perfluoro ketones by the organometallic route were reported earlier from this laboratory [1, 2, 5, 6, 15, 16] and elsewhere [14]. We have now extended our studies to preparing a series of high molecular weight perfluoroalkylether ketones and tertiary alcohols.

Experimental

General comments

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. All the solvents were dried before use. All chemicals used were commercially available except $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)OMe$ which was obtained from Exfluor Research Corporation, $C_3F_7O(CF_2CF_2)_xI$ ($x=1$ and 2) which were obtained from Allied Chemical Co., $C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2I$ and $C_2F_5O(C_2F_4O)_yCF_2C(O)OMe$ ($y=4$ and 5) which were obtained from PCR Inc. Gas Chromatographic (GC) analyses were performed on a Perkin–Elmer Sigma I instrument with a 10% SP-2100 on 100/120 mesh Supelcoport packed 1/4″ (d)×6′ stainless-steel column or a Sigma IIB instrument with a 1/4″ (d)×2′, 5% Dexsil 400 on 100/120 mesh Supelcoport packed column. The GC/MS analyses were performed on a Finnigan 4021 mass spectrometer using either chemical ionization or electron impact mode, or both if necessary. The highest masses in the fragmentation peaks were reported except for those compounds which have molecular ion peaks over 1000, beyond the limit of the spectrometer. Infrared (IR) spectra were recorded on a Beckman Microlab 600 spectrophotometer using a neat liquid capillary film between NaCl plates. Most compounds were characterized by a combination of analytical techniques, *e.g.* IR, GC/MS and combustion analyses (see Tables 2 and 4). All boiling points are uncorrected. Yields of products are reported as isolated yields, GC area % or both (see Tables 2, 3 and 4). Some perfluoroketones and all perfluoro tertiary alcohols were prepared following typical procedures.

Attempted preparation of $(n\text{-}C_6F_{13})_3COH$ and synthesis of $(n\text{-}C_6F_{13})_2C(O)$ (IIa)

Into a diethyl ether (300 ml) solution of $n\text{-}C_6F_{13}I$ (15.61 g, 35.0 mmol) was slowly added EtMgBr (12.3 ml of a 2.85 M diethyl ether solution, 35.0 mmol) with stirring at −78 °C over a period of 6 min. After an additional 30 min, diethyl carbonate (4.00 g, 33.9 mmol) was added at −78 °C. The reaction mixture was warmed to −60 °C and stirred for an additional 3 h and then allowed to warm up to room temperature during ~1 h and stirred for another 20 min. The reaction mixture was again cooled to −78 °C. An additional amount of $n\text{-}C_6F_{13}I$ (20.0 g, 44.8 mmol) and then MeLi (32.0 ml of a 1.4 M diethyl ether solution, 44.8 mmol) were added. After 30 min, the GC analysis showed 95% of $(n\text{-}C_6F_{13})_2C(O)$. The reaction mixture was warmed to room temperature during ~1 h, maintained at room temperature for 5 min and then cooled to −78 °C. More $n\text{-}C_6F_{13}I$ (20.0 g, 44.8 mmol) and MeLi (32.0 ml of a 1.4 M diethyl ether solution, 44.8 mmol) were added again. Aliquot samples were removed periodically, hydrolyzed and analyzed by GC methods. The results indicated that no $(n\text{-}C_6F_{13})_3COH$ was formed. After 3 h, the reaction mixture was hydrolyzed with conc. HCl (5.0 ml) at −78 °C and then poured into 2 N HCl (100 ml). The organic layer was separated and dried over $MgSO_4$. Distillation yielded the ketone (**IIa**) (18.65 g, b.p., 138 °C/80 mmHg, 83% yield).

Compound **IIb** was prepared from $(CF_3)_2CFOCF_2CF_2I$ and $(EtO)_2C(O)$ according to the known procedure which we have previously reported [15].

Attempted preparation of $[(CF_3)_2CFOCF_2CF_2]_3COH$ *(**IIIb**) by a one-pot reaction*

To a diethyl ether solution (80 ml) of $(CF_3)_2CFOCF_2CF_2I$ (13.6 g, 33 mmol) was slowly added MeLi (15.7 ml of a 1.4 M diethyl ether solution, 22 mmol) at −78 °C over a period of 20 min. After an additional 15 min, $(EtO)_2C(O)$ (1.18 g, 10 mmol) in diethyl ether (2.0 ml) was added over a period of 5 min. After an additional 20 min, the reaction mixture was warmed to −40 °C during ~20 min and maintained for 30 min. It was again cooled to −78 °C. An additional amount of MeLi (7.8 ml of a 1.4 M diethyl ether solution, 11 mmol) was added. Aliquot samples were removed periodically, hydrolyzed and analyzed by GC methods. The major product identified by GC/MS was the ketone **IIb** in addition to the typical decomposition products of $(CF_3)_2CFOCF_2CF_2Li$. Compound IIIb was not produced.

Typical procedure for the synthesis of perfluoro ketones from perfluoro esters – $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)C_2F_4OCF(CF_3)_2$ *(**IIc**)*

To a diethyl ether solution (200 ml) of $(CF_3)_2CFOCF_2CF_2I$ (25.8 g, 62.6 mmol) was slowly added MeLi (44.7 ml of a 1.4 M in diethyl ether solution, 62.6 mmol) at −78 °C over a period of 40 min. After an additional 30 min, a $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)OMe$ (33.8 g, 58.7 mmol) solution in diethyl ether (10 ml) was added at −78 °C over a period of 50 min. After an additional 1.5 h, the reaction mixture was hydrolyzed with conc. HCl (5.0 ml) at −78 °C and then poured into 2 N HCl (100 ml). The organic layer was separated, washed with H_2O (50 ml) and dried ($MgSO_4$). A GC/MS analysis of the solution indicated the ketone (**IIc**) in 98 GC area %. Distillation of the mixture yielded 46.6 g (96%) of compound **IIc** (b.p., 200 °C).

Compounds **IId**, **IIe** and **IIf** were prepared by a similar procedure as described above except that **IIe** was prepared by the *in situ* reaction and **IIf** was prepared in perfluoro-2-n-butyltetrahydrofuran (12 mmol of R_f^2I in 40 ml of $2\text{-}C_4F_9C_4F_7O$) instead of diethyl ether. The reactions were assumed complete when the GC analyses of aliquot samples indicated maximum product formation. The yield, b.p., IR, MS and combustion data of all the ketones are listed in Table 2.

Typical procedure for the synthesis of perfluoro tertiary alcohols — *$[(CF_3)_2CFOCF_2CF_2]_3COH$ (**IIIb**)*

To a diethyl ether solution (50 ml) of $(CF_3)_2CFOCF_2CF_2I$ (6.2 g, 15 mmol) was slowly added MeLi (10.7 ml of a 1.4 M in diethyl ether solution, 15 mmol) at −78 °C over a period of 6 min. After an additional 10 min, a ketone, $[(CF_3)_2CFOCF_2CF_2]_2C(O)$ (**IIb**) (6.50 g, 11 mmol) was added at −78 °C over a period of 10 min. The reaction mixture, while being stirred, was left in the −78 °C bath overnight. At the end of 20 h, the temperature has increased to ~ −70 °C. The reaction mixture was hydrolyzed with conc. HCl (2 ml) at −78 °C and then poured into 2 N HCl (30 ml) and diethyl ether (50 ml). The organic layer was separated, washed with H_2O (30 ml) and dried over $MgSO_4$. Distillation yielded compound **IIIb** (7.3 g, b.p., 117 °C/25 mmHg, 75%).

Compounds **IIIa**, **IIIc**, **IIId**, **IIIe**, **IIIf** and **IIIg** were prepared by a procedure similar to that described above except that the molar ratios of reactants, reaction times and solvents were varied (see Table 3). The physical measurements and analyses of all the alcohols are summarized in Table 4.

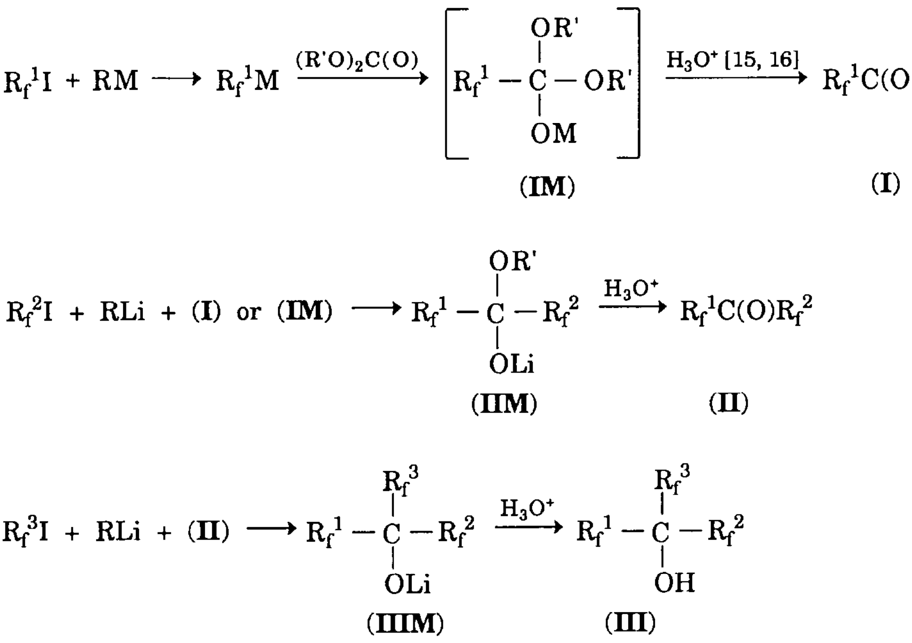
Results and discussion

As far as the reactions between perfluoroorganometallic reagents and diethyl carbonate, perfluoroesters or perfluoroketones are concerned, the following mechanism [eqns. (1)–(3)] may be suggested on the basis of previous studies [15, 18–21] and by analogy with similar reactions among hydrocarbons [17] (see Scheme 1).

The formation of the products **I**, **II** or **III** in these reactions depends on the stability of the appropriate intermediates designated as **IM**, **IIM** and **IIIM**, respectively. The thermal stability of these intermediates, **IM** and **IIM**, has been discussed in detail in an earlier publication [15]. The intermediate **IM**, M = MgBr is unstable at room temperature in diethyl ether and eliminates a molecule of R'OM to yield the ester **I**. The hydrolysis step shown in eqn. (1) was needed only for the isolation of the ester. In fact, attempts to isolate **IM**, $R_f^1 = n\text{-}C_8F_{17}$; $R' = C_2H_5$; M = MgBr at room temperature were unsuccessful due to its thermal instability [15].

The intermediate **IIM**, on the other hand, is stable at room temperature in diethyl ether and cannot eliminate R'OLi to yield the ketone without hydrolysis.

These aspects of the thermal stability of **IM** and **IIM** are reflected in the attempted preparations of the alcohols $(n\text{-}C_6F_{13})_3COH$ and **IIIb** by one-pot reactions (see Experimental). The warming and cooling cycles were used in an attempt to generate the required carbonyl species, **I** and **II**, in the reaction medium for *in-situ* reactions with the thermally labile R_fLi generated



$$R_f^1I + RM \longrightarrow R_f^1M \xrightarrow{(R'O)_2C(O)} \underset{\text{(IM)}}{\left[R_f^1-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OM}{|}}{C}}-OR' \right]} \xrightarrow{H_3O^+\,[15,\,16]} \underset{\text{(I)}}{R_f^1C(O)OR'} \qquad (1)$$

$$R_f^2I + RLi + \text{(I) or (IM)} \longrightarrow \underset{\text{(IIM)}}{R_f^1-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OLi}{|}}{C}}-R_f^2} \xrightarrow{H_3O^+} \underset{\text{(II)}}{R_f^1C(O)R_f^2} \qquad (2)$$

$$R_f^3I + RLi + \text{(II)} \longrightarrow \underset{\text{(IIIM)}}{R_f^1-\overset{\overset{\displaystyle R_f^3}{|}}{\underset{\underset{\displaystyle OLi}{|}}{C}}-R_f^2} \xrightarrow{H_3O^+} \underset{\text{(III)}}{R_f^1-\overset{\overset{\displaystyle R_f^3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R_f^2} \qquad (3)$$

R, R' = CH_3 or C_2H_5; M = MgBr or Li
R_f^1, R_f^2, R_f^3 = perfluoroalkyl or perfluoroalkylether
Scheme 1.

from R_fI. While this approach was successful in the conversion of ester **I** to ketone **II** due to the instability of **IM**, the reaction stopped at the ketone stage due to the stability of **IIM**. Hence the ketones **II** had to be isolated by hydrolysis for reaction with R_f^3Li in order to prepare the tertiary alcohols **III**.

Although the possibility of R_f^2Li reacting with **IM**, M = MgBr to yield **IIM** directly at −78 °C cannot be completely ruled out, our earlier studies [15] suggest the probable formation of free ester **I** from **IM** by just raising the temperature.

Synthesis of perfluoroalkyl and perfluoroalkylether ketones

In our present study we have synthesized the ketones $(n\text{-}C_6F_{13})_2C(O)$ (**IIa**), $[(CF_3)_2CFOCF_2CF_2]_2C(O)$ (**IIb**), $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)$-$CF_2CF_2OCF(CF_3)_2$ (**IIc**), $C_2F_5O(C_2F_4O)_4CF_2C(O)CF_2CF_2[OCF_2CF(CF_3)]_2O$-$C_3F_7$ (**IId**), $C_2F_5O(C_2F_4O)_5CF_2C(O)(CF_2CF_2)_2OCF(CF_3)_2$ (**IIe**) and $C_2F_5O(C_2F_4O)_5CF_2C(O)CF_2CF_2OCF(CF_3)_2$ (**IIf**) by the methods which we have previously reported [15, 16] from diethyl carbonate [eqns. (1) and (2)] or perfluoroalkylether ester [eqn. (2) only]. The starting materials for the synthesis of ketones are summarized in Table 1.

The lithium salt of **I**, unlike its magnesium counterpart, is less stable and forms the ester **I** which can further react with R_fLi to form ketone **II**.

TABLE 1

Starting materials for the synthesis of perfluoroalkyl or perfluoroalkylether ketones

Compound	Starting materials	
IIa	eqn. (1):	$R_f^1 = n\text{-}C_6F_{13}$, R and $R' = C_2H_5$, $M = MgBr$
	eqn. (2):	$R_f^2 = n\text{-}C_6F_{13}$, $R = CH_3$, $M = Li$
IIb	eqns. (1) and (2):	R_f^1 and $R_f^2 = (CF_3)_2CFOCF_2CF_2$, $R = CH_3$, $R' = C_2H_5$, $M = Li$
IIc	eqn. (2):	$R_f^1 = CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$, $R_f^2 = (CF_3)_2CFOCF_2CF_2$, R and $R' = CH_3$
IId	eqn. (2):	$R_f^1 = C_2F_5O(C_2F_4O)_4CF_2$, $R_f^2 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$, R and $R' = CH_3$
IIe	eqn. (2):	$R_f^1 = C_2F_5O(C_2F_4O)_5CF_2$, $R_f^2 = (CF_3)_2CFO(CF_2CF_2)_2$, R and $R' = CH_3$
IIf	eqn. (2):	$R_f^1 = C_2F_5O(C_2F_4O)_5CF_2$, $R_f^2 = (CF_3)_2CFOCF_2CF_2$, R and $R' = CH_3$

It is known that perfluoroalkyl lithium and perfluoroalkylether lithium without an oxygen β to the reaction center are quite unstable at -78 °C in diethyl ether and must be prepared and reacted immediately with substrates in an *in-situ* manner. Hence, compound **IIa** was prepared from diethyl carbonate using the Grignard reagent [eqn. (1)] and the lithium reagent [eqn. (2)]. By the combination of the Grignard and lithium reagent method, the yield of **IIa** was increased to 95% in comparison to 55% for $(n\text{-}C_8F_{17})_2C(O)$ which was produced by the use of lithium reagent [15]. Compound **IIb** was prepared by the reported method [15]. Compounds **IIc**, **IId**, **IIe** and **IIf** were synthesized from the perfluoro ester **I** and lithium reagent according to eqn. (2) by the typical procedure used for the preparation of ketones in diethyl ether except that **IIe** was prepared by the *in-situ* reaction. Compound **IIf** was synthesized in perfluoro-2-butyltetrahydrofuran instead of diethyl ether. The reaction conditions for the preparation and characterization of all the perfluoroketones are listed in Table 2. These ketones (**II**) likewise formed the hydrate in air quite rapidly as previously reported [15, 16].

Synthesis of perfluorinated tertiary alcohols

The high molecular weight perfluoroalkylether tertiary alcohols (**IIIa** to **IIIg**) were prepared by the reaction of the perfluoro ketones, **IIa** to **IIf**, and the perfluoroalkylether lithium reagents (R_f^3Li) with an oxygen atom β to the carbon atom attached to lithium according to eqn. (3) and are summarized as follows.

IIIa: $R_f^1 = R_f^2 = n\text{-}C_6F_{13}$, $R_f^3 = (CF_3)_2CFOCF_2CF_2$
IIIb: $R_f^1 = R_f^2 = R_f^3 = (CF_3)_2CFOCF_2CF_2$

TABLE 2

Preparation and characterization of perfluoro ketones

Compound	Molar[a] ratio	Solvent	Isolated yield (GC area %)	Boiling point (°C/mmHg)	IR: (C=O) (cm^{-1})	MS	Combustion data: (calcd./Found) %C	Combustion data: (calcd./Found) %H
IIa (nc)	3.7	Et_2O	83 (95)	138/80	1787	647 $(M-F)^+$	23.44/22.95	0.00/0.09
IIb[b]	2.2	Et_2O	86[c]	130	1786	579 $(M-F)^+$	—	—
IIc (nc)	1.1	Et_2O	96 (98)	200	1790	811 $(M-F)^+$	21.70/21.43	0.00/0.15
IId (nc)	1.2	Et_2O	60 (65)	88/0.01	1810	777 $(R_f^1COC_2F_4)^{+d}$ 501 $(R_f^2-C_2F_4O)^+$	21.43/20.98	0.00/0.12
IIe (nc)	3.7	Et_2O	30 (43)	110/2.2	1802	927 $(M-C_2F_5OC_2F_4O)^{+d}$	21.41/21.46	0.00/0.00
					1787	811 $(M-C_2F_5O(C_2F_4O)_2)^+$		
IIf (nc)	1.2	$2\text{-}C_4F_9C_4F_7O$[e]	93 (98)	152/30	1802	827 $(M-C_2F_5OC_2F_4O)^{+d}$ 711 $(M-C_2F_5O(C_2F_4O)_2)^+$	21.17/21.14	0.00/<0.2

[a] For compounds **IIa** and **IIb**: $R_f^1I/(EtO)_2C(O)$; for compounds **IIc** to **IIf**: $R_f^2I/R_f^1C(O)OR$.

[b] Known compound, see ref. 15.

[c] Solvent peaks interfered with product identification.

[d] Molecular ion peaks (> 1000) were beyond the limit of the spectrometer; however, fragmentation peaks were consistent with structure.

[e] $2\text{-}C_4F_9C_4F_7O$: perfluoro-2-butyltetrahydrofuran.

IIIc: $R_f^1 = CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$, $R_f^2 = R_f^3 = (CF_3)_2CFOCF_2CF_2$

IIId: $R_f^1 = C_2F_5O(C_2F_4O)_4CF_2$, $R_f^2 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$, $R_f^3 = (CF_3)_2CFOCF_2CF_2$

IIIe: $R_f^1 = C_2F_5O(C_2F_4O)_5CF_2$, $R_f^2 = (CF_3)_2CFO(CF_2CF_2)_2$, $R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$

IIIf: $R_f^1 = C_2F_5O(C_2F_4O)_5CF_2$, $R_f^2 = (CF_3)_2CFOCF_2CF_2$, $R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$

IIIg: $R_f^1 = CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$, $R_f^2 = (CF_3)_2CFOCF_2CF_2$, $R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2$

With a better understanding of the thermal stability of perfluoroorganometallic reagents and their reactivity toward diethylcarbonate, perfluoroesters and perfluoroketones, we have synthesized the perfluoro alcohols **IIIa** to **IIIf** from the ketones **IIa** to **IIf**, respectively, and **IIIg** from **IIc**. The reaction conditions, such as the molar ratio of reactants, time and solvent, are listed in Table 3. The characterization of perfluoro tertiary alcohols is listed in Table 4.

Effect of perfluoroorganometallic reagent

For the conversion of ketones **II** to tertiary alcohols **III**, perfluoroalkylether lithium containing an ether oxygen β to the reaction center had to be used as these were quite stable at −78 °C in diethyl ether and could be added to the carbonyl group of the ketones. When less stable R_f^3Li, such as perfluoroalkyl lithium or perfluoroalkylether lithium, without the stabilizing β-oxygen atom, were generated from the iodides at −78 °C in the presence of ketones, it appeared that these organometallic species decomposed at a rate faster than their addition to the ketones. Consequently no alcohols were formed. With R_f^3MgBr, the rate of reaction with ketones is too slow to be of preparative value.

Effect of mode of addition

The mode of addition is also very important. The less stable type of perfluoroalkyl lithium or perfluoroalkylether lithium without a β-oxygen atom must be prepared and reacted with substrates in an *in-situ* manner for the high-yield synthesis of ketones (see Table 2, compounds **IIa** and **IIe**). The stable type of perfluoroalkylether lithium with a β-oxygen atom can be preformed and then reacted with the substrate (see Table 2, compounds **IIc**, **IId**, and **IIf**, and Table 3, compounds **IIIa** to **IIIg**) or can also be reacted with the substrate in an *in-situ* manner (see Table 2, compound **IIb**).

Effect of the solvent

From the experimental results (see Table 2, compounds **IIa** to **IIe**, and Table 3, compounds **IIIa** to **IIId**), it can be seen that the higher the molecular weight of the perfluoro ketones and alcohols, the lower the yield obtained in diethyl ether. For high molecular weight perfluoro iodides, esters and ketones, we have found that perfluoro-2-butyltetrahydrofuran was a better

TABLE 3

Preparation of perfluoro tertiary alcohols

Compound	Molar ratio $R_f^3I/R_f^1C(O)R_f^2$	Solvent	Time (h)	GC area %		
				Unreacted ketones	Products	
					Alcohols	Unknowns
IIIa	2.0	Et_2O	20	15	81	4
IIIb	1.4	Et_2O	20	–	75[a]	–
IIIc	1.1	Et_2O	18	14	78	6
IIIc	1.2	$2\text{-}C_4F_9C_4F_7O$[c]	2.0	1	98	1
IIId	2.9	Et_2O	22	47	48	5
IIIe	2.0	Et_2O, Freon E2[b]	20	21	71	8
IIIf	2.0	$2\text{-}C_4F_9C_4F_7O$[c]	4.5	2	96	2
IIIg	1.3	Et_2O, Freon E2[b]	20	24	64	12

[a] Isolated yield, solvent peak interfered with starting materials, ketone **IIb**.

[b] Freon E2: $C_3F_7OCF(CF_3)CF_2OCF(H)CF_3$. To R_f^3Li solution in Et_2O was slowly added the $R_f^1C(O)R_f^2$ solution in Freon E2 (~25% by weight).

[c] $2\text{-}C_4F_9C_4F_7O$: perfluoro-2-butyltetrahydrofuran. 4.8 mmol of R_f^3I (**IIIc**) or 8.0 mmol of R_f^3I (**IIIf**) in 40 ml $2\text{-}C_4F_9C_4F_7O$ and 4.0 mmol of $R_f^1C(O)R_f^2$ in 8 ml $2\text{-}C_4F_9C_4F_7O$.

TABLE 4

Characterization of perfluoro tertiary alcohols

Compound	Boiling point (°C/mmHg)	IR: (OH) (cm^{-1})	Isolated yield (GC area %)	Combustion data (Calcd./Found)		MS (chemical ionization)
				%C	%H	
IIIa	189/80	3621	49 (81)	21.71	0.11	933 $(M-F)^+$
(nc)				21.21	0.18	914 $(M-2F)^+$
IIIb	117/25	3614	75 (–)[a]	21.74	0.11	845 $(M-HF-F)^{+c}$
(nc)				21.50	0.16	
IIIc	159/25	3613	95 (98)	21.52	0.09	911 $(M-HF-OC_3F_7)^{+c,d}$
(nc)				21.32	0.18	
IIId	177[b]	3614	– (48)	21.28	0.06	
(nc)				21.04	0.10	
						961 $(R_f^2 \overset{\overset{\text{OH}}{\vert}}{C} (R_f^3)CF_2-HF)^{+d}$ 911 $(R_f^2C(R_f^3)(OH)-HF)^+$
IIIe	103/0.30	3614	45 (71)	21.40	0.06	911 $(R_f^3C(O)C_4F_8OCF_2)^{+d}$
(nc)				21.40	0.16	679 $(R_f^2C(O)C_2F_4OC_3F_6)^+$
IIIf	123/0.05	3612	89 (96)	21.24	0.06	811 $(R_f^3C(O)C_2F_4OCF_2)^{+d}$
(nc)				21.09	0.15	579 $(R_f^2C(O)C_2F_4OC_3F_6)^+$
IIIg	147/0.45	3616	48 (64)	21.56	0.07	911 $(R_f^1\overset{\overset{\text{O}}{\vert}}{C}(R_f^2)C_2F_3)^{+d}$
(nc)				21.31	0.14	579 $(R_f^2C(O)C_2F_4OC_3F_6)^+$ 501 $(R_f^3-C_2F_4O)^+$

[a] Solvent peak interfered with starting material peak.

[b] Determined by TGA analysis.

[c] Determined by electron impact mode.

[d] Molecular ion peaks (> 1000) were beyond the limit of the spectrometer; however, fragmentation peaks were consistent with structure.

solvent than diethyl ether and Freon E2/diethyl ether (see Table 2, compound **IIf**, and Table 3, compounds **IIIc** and **IIIf**). Higher reactivity and improved solubility were realized.

By controlling the reaction conditions, it has thus been possible to synthesize a variety of high molecular weight perfluoro tertiary alcohols (**IIIa** to **IIIg**) in 45–95% isolated yields. This study has been extended to high molecular weight difunctional perfluoroalkylether tertiary alcohols as well as polyfunctional tertiary alcohols. The results will be published in forthcoming communications.

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