

Synthesis of perfluoro-(1,1-dimethylbutyl)methyl ethers by *vic*-oxymethylfluorination of perfluoro-2-methyl-2-pentene with chloromethyl ethers

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Abstract

Perfluoro-2-methyl-2-pentene was successfully converted to perfluoro-(1,1-dimethylbutyl)methyl ethers by *vic*-oxymethylfluorination with chloromethyl ethers in the presence of KF in aprotic polar solvents such as *N,N*-dimethylformamide and *N*-methylpyrrolidone. By the addition of a catalytic amount of quaternary ammonium salt, the reaction was accelerated and the yield of product greatly increased.

1. Introduction

Fluorine-containing organic compounds are much used as high performance materials. Perfluoroalkyl compounds exhibit low surface energy and play an important role in improving the surfaces of solids and liquids.

Perfluoro-2-methyl-2-pentene (**1**) has been reported to have a very interesting reactivity. This olefin reacts with various nucleophiles to give a carbanion, followed by the elimination of fluoride ion to generate substituted olefins [1–6], or followed by reaction with electrophiles to give addition products [7–10]. Although the intermediacy of a carbanion has been postulated in these reactions, its reactivity has not been well studied. It seems worthwhile to discuss the reactivity of the postulated perfluoro carbanion further.

Olefin **1** is a promising material, since it is obtained with complete selectivity by the anionic dimerization of perfluoropropylene as one of the isomers, and is prepared industrially [11–13].

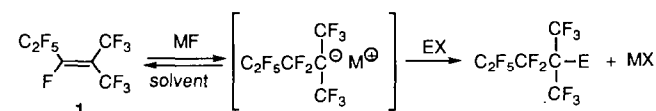
In the present work, in view of the possibility of the *vic*-oxymethylfluorination of perfluoro-olefin **1**, its reaction with chloromethyl ethers has been studied.

2. Results and discussion

Perfluoro-olefin **1** is reported to react with fluoride ion to afford a perfluoro-*t*-carbanion. Under appropriate conditions, this carbanion reacts with a specific elec-

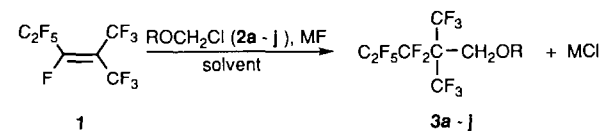
trophile to afford addition products, such as perfluoro-(1,1-dimethylbutyl)methylbenzene [7, 8]. The probable reaction pathway is shown in Scheme 1. However, it has still not been established what kind of electrophile is reactive toward this carbanion. Chloromethyl ethers are possible electrophiles which may give products by the *vic*-oxymethylfluorination of perfluoro-olefin **1** (Scheme 2). To investigate the reactivity of chloromethyl ethers, CsF/diglyme and KF/*N,N*-dimethylformamide (DMF) systems have been employed [7–10].

As a general example, the chloromethyl ether was added to the suspension of the fluoride salt in a mixture of perfluoro-olefin **1** and solvent, and the mixture stirred.



MF = CsF, KF
EX = PhCH₂Br [7,8], RX [9]. R = Me, Et, C₃H₇, C₄H₉. CH₂=CHCH₂; X = I, Br

Scheme 1. Generation of the perfluoro-*t*-carbanion and its reaction with an electrophile.



MF = CsF, KF
a; R = C₈H₁₇ e; R = CH₂=CHCH₂OCH₂CH₂
b; R = Ph f; R = CH₂=CH(CH₂)₈
c; R = PhCH₂ g - i; R = ClCH₂CH₂(OCH₂CH₂)_n, n = 0, 1, 2
d; R = CH₂=CHCH₂ j; R = Cl(CH₂)₆

Scheme 2. The *vic*-oxymethylfluorination of perfluoro-2-methyl-2-pentene.

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TABLE 1. Temperature dependency of the *vic*-oxymethylfluorination reaction^a

Run No.	Temp. (°C)	Time ^b (h)	Yield ^c (%)
1	25	3	74
2	50	3	52
3	80	2	50

^a1/2a/KF = 1.5:1:1, molar ratio.^bTime needed for the consumption of raw chloromethyl octyl ether.^cGLC yield.

The reaction was fairly clean and two new peaks were generated in the GLC trace. One occurred just before the peak for the chloromethyl ether, and the other was nearly at the midpoint between those for the olefin and the chloromethyl ether. After confirming the consumption of raw chloromethyl ether by GLC methods, the suspension was washed with an aqueous 5% HCl solution and then with water. The new products were isolated by fractional distillation. From the ¹H NMR, ¹⁹F NMR and mass spectrum, and by elemental analysis, the product with the longer retention time was identified as perfluoro-(1,1-dimethylbutyl)methyl ether. The other product was confirmed as the fluoromethyl ether FCH₂OR by an independent experiment. On heating at 80 °C for 2 h in the suspension of excess KF in DMF, the chloromethyl alkyl ether was converted quantitatively to the corresponding fluoromethyl ether.

This fluoromethyl ether did not afford the *vic*-oxymethylfluorination product on heating with KF at 50–150 °C under the same reaction conditions. The ether

remained unreacted and was recovered quantitatively after heating.

As shown in Table 1, the lower the temperature, the higher the yield obtained, indicating that the side reaction, i.e. the formation of the fluoromethyl ether, proceeded more slowly at lower temperature.

The selection of fluoride salt and solvent affected the results obtained from this reaction. Yields are summarized in Table 2. The use of a polar solvent was better for KF, but a less polar solvent also showed good results for CsF. For NaF, however, DMF was still unsatisfactory.

It was found that the addition of a catalytic amount of a quaternary ammonium salt improved the yield in the reaction. In the KF/DMF/tetrabutylammonium chloride (TBAC) system, the expected product was obtained almost quantitatively and the fluoromethyl ether was absent. The particular quaternary ammonium salt employed did not affect the yield to any great extent. However, NaF did not exhibit satisfactory results even when TBAC was used.

Yields of product against time during *vic*-oxymethylfluorination are shown in Fig. 1. On adding TBAC, the reaction rate increased greatly.

The results of *vic*-oxymethylfluorination with various chloromethyl ethers are shown in Table 3. Yields were usually very good; however, in the case of the allyl ether, the yield was low. This latter result may have been caused by the substantial loss of product during the work-up process, due to its high vapor pressure. In contrast with the chloromethyl ethers, β -chloroethyl ether and diethylene glycol bis(2-chloroethyl) ether showed no reactivity.

TABLE 2. Effect of solvent and quaternary ammonium salt on *vic*-oxymethylfluorination^a

MF	Solvent	Temp. (°C)	Time (h)	Ammonium salt	Yield (%) ^b	
					Quat. ammonium salt	
					With	Without
CsF	diglyme ^c	25	3	TBAC	–	42
KF	diglyme	25	3	TBAC	2	1
CsF	DMF	25	3	TBAC	–	73
KF	DMF	25	3	TBAC	95	74
KF	DMSO	25	3	TBAC	5	1
KF	NMP ^d	25	3	TBAC	–	63
KF	DMF	25	3	BTMAC ^e	88	74
NaF	DMF	25	3	TBAC	6	4
KF	DMF	50	3	TBAC	69	52
KF	DMF	80	2	TBAC	70	50

^a1/2a/MF = 1.5:1:1, molar ratio.^bGLC yield.^cDiglyme = diethylene glycol dimethyl ether.^dNMP = *N*-methylpyrrolidone.^eBTMAC = benzyltrimethylammonium chloride.

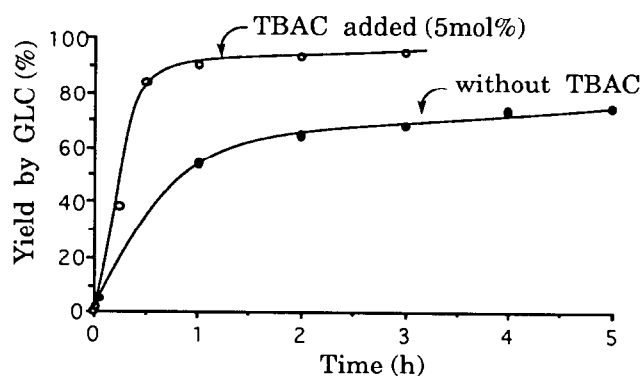
TABLE 3. The vic-oxymethylfluorination of perfluoro-olefin 1 with chloromethyl ethers, ROCH₂Cl

Comp. No. (R)	Yield (%)	B.p. ^a (°C/Torr)	¹⁹ F NMR ^b (CDCl ₃ , δ ppm)	¹ H NMR (CDCl ₃ , δ ppm)	MS (<i>m/z</i>) (M ⁺)	Analysis (%)
						Found (Calc.)
3a (C ₈ H ₁₇)	90	50/0.1	1.11 (quint, 6F); 17.42 (t, 3F); 45.32 (m, 2F); 60.31 (m, 2F)	0.89 (t, 3H); 1.27 (m, 10H); 1.57 (quint, 2H); 3.47 (t, 2H); 4.03 (s, 2H)	461	C, 38.97 (38.97); H, 4.12 (4.14)
3b (Ph)	81	25/0.15	0.89 (quint, 6F); 17.38 (t, 3F); 45.11 (m, 2F); 60.08 (m, 2F)	4.58 (s, 2H); 6.94 (d, 2H); 7.08 (t, 1H); 7.35 (t, 2H)	414	C, 36.78 (36.64); H, 1.48 (1.66)
3c (PhCH ₂)	82	85/4	0.95 (quint, 6F); 17.42 (t, 3F); 45.21 (m, 2F); 60.28 (m, 2F)	4.07 (s, 2H); 4.62 (s, 2H); 7.32–7.40 (m, 5H)	440	C, 37.97 (38.20); H, 2.16 (2.06)
3d (CH ₂ =CHCH ₂)	50	135/760	1.01 (quint, 6F); 16.25 (t, 3F); 42.50 (m, 2F); 56.56 (m, 2F)	4.03 (s, 2H); 4.05 (d, 2H); 5.26 (dd, 1H); 5.32 (dd, 1H); 5.86 (ddt, 1H)	390	C, 31.05 (30.79); H, 1.66 (1.81)
3e (CH ₂ =CHCH ₂ OC ₂ H ₄)	85	50/1	0.98 (quint, 6F); 17.32 (t, 3F); 45.24 (m, 2F); 60.15 (m, 2F)	3.63 (t, 2H); 3.69 (t, 2H); 4.03 (d, 2H); 4.18 (s, 2H); 5.18 (dd, 1H); 5.26 (dd, 1H); 5.88 (ddt, 1H)	434	C, 33.25 (33.20); H, 2.44 (2.55)
3f (CH ₂ =CH(CH ₂) ₈)	86	85/0.55	1.15 (quint, 6F); 17.48 (t, 3F); 45.34 (m, 2F); 60.33 (m, 2F)	1.2–1.5 (m, 10H); 1.57 (quint, 2H); 2.04 (q, 2H); 3.48 (t, 2H); 4.03 (s, 2H); 4.94 (dd, 1H); 5.01 (dd, 1H); 5.83 (ddt, 1H)	489	C, 42.10 (41.81); H, 4.45 (4.33)
3g (ClC ₂ H ₄)	70	65/16	1.03 (quint, 6F); 17.45 (t, 3F); 45.27 (m, 2F); 60.22 (m, 2F)	3.63 (t, 2H); 3.79 (t, 2H); 4.18 (s, 2H)	413	C, 26.17 (26.20); H, 1.60 (1.47)
3h (ClC ₂ H ₄ OC ₂ H ₄)	83	98/20	1.05 (quint, 6F); 17.45 (t, 3F); 45.29 (m, 2F); 60.23 (m, 2F)	3.62 (t, 2H); 3.70 (m, 4H); 3.75 (t, 2H); 4.18 (s, 2H)	457	C, 29.09 (28.93); H, 2.41 (2.21)
3i (ClC ₂ H ₄ (OC ₂ H ₄) ₂)	75	92/0.55	1.07 (quint, 6F); 17.47 (t, 3F); 45.29 (m, 2F); 60.23 (m, 2F)	3.62 (t, 2H); 3.65–3.71 (m, 8H); 3.76 (t, 2H); 4.17 (s, 2H)	501	C, 31.14 (31.19); H, 3.14 (2.82)
3j (Cl(CH ₂) ₆)	88	55/0.08	1.14 (quint, 6F); 17.46 (t, 3F); 45.36 (m, 2F); 60.33 (m, 2F)	1.38 (quint, 2H); 1.47 (quint, 2H); 1.60 (quint, 2H); 1.79 (quint, 2H); 3.49 (t, 2H); 3.54 (t, 2H); 4.03 (s, 2H)	469	C, 33.50 (33.32); H, 3.03 (3.01)

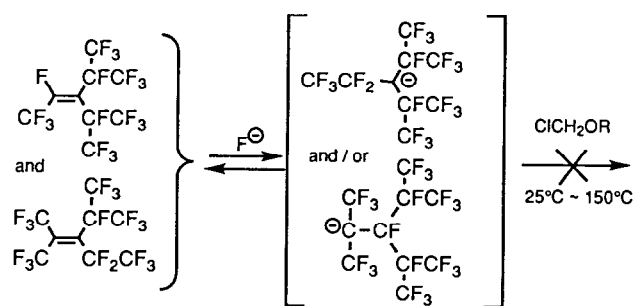
^aKugelrohr distillation.^bExternal standard, PhCF₃ (63.78 ppm).

TABLE 4. Relevant data for chloromethyl ethers **2e**, **2f** and **2h-j**

Chloromethyl ether [$\delta(^1\text{H})$] ^a	B. p. ($^{\circ}\text{C}/\text{Torr}$)
2e $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{Cl}$ 5.21 (dd, 1H) 3.66 (t, 2H) 5.56 (s, 2H) 5.29 (dd, 1H) 5.93 (ddt, 1H) 4.04 (d, 2H) 3.87 (t, 2H)	87/30
2f $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{Cl}$ 4.94 (dd, 1H) 1.30 (m, 6H) 5.00 (dd, 1H) 1.37 (m, 4H) 5.82 (ddt, 1H) 2.05 (q, 2H) 1.62 (q, 2H) 3.69 (t, 2H) 5.51 (s, 2H)	87/3
2h $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{Cl}$ 3.65 3.75 3.78 3.88 5.55 (s, 2H) (t, 2H)	66/1
2i $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{Cl}$ 3.64 3.68 3.68 3.73 3.77 3.87 5.55 (s, 2H) (t, 2H)	88/0.18
2j $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2\text{Cl}$ 3.55 (t, 2H) 1.65 (q, 2H) 1.48 (q, 2H) 1.79 (q, 2H) 5.51 (s, 2H) 1.42 (q, 2H) 3.70 (t, 2H)	50/0.15

^a δ in ppm.Fig. 1. Plots of time versus yield of perfluoroalkylmethyl octyl ether during *vic*-oxymethylfluorination in KF/DMF at 25 °C.

In contrast to perfluoro-olefin **1**, the perfluoropropylene trimer showed no reactivity toward chloromethyl ethers at 25–150 °C under similar reaction conditions.



Scheme 3. Perfluoropropylene trimers and assumed t-carbanions generated.

The trimer is composed of the isomers shown in Scheme 3. The carbanions expected to be generated are very bulky, which may be why the reaction with chloromethyl ether did not proceed.

3. Experimental details

Boiling points are uncorrected. ^1H NMR spectra were obtained with a Bruker AM-600 spectrometer operating at 600 MHz. ^{19}F NMR spectra were obtained with a JEOL JNM-GSX 400 spectrometer at 376 MHz; chemical shifts were calculated in ppm upfield from benzotrifluoride (63.78 ppm) as external standard. Mass spectra were recorded on a JEOL JMS-BX 303-HF spectrometer; m/z values are quoted for the lowest isotopic species. GLC studies were carried out on a Shimadzu model GC-8A instrument equipped with a thermal conductivity detector. The column was Silicone SE-30 on Uniport B (60–80 mesh, 1 m \times 3.2 mm).

The perfluoro-olefin **1** was donated by Neos Co. Ltd., Kobe, Japan, and redistilled under atmospheric pressure at 51 °C before use. The chloromethyl ethers were prepared by bubbling HCl gas into the solution of the corresponding alcohol and 1,3,5-trioxane in dichloromethane [14–17]. Relevant data for the chloromethyl ethers **2e**, **2f** and **2h–j** are listed in Table 4. Chloromethyl ethers **2a–d** and **2g** were identified by comparison with reported data [14–17].

DMF (manufacturer's guaranteed grade) was stirred for 1 d over CaH_2 and then distilled at 58 °C/26 Torr. Diglyme (reagent grade) was heated to reflux for 10 h in the presence of sodium metal and then distilled at 63 °C/19 Torr. KF and CsF were donated by Morita Chemical Industry Co. Ltd., Osaka, Japan, dried at 200 °C for 20 h and stored over P_2O_5 in a desiccator. TBAC and BTMAC were obtained from a commercial source.

Preparation of perfluoro-(1,1-dimethylbutyl)-methyl octyl ether (3a)

A typical procedure was as follows. Under an argon atmosphere, KF (10 mmol, 0.58 g), TBAC (0.5 mmol, 0.14 g), DMF (5 ml), perfluoro-olefin **1** (15 mmol, 4.50 g) and chloromethyl octyl ether (10 mmol, 1.78 g) were placed in a two-necked flask, and stirred for 3 h at 25 °C. The reaction mixture was filtered off and the solid washed with ether. The solutions and pyridine (1 ml) were combined and stirred for 1 h at room temperature. The resulting solution was washed successively with

water (150 ml), aqueous 5% HCl solution (150 ml) and water (150 ml \times 2). The organic layer was dried over MgSO_4 and the solvent evaporated. Using Kugelrohr distillation, a colorless liquid was obtained (4.12 g, yield 90%).

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References

- 1 I. Ikeda, M. Umino and M. Okahara, *J. Org. Chem.*, **51** (1986) 569.
- 2 N. Ishikawa and A. Nagashima, *Bull. Chem. Soc. Jpn.*, **49** (1976) 502.
- 3 S. Yanagida, Y. Noji and M. Okahara, *Tetrahedron Lett.*, **27** (1977) 2337.
- 4 I. Ikeda, T. Ineyama, T. Tsukamoto and M. Okahara, *Nippon Kagaku Kaishi*, **10** (1985) 1995; [*Chem. Abs.*, **105** (1986) 133 796x].
- 5 I. Ikeda, Y. Kogame and M. Okahara, *J. Org. Chem.*, **50** (1985) 3640.
- 6 I. Ikeda, T. Tsukamoto and M. Okahara, *Chem. Lett.*, (1980) 583.
- 7 K.M. Makarov, L.L. Gervits and I.L. Knunyants, *J. Fluorine Chem.*, **10** (1977) 157.
- 8 I. Ikeda, M. Tsuji and M. Okahara, *J. Fluorine Chem.*, **36** (1987) 171.
- 9 W. Dmowski and R. Wozniacki, *J. Fluorine Chem.*, **36** (1987) 385.
- 10 H. Suzuki, H. Satake, H. Uno and H. Shimizu, *Bull. Chem. Soc. Jpn.*, **60** (1987) 4471.
- 11 Du Pont, US Patent 2 918 501, 1959.
- 12 R.D. Dresdner, F.N. Tlumac and J.A. Young, *J. Org. Chem.*, **30** (1965) 3524.
- 13 W. Brunskill, W.T. Flowers, R. Gregory, R.N. Haszeldine, *Chem. Commun.*, (1970) 1444.
- 14 Arthur J. Hill and Dewitt T. Keach, *J. Am. Chem. Soc.*, **48** (1926) 257.
- 15 C.S. Marvel and P.K. Porter, *Org. Synth., Coll. Vol. 1*, (1941) 377.
- 16 L. Summers, *Chem. Rev.*, **55** (1955) 301.
- 17 D.S. Connor, G.W. Klein and G.N. Taylor, *Org. Synth.*, **52** (1972) 16.