Journal of Fluorine Chemistry, 59 (1992) 113–125

Perfluoro tertiary alcohols
II. Synthesis of high molecular weight perfluorinated diketones, keto alcohols and tertiary dialcohols

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(Received October 25, 1991; accepted December 20, 1991)

Abstract

A variety of perfluorinated diketones, $R_f^1C(O)R_f^aC(O)R_f^1$ (**I**), keto alcohols, $R_f^1R_f^2C(OH)R_f^aC(O)R_f^1$ (**II**), and dialcohols, $R_f^1R_f^2C(OH)R_f^aC(OH)R_f^1R_f^2$ (**III**), $R_r^1 = (CF_3)_2CFO(CF_2)_2$, $(CF_3)_2CFO(CF_2)_4$ and $CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$; $R_f^2 = (CF_3)_2CFO(CF_2)_2$ and $C_3F_7O[CF(CF_3)CF_2O]_2(CF_2)_2$; and $R_f^a = (CF_2)_3$, $(CF_2)_8$, $CF_2OCF_2CF_2OCF_2$, $(CF_2)_2O(CF_2)_5O(CF_2)_2$ and $(CF_2)_4O(CF_2)_4O(CF_2)_4$, have been prepared via perfluoroalkylether lithium intermediates. In the reaction of diketones with perfluoro lithium reagents, the solvent and the nature of the R_f^a groups play important roles in determining the yield and the nature of the reaction products formed. The reaction of diketone **I** [where R_f^a is other than $(CF_2)_3$] with excess perfluoroalkylether lithium yielded the diol **III** as the principal product and keto alcohol **II** as the minor product. However, when $R_f^a = (CF_2)_3$, the product is exclusively keto alcohol **II**.

Introduction

We have previously reported [1] on the synthesis of high molecular weight perfluoroalkylether-substituted tertiary monoalcohols via organometallic intermediates. Subsequently, the study was extended to the synthesis of high molecular weight perfluoroalkylether-substituted tertiary dialcohols.

The reactions between perfluoroalkyl and perfluoroalkylether lithium with diethyl oxalate, diethyl hexafluoroglutarate and diethyl tetrafluorosuccinate were utilized by us earlier [2, 3] in the preparation of diketones. Perfluorinated dialcohols, $HOC(CF_3)_2R_f^aC(CF_3)_2OH$, $R_f^a = (CF_2)_6$, 1,4-C_6F_4 and 4,4'-$C_6F_4C_6F_4$, have been prepared from hexafluoroacetone and bis-organometallic reagents [4, 5]. Other reported methods of synthesis of perfluoro dialcohols include preparation of $[(C_6F_5)C(CF_3)OH]_2$ from octafluoroacetophenone by photolysis [6] and the reaction of hexafluoroacetone with triethyl phosphate [7]. However, high molecular weight perfluoroalkylether-substituted tertiary dialcohols have not been described.

We wish to report an improved method which has facilitated the synthesis of a number of this type of dialcohols in excellent yield. We also report the by-products, keto alcohols and the intermediate products, diketones.

0022-1139/92/$5.00

Results and discussion

Synthesis of perfluorinated diketones

In our present study, we have synthesized these high molecular weight perfluoroalkylether diketones by two different procedures; the addition of diester to the preformed $R_f{}^1Li$ (method A: for $R_f{}^1 = (CF_3)_2CFO(CF_2)_2-$) or the reaction between the diester and $R_f{}^1Li$ generated *in situ* (method B: for $R_f{}^1 = (CF_3)_2CFO(CF_2)_4-$) [see eqn. (1)].

$$2R_f{}^1I + 2MeLi + ROC(O)R_f{}^aC(O)OR \xrightarrow[-78\ ^\circ C]{\text{solvent}} \underset{\textbf{I}}{R_f{}^1C(O)R_f{}^aC(O)R_f{}^1} \qquad (1)$$

Ia: $R_f{}^1 = (CF_3)_2CFO(CF_2)_2$, $R_f{}^a = -(CF_2)_3-$, $R = C_2H_5$
Ib: $R_f{}^1 = (CF_3)_2CFO(CF_2)_4$, $R_f{}^a = -(CF_2)_3-$, $R = C_2H_5$
Ic: $R_f{}^1 = (CF_3)_2CFO(CF_2)_4$, $R_f{}^a = -(CF_2)_8-$, $R = C_2H_5$
Id: $R_f{}^1 = (CF_3)_2CFO(CF_2)_2$, $R_f{}^a = -CF_2OCF_2CF_2OCF_2-$, $R = CH_3$
Ie: $R_f{}^1 = (CF_3)_2CFO(CF_2)_4$, $R_f{}^a = -CF_2OCF_2CF_2OCF_2-$, $R = CH_3$
If: $R_f{}^1 = (CF_3)_2CFO(CF_2)_2$, $R_f{}^a = -(CF_2)_4O(CF_2)_4O(CF_2)_4-$, $R = C_2H_5$

All the diketones except **Ig** were prepared by methods A and B which we have also previously reported [1–3]. Compound **Ig** was prepared from the diiodide and monoester as in eqn. (2).

$$IR_f{}^aI + 2MeLi + 2R_f{}^1C(O)OR \xrightarrow[-78\ ^\circ C]{\text{solvent}} \underset{(\text{I})}{R_f{}^1C(O)R_f{}^aC(O)R_f{}^1} \qquad (2)$$

Ig: $R_f{}^1 = CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$, $R_f{}^a = -(CF_2)_2O(CF_2)_5O(CF_2)_2-$, $R = CH_3$

The results are listed in Table 1. From the experimental results (see Table 1), it can be seen that a greater excess of $R_f{}^1I$ was required to improve the yield (exp. 1 and 2). For a high molecular weight $R_f{}^a$, the perfluoro-2-butyltetrahydrofuran (PBTH) was a better solvent than diethyl ether in achieving a high yield of product (exp. 7).

The reaction of the diiodide [eqn. (2)] was more complicated than that of the diester and gave a lower yield of the desired product. Table 2 provides a summation of the yield of the reaction products based on a variation in the experimental conditions. The low yield of desired product in diethyl ether was probably due to the low solubility of the reactants, $IR_f{}^aI$ and $R_f{}^1C(O)OMe$ (see Table 2, exp. 1). The rate of the competing side-reaction between $R_f{}^1C(O)OMe$ and MeLi depended on the solvents. The percentage yield of $R_f{}^1C(O)Me$ was PBTH (23) $\gg$ Et_2O:Freon E2 (10,3) $>$ Et_2O (8) (see Table 2). An attempt to prepare compound **Ig** by addition of $R_f{}^1C(O)OMe$ to preformed $LiR_f{}^aLi$ in PBTH under similar conditions was unsuccessful. This suggests that the dilithium, $LiR_f{}^aLi$, is less stable in PBTH than in Et_2O (see Table 2, exp. 1). Characterization of the diketones was as shown in Table 3.

Synthesis of keto alcohols and dialcohols

All the high molecular weight perfluoroalkylether-substituted keto alcohols (**IIa** to **IIg**) and dialcohols (**IIIc** to **IIIg**) were prepared by the addition of

TABLE 1

Preparation of perfluoro diketones from diesters

Exp.	Compound	Method[a]	Molar ratio R_f^1I: diester	Solvent	Reaction time (h)	Products (GC area %)		
						$R_f^1\overset{\overset{O}{\|}}{C}R_f^a\overset{\overset{O}{\|}}{C}Me$	$R_f^1\overset{\overset{O}{\|}}{C}R_f^a\overset{\overset{O}{\|}}{C}OR$	$R_f^1\overset{\overset{O}{\|}}{C}R_f^a\overset{\overset{O}{\|}}{C}R_f^1$
1	**Ia**	A	2.2	Et_2O	12	0	15	85
2	**Ia**	A	2.5	Et_2O	17	0	2	98
3	**Ib**	B	3.6	Et_2O	2.5	7	11	81
4	**Ic**	B	3.6	Et_2O	4.5	9	13	78
5	**Id**	A	2.4	Et_2O	4.0	0	4	96
6	**Ie**	B	3.1	Et_2O	2.0	11	16	73
7	**If**	A	3.0	PBTH[b]	2.5	0	1	99

[a] Method A: diester was added to preformed R_f^1Li. Method B: *in situ* reaction.
[b] PBTH = perfluoro-2-butyltetrahydrofuran.

TABLE 2

Preparation of perfluoro diketone $R_f^1C(O)R_f^aC(O)R_f^1$ (**Ig**) from diiodide[a]

Exp.	Molar ratio $R_f^1C(O)OMe/IR_f^aI$	Solvent (vol. ratio)	Time (h)	GC area (%)					
				Unreacted $R_f^1C(O)OMe$	Products				
					Ig	$R_f^1C(O)Me$	$R_f^1C(O)R_f^aH$	HR_f^aH	Unknown
1[b]	1.8	Et_2O	22	24	34	8	11	6	17[c]
2	1.8	Et_2O:Freon E2[d] (6:1)	4	4	54	13	25	2	2
3	2.1	Et_2O:Freon E2[d] (4:1)	3	8	61	10	17	2	2
4	2.1	PBTH[e]	2	3	48	23	19	3	4
5	2.2	Et_2O:PBTH[e] (1:1)	3	9	57	20	10	1	3

[a] $R_f^1 = CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$; $R_f^a = -(CF_2)_2O(CF_2)_5O(CF_2)_2-$; *in situ* method used.

[b] Method A: $R_f^1C(O)OMe$ was added to preformed LiR_f^aLi.

[c] 8% IR_f^aI, 8% $R_f^1C(O)R_f^aI$.

[d] Freon E2 = $C_3F_7OCF(CF_3)CF_2OCF(H)CF_3$.

[e] PBTH = perfluoro-2-butyltetrahydrofuran.

TABLE 3

Characterization of perfluoro diketones

Compound	B.p. (°C/mmHg)	Isolated (GC area) yield (%)	IR[c] (C=O, cm^{-1})	MS (*m*/*z*)[d]	Combustion data (calc./found)	
					C (%)	H (%)
Ia (nc)	215	82 (98)[a]	1790	757 $(M-F)^+$	23.21 23.02	0 0.00
Ib (nc)	162/30	64 (81)	1790	975 $(M-F)^+$	23.38 22.90	0 0.12
Ic (nc)	107/0.01	58 (78)	1790	813[e] $[R_f^1C(O)C_8F_{16}]^+$	23.51 22.98	0 0.12
Id (nc)	99/10	79 (96)	1799	839 $(M-F)^+$	22.39 21.80	0 0.06
Ie (nc)	108/22	49 (73)	1799	579[e] $[R_f^1C(O)CF_2O(CF_2)_2]^+$	22.70 22.04	0 0.19
If (nc)	112/0.2	94 (99)	1788	807[e] $[FC(O)R_f^aC(O)(CF_2)_2]^+$ 513 $[R_f^1C(O)(CF_2)_4]^+$	22.91 22.47	0 0.07
Ig (nc)	131/0.01	62 (61)[b]	1791	645[e] $[R_f^1C(O)(CF_2)_2]^+$ 557 $[FC(O)R_f^aC(O)]^+$	22.15 22.24	0 0.00

[a] From exp. 2 in Table 1.

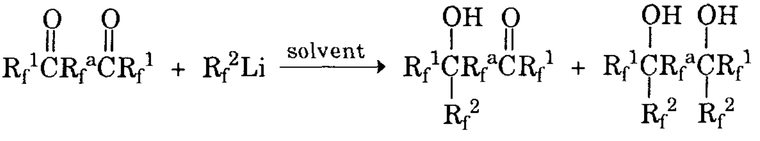
[b] From exp. 3 in Table 2, isolated yield based on IR_f^aI used.

[c] Neat liquid, capillary film between NaCl plates.

[d] Determined by electron impact or chemical ionization.

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

diketones (**Ia** to **Ig**) to the preformed perfluoroalkylether lithium reagents (R_f^2Li) containing an oxygen atom β to the carbon atom attached to lithium, according to eqn. (3).



$$R_f^1\overset{O}{\overset{\|}{C}}R_f^a\overset{O}{\overset{\|}{C}}R_f^1 + R_f^2Li \xrightarrow{\text{solvent}} R_f^1\underset{R_f^2}{\overset{OH}{C}}R_f^a\overset{O}{\overset{\|}{C}}R_f^1 + R_f^1\underset{R_f^2}{\overset{OH}{C}}R_f^a\underset{R_f^2}{\overset{OH}{C}}R_f^1 \qquad (3)$$

(I) (II) (III)

IIa: $R_f^1 = R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -(CF_2)_3-$
IIb: $R_f^1 = (CF_3)_2CFO(CF_2)_4$; $R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -(CF_2)_3-$
IIc, IIIc: $R_f^1 = (CF_3)_2CFO(CF_2)_4$; $R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -(CF_2)_8-$
IId, IIId: $R_f^1 = R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -CF_2OCF_2CF_2OCF_2-$
IIe, IIIe: $R_f^1 = (CF_3)_2CFO(CF_2)_4$; $R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -CF_2OCF_2CF_2OCF_2-$
IIf, IIIf: $R_f^1 = (CF_3)_2CFO(CF_2)_2$; $R_f^2 = C_3F_7O[CF(CF_3)CF_2O]_2(CF_2)_2$; $R_f^a = -(CF_2)_4O(CF_2)_4O(CF_2)_4-$
IIg, IIIg: $R_f^1 = CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$; $R_f^2 = (CF_3)_2CFO(CF_2)_2$; $R_f^a = -(CF_2)_2O(CF_2)_5O(CF_2)_2-$

All the reactions are listed in Table 4. The physical properties and analyses of the keto alcohols and dialcohols are summarized in Tables 5 and 6. All the keto alcohols except compounds **IIa** and **IIb** are minor products of the reactions. Compounds **IIc, IId, IIg** and **IIf** were isolated by preparation GC and have not been fully characterized. In our present study we have examined in detail the preparation of the dialcohol III. The reactions were carried out under various experimental conditions (see Table 4).

Effect of solvent

In our previous study [1] we found that PBTH was a better solvent than diethyl ether and Freon E2 for the synthesis of high molecular weight perfluoro tertiary alcohols. This is also true for the preparations of the dialcohols, probably due to the improved solubility and increased nucleophilic character of the lithium reagents. Under comparable conditions, the reactions of the diketones and the perfluoroalkylether lithium reagents occurred at a faster rate and provided a higher yield and cleaner reaction in PBTH than in Et_2O:Freon E2 mixtures and in Et_2O (see Table 4, exp. 4, 5 and 6).

Experiments (exp. 12–16, Table 4) in either PBTH or Et_2O:PBTH mixtures yielded the keto alcohol **IIg** and the dialcohol **IIIg**, except that they showed different percentage GC areas. GC analysis of **IIIg** showed only one sharp peak. However, compound **IIIg** when prepared in an Et_2O:Freon E2 mixture (exp. 11, Table 4) gave a broad GC peak. The IR, MS and elemental analysis of the two samples did not show any significant differences. Similar results were also obtained for other dialcohols such as **IIIc** (exp. 5, Table 4) and **IIIe** (exp. 8, Table 4). The reason for this behaviour is not clear.

TABLE 4

Preparation of perfluoro keto alcohols and dialcohols[a]

Exp.	Reactant diketone	Molar ratio R_f^2I/diketone	Solvent (volume ratio)	Time (h)	GC area (%)			
					Unreacted diketone	Products		
						keto alcohol	dialcohol	unknowns
1	**Ia**	3.1	Et_2O	20	**Ia**, 1	**IIa**, 99	**IIIa**, 0	0
2	**Ib**	3.4	Et_2O	24	**Ib**, 29	**IIb**, 65	**IIIb**, 0	6
3	**Ib**	4.0	PBTH[c]	4	**Ib**, 0	**IIb**, 99	**IIIb**, 0	1
4	**Ic**	4.7	Et_2O	27	**Ic**, 75	**IIc**, 3	**IIIc**, 17	5
5	**Ic**	4.0	Et_2O:Freon E2[b] (3:1)	21	**Ic**, 9	**IIc**, 9	**IIIc**, 82[d]	0
6	**Ic**	4.0	PBTH[c]	6	**Ic**, 0	**IIc**, 6	**IIIc**, 92	2
7	**Id**	4.0	Et_2O	21	**Id**, 13	**IId**, 10	**IIId**, 64	13
8	**Ie**	3.5	Et_2O:Freon E2[b] (6:1)	19	**Ie**, 9	**IIe**, 12	**IIIe**, 79[d]	0
9	**Ie**	4.0	PBTH[c]	5.5	**Ie**, 3	**IIe**, 14	**IIIe**, 80	3
10	**If**	4.0	PBTH[c]	3.5	**If**, 2	**IIf**, 12	**IIIf**, 86	0
11	**Ig**	4.0	Et_2O:Freon E2[b] (3:1)	20	**Ig**, 0	**IIg**, 2	**IIIg**, 98[d]	0
12	**Ig**	4.0	Et_2O:PBTH[c] (3:1)	24	**Ig**, 0	**IIg**, 4	**IIIg**, 92	4
13	**Ig**	3.0	Et_2O:PBTH[c] (3:2)	6.0	**Ig**, 2	**IIg**, 11	**IIIg**, 84	3
14	**Ig**	4.0	Et_2O:PBTH[c] (3:2)	5.0	**Ig**, 0	**IIg**, 2	**IIIg**, 98	0
15	**Ig**	2.5	PBTH[c]	4.5	**Ig**, 6	**IIg**, 17	**IIIg**, 77	0
16	**Ig**	4.0	PBTH[c]	2.0	**Ig**, 0	**IIg**, 2	**IIIg**, 98	0

[a] Diketones: $R_f^1C(O)R_f^aC(O)R_f^1$ (**I**); keto alcohols: $R_f^1R_f^2C(OH)R_f^aC(O)R_f^1$ (**II**); dialcohols: $R_f^1R_f^2C(OH)R_f^aC(OH)R_f^2R_f^1$ (**III**).

[b] Freon E2 = $C_3F_7OCF(CF_3)CF_2OCF(H)CF_3$.

[c] PBTH = perfluoro-2-butyltetrahydrofuran.

[d] Compounds **IIIc**, **IIIe** and **IIIf** prepared in Et_2O:Freon E2 mixture differed from the same samples prepared in other solvents in giving broader GC peaks, although IR, MS and elemental analysis were similar. The reason for this behavior is not clear.

TABLE 5

Characterization of perfluoro keto alcohols[a]

Compound	B.p. (°C/mmHg)	Isolated (GC area) (%)	IR (cm^{-1})[b]		MS (m/z)[c]	Combustion data (calc./found)	
			C=O	OH		C (%)	H (%)
IIa (nc)	78/0.01	77 (99)	1790	3608	857 $(M-HF-C_3F_7O)^+$ 729 $(M-HF-C_3F_7OC_2F_4)^+$	22.62 22.19	0.09 0.19
IIb (nc)	114/0.05[d]	30 (65)	1790	3612	839 $(M-HF-C_3F_7OC_4F_8C(O))^+$ 563 $(C_3F_7OC_4F_8C(O)C_3F_6)^+$	22.84 22.29	0.08 0.15
IIe (nc)	–[e]	6 (12)	1800	3608	845[f] $(R_f^1R_f^2C(O)CF_2OC_2F_3)^+$	22.34 21.97	0.07 0.15

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[a] Keto alcohols: $R_f^1R_f^2C(OH)R_f^aC(O)R_f^1$ (II). Compounds **IIc**, **IId**, **IIf** and IIg were determined by IR and MS, and the results were consistent with the structure.

[b] Neat liquid, capillary film between NaCl plates.

[c] Determined by electron impact or chemical ionization; molecular ion peaks (>1000) were beyond the limit of the spectrometer; however, fragmentation peaks were consistent with the structure.

[d] Small scale of reaction (2.1 mmol diketone).

[e] Compounds **IIc**, **IId**, **IIe**, **IIf** and **IIg** were minor products isolated by preparative GC.

[f] $R_f^1=(CF_3)_2CFO(CF_2)_4$; $R_f^2=(CF_3)_2CFO(CF_2)_2$.

TABLE 6

Characterization of perfluoro dialcohols[a]

Compound	B.p. (°C/mmHg)	Isolated (GC area) (%)	IR[b] (OH, cm^{-1})	MS (m/z)[c]	Combustion data (calc./found)	
					C (%)	H (%)
IIIc (nc)	169/0.01	75(92)	3620	679 $(C_3F_7OC_4F_9C(O)C_2F_4OC_3F_6)^+$	22.71 23.16	0.11 0.27
IIId (nc)	117/0.01	33 (64)	3609	765 $((C_3F_7OC_2F_4)_2C(OH)CF_2OC_2F_4)^+$	21.83 21.42	0.14 0.23
IIIe (nc)	141/0.03	63 (80)	3607	$845^d\ (R_f^1R_f^2\overset{\overset{O}{\|}}{C}CF_2OC_2F_3)^+$	22.10 22.12	0.12 0.20
IIIf (nc)	198/0.03	68 (86)	3617	2454^e (M − 2HF)$^+$ 2435 (M − 2HF − F)$^+$	22.15 21.75	0.08 0.17
IIIg (nc)	171/0.03	96 (98)	3614	2104^e (M − 2HF)$^+$ 2085 (M − 2HF − F)$^+$	21.85 22.08	0.09 0.10

[a] Dialcohols: $R_f^1R_f^2C(OH)R_f^aC(OH)R_f^2R_f^1$ (**III**).

[b] Neat liquid, capillary film between NaCl plates.

[c] Determined by electron impact or chemical ionization. Molecular ion peaks (>1000) were beyond the limit of the spectrometer; however, fragmentation peaks were consistent with the structures.

[d] $R_f^1=(CF_3)_2CFO(CF_2)_4$; $R_f^2=(CF_3)_2CFO(CF_2)_2$.

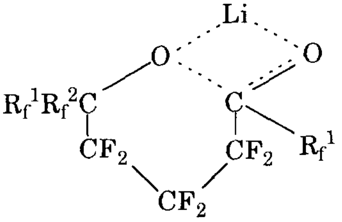
[e] GC/MS analyses performed by Middle Atlantic MS Laboratory, Baltimore, MD, USA.

Effect of the molar ratio of reactants

From the experimental results, it can be seen that increasing the molar ratio of R_f^2I and diketone from 2.5 to 4, (exp. 15 and 16, Table 4) and from 3 to 4 (exp. 13 and 14, Table 4), increased the yield of dialcohol from 77 to 98% and from 84 to 98%, respectively. Hence, the molar ratio of reactants is an important factor in producing high yields in these reactions.

Effect of the nature of the $-R_f^a-$ group

The nature of the $-R_f^a-$ group also plays an important role in determining the reaction product formed, and the yield of the product, for the reaction of diketones and perfluoro lithium reagents (R_f^2Li), but has no effect in the formation of diketones. From Table 4, exp. 3, 9, 6 and 16, it can be seen that under comparable conditions [$R_f^2 = (CF_3)_2CFOCF_2CF_2$; solvent = PBTH] the yields of dialcohols increase in the following order; $R_f^a = -(CF_2)_3-$ (0%) < $-CF_2OCF_2CF_2OCF_2-$ (80%) < $-(CF_2)_8-$ (92%) < $-(CF_2)_2O(CF_2)_5$-$(CF_2)_2-$ (98%). The yield of keto alcohols decreases in the same order. When $R_f^a = -(CF_2)_3-$, the product was exclusively the keto alcohols **IIa** and **IIb** (see exp. 1, 2 and 3, Table 4). This may be due to the formation of a stable six-membered cyclic intermediate,



which loses the property of a ketone. This result is similar to the data described for the fluorination of $C_6H_5C(O)(CF_2)_3C(O)C_6H_5$ by SF_4/HF [10]. Under similar conditions, when $R_f^a = -(CF_2)_8-$, the dialcohol **IIIc** was formed in 17 and 92 GC area % in diethyl ether and PBTH solvent, respectively (see Table 4, exp. 4 and 6). This is probably due to the fact that the stability of the cyclic intermediate decreases when the ring size increases (>6). When $R_f^a = -(CF_2)_4O(CF_2)_4O(CF_2)_4-$ (Table 4, exp. 10), the yield of dialcohol **IIIf** (86%) was lower than expected. This is probably due to the high molecular weight and diminished solubility of $C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2Li$ used.

Experimental

General comments

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. All solvents were dried prior to use. $CF_3O[CF_2CF(CF_3)O]_2$-$CF_2CF_2C(O)OMe$ was obtained from Exfluor Research Corporation. $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ and $(CF_3)_2CFO(CF_2CF_2)_xI$ ($x = 1$ and 2) were obtained from Allied Chemical Co., and $EtO(O)C(CF_2)_8C(O)OEt$ and $C_3F_7O[CF$-

$(CF_3)CF_2O]_2CF_2CF_2I$ were from PCR, Inc. $MeO(O)CCF_2OCF_2CF_2OCF_2C(O)OMe$ was from the 3M Corporation. $EtO(O)C(CF_2)_4O(CF_2)_4O(CF_2)_4C(O)OEt$ was prepared by known procedures [8, 9]. Gas chromatographic analyses (GC) were performed on a Perkin-Elmer Sigma Instrument using 10% SP-2100 on a 100/120 mesh Supelcoport 1/4 in. (d)×6 ft. stainless-steel packed column or a Sigma IIB instrument with a 1/4 in. (d)×2 ft. column containing 5% Dexsil 400 on 100/120 mesh Supelcoport. All GC/MS analyses, except those for compounds **IIIf** and **IIIg**, were performed on a Finnigan 4021 mass spectrometer using either the chemical ionization or electron impact mode or both if necessary. The highest mass in the fragmentation peaks is reported except for those compounds which have molecular ion peaks over 1000, beyond the limit of the spectrometer. Infrared 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 3, 5 and 6). All temperatures are reported uncorrected. Yields of products are reported as isolated yield or GC area % or both (see Tables 1, 2, 3, 4, 5 and 6). Some perfluoroketones, keto alcohols and all dialcohols were prepared following typical procedures.

Typical procedure for the preparation of perfluorinated diketones from diesters – $(CF_3)_2CFOCF_2CF_2C(O)(CF_2)_3C(O)CF_2CF_2OCF(CF_3)_2$ (Ia)

To a diethyl ether solution (500 ml) of $(CF_3)_2CFOCF_2CF_2I$ (28.0 g, 68.0 mmol) was slowly added MeLi (48.0 ml of a 1.4 M solution in diethyl ether, 67.2 mmol) at −78 °C over a period of 20 min. After an additional 20 min, a diethyl hexafluoroglutarate (8.0 g, 27.0 mmol) solution in diethyl ether (20 ml) was added at −78 °C over 25 min. After an additional 17 h, the reaction mixture was hydrolyzed with conc. HCl (10 ml) and then poured into 2 N HCl (200 ml). The organic layer was separated, washed with H_2O (60 ml) and dried ($MgSO_4$). Distillation yielded th diketone **Ia** (17.1 g; b.p., 215 °C; 82%).

The other diketones **Ib, Ic, Id, Ie** and **If** were synthesized by a similar procedure as described above, except that the molar ratio of reactants, the reaction time and the solvent were varied (see Table 1). The products, yield, b.p., MS and analysis data of the diketones are listed in Table 3.

Synthesis of perfluorinated diketones from diiodide – $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)(CF_2)_2O(CF_2)_5O(CF_2)_2C(O)CF_2CF_2[OCF(CF_3)CF_2]_2OCF_3$ (Ig)

To a mixture of diethyl ether (480 ml) and a Freon E2 (120 ml) solution containing $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$ (14.72 g, 20.0 mmol) and $CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2C(O)OMe$ (24.49 g, 42.5 mmol) was slowly added MeLi (28.6 ml of a 1.4 M solution in diethyl ether, 40.0 mmol) at −78 °C over a period of 45 min. The solution was stirred at −78 °C for an additional 10 min. An aliquot sample was removed, hydrolyzed with 2 N HCl and analyzed by GC/MS which indicated five major peaks, i.e. $R_f^1C(O)Me$ (8 GC area %), $R_f^1C(O)OMe$ (13 GC area %), $R_f^1C(O)R_f^aH$ (13 GC area %), $R_f^1C(O)R_f^aI$ (6 GC area %) and $R_f^1C(O)R_f^aC(O)R_f^1$ (**Ig**, 58 GC area %) ($R_f^1 = CF_3O[CF_2CF(CF_3)O]_2CF_2CF_2$; $R_f^a = (CF_2)_2O(CF_2)_5O(CF_2)_2$). An additional amount of MeLi (5.0 ml of a 1.4 M solution in diethyl ether, 7.0 mmol) was added. After another 1.5 h (or a total of 3 h), the reaction mixture was hydrolyzed with conc. HCl (10 ml) at −78 °C and then poured over 2 N HCl (200 ml). The organic layer was separated and dried over $MgSO_4$. A GC/MS analysis of the reaction mixture showed HR_f^aH (2%), $R_f^1C(O)Me$ (10%), $R_f^1C(O)OMe$ (8%), $R_f^1C(O)R_f^aH$ (17%) and **Ig** (61%). Distillation on a spinning-band column yielded the pure diketone **Ig** (19.5 g; b.p., 131 °C/ 0.01 mmHg; 62% yield based on IR_f^aI used) (see Table 3).

Four other experiments (see Table 2, exp. 1, 2, 4 and 5) were carried out under slightly different conditions, the conditions and the results being listed in Table 2.

Another experiment was conducted under similar conditions by method A ($R_f^1C(O)OMe$ was added to preformed LiR_f^aLi) in perfluoro-2-butyltetrahydrofuran (PBTH) but did not yield the desired product ***Ig***.

*Synthesis of perfluorinated keto alcohols — $R_f^1R_f^2C(OH)(CF_2)_3C(O)R_f^1[R_f^1 = R_f^2 = (CF_3)_2CFO(CF_2)_2]$ (**IIa**)*

To a diethyl ether solution (250 ml) of R_f^1I (12.73 g, 30.9 mmol) was slowly added MeLi (22.0 ml of a 1.4 M solution in diethyl ether, 30.8 mmol) at −78 °C over a period of 25 min. After an additional 25 min, an $R_f^1C(O)(CF_2)_3C(O)R_f^1$ (7.85 g, 10.1 mmol) solution in diethyl ether (5.0 ml) was added at −78 °C over 5 min. After an additional 20 h, the reaction mixture was hydrolyzed with conc. HCl (5.0 ml) and then poured into 2 N HCl (100 ml). The organic layer was separated and dried over $MgSO_4$. A GC/MS analysis indicated that only the keto alcohol was formed. There was no evidence of dialcohol formation. The crude product was distilled to yield the keto alcohol (8.31 g; b.p., 78 °C/0.01 mmHg; 77%) (see Tables 4 and 5).

*Typical procedure for the preparation of the perfluorinated dialcohols **III** and the keto alcohols **II***

To a PBTH solution (30 ml) of $(CF_3)_2CFOCF_2CF_2I$ (3.30 g, 8.00 mmol) was slowly added MeLi (5.60 ml of a 1.4 M solution in diethyl ether, 7.80 mmol) at −78 °C over 15 min. After an additional 15 min, an $R_f^1C(O)R_f^aC(O)R_f^1$ (**Ig**) ($R_f^1 = CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$, $R_f^a = -(CF_2)_2O(CF_2)_5O(CF_2)_2-$) (3.15 g, 2.00 mmol) solution in PBTH (5.0 ml) was added at −78 °C over 15 min. Aliquot samples were removed periodically, hydrolyzed and analyzed by GC. After an additional 2.0 h, the reaction mixture was hydrolyzed with conc. HCl (2.0 ml) at −78 °C and then poured into 2 N HCl (10 ml). The organic layer was separated, washed with H_2O (10 ml) and dried over $MgSO_4$. A GC/MS analysis of the reaction mixture indicated the following products: keto alcohol (**IIg**) (2 GC area %) and dialcohol (**IIIg**) (98 GC area %).

Distillation yielded compound **IIIg** (4.1 g, b.p. 171 °C/0.03 mmHg) in 96% yield (see Table 4, exp. 14 and Table 6). GC analysis of compound **IIIg** showed one sharp peak.

Five other experiments (see Table 4, exp. 11, 12, 13, 15 and 16) were carried out under slightly different conditions, i.e. variation of molar ratio of reactants, solvent and reaction time. The conditions and the results are listed in Table 4. The minor product, keto alcohol **IIg**, was isolated from exp. 15 by preparative GC. All experiments except exp. 11 showed the same products as in exp. 14 but in different ratios. From exp. 11 in Table 4, compound **IIIg** (b.p., 178–183 °C/0.08 mmHg), which has a similar IR, MS spectral and elemental analysis to that of compound **IIIg** (Table 4, exp. 14), was isolated in 98% yield. GC analysis of **IIIg** (exp. 11) showed a broad peak.

The other keto alcohols **IIb, IIc, IId, IIe** and **IIf** and the dialcohols **IIIc, IIId, IIIe** and **IIIf** were synthesized by procedures similar to that described above. The results are listed in Table 4, 5 and 6.

Acknowledgements

This work was supported by the Materials Directorate of the Wright Laboratory, Wright-Patterson Air Force Base, OH. The authors thank Dr Chi Yu of Chemsys Inc., Dayton, OH and Dr Robert J. Cotter of the Middle Atlantic Mass Spectrometry Laboratory, Baltimore, MD for their mass spectral analyses and interpretation, and Mr Car E. Snyder Jr., Wright-Patterson Air Force Base, OH and Dr K. C. Eapen, University of Dayton Research Institute for useful suggestions.

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