The electrochemical fluorination of nitrogen-containing carboxylic acids.* Fluorination of methyl esters of 3-dialkylamino propionic acids

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Abstract

Six methyl esters of 3-dialkylamino-substituted propionic acids were subjected to electrochemical fluorination to give the corresponding perfluoroacid fluorides The following dialkylamino substituents were investigated. diethylamino, di-*n*-propylamino, di-*n*-butylamino, pyrrolidino, morpholino and piperidino groups These perfluoroacid fluorides, which were obtained in fair yields, are considered to be prospective key precursors for preparing soft-type (degradable) fluorochemicals. The salts show a considerable lowering of surface tension in aqueous solution The physical properties of all the perfluoroacid fluorides obtained are reported, together with their spectroscopic data (^{19}F NMR, mass and IR spectra)

Introduction

Perfluorocarboxylic acids containing as heteroatoms nitrogen and/or oxygen in the chain may be regarded as soft-type (degradable) materials in terms of environmental impact compared with those containing saturated perfluoroalkyl groups which are characteristically strong (hard-type; non-degradable). This arises because, on introduction of the heteroatom into the perfluoroalkly group, the α-fluorine is considerably labilized and shows moderate reactivity towards $AlCl_3$ [1], SO_3 [2] and fuming sulfuric acid [3]. Thus, perfluorocarboxylic acids which contain a nitrogen in the alkyl group are prospective key intermediates to meet the requirements for environmental protection by making, for example, soft-type (degradable) fluorochemicals such as surfactants, water/oil repellents, etc.

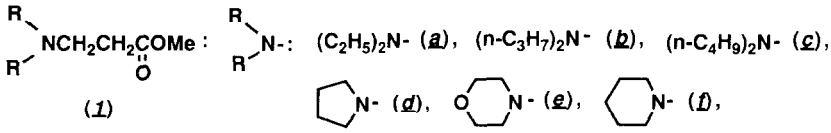
In earlier papers, we have reported the electrochemical fluorination of various dialkylamino-substituted carboxylic acid derivatives related to

*Preceding paper of this series, see ref 4

0022-1139/92/$5 00

glycine and alanine, and also methyl 3-dimethylaminopropionate and methyl 3-hexamethyleneimino propionate which are related to β-alanine [4, 5]. Although fluorinations of several kinds of 3-(dialkylamino)-substituted propionyl chloride hydrochloride salts to give perfluoro-(3-dialkylaminopropionyl fluorides) have been described in the patent literature [6], data on the products are thin and the procedure using acid chloride hydrochloride salts is inconvenient because of the preparation of the starting materials which requires a multi-step synthesis.

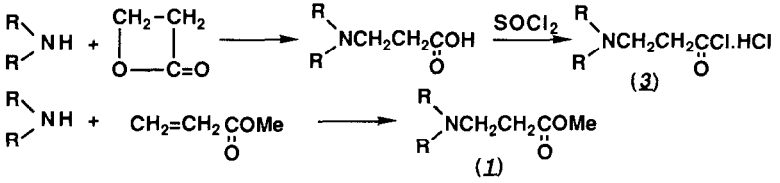
In this paper, we describe experimental details on the synthesis of several perfluoro-(3-dialkylaminopropionyl fluorides) by fluorination of the methyl esters of 3-(dialkylamino)-substituted propionic acids (**1a** to **f**):



Results and discussion

In terms of the starting materials for the preparation of perfluoro-(3-dialkylaminopropionyl fluorides) (**2**), methyl 3-dialkylaminopropionates (**1**) have advantages over 3-dialkylaminopropionyl chloride hydrochlorides (**3**) in ease of preparation, cost and also cell operation.

While **3**, which are moisture-sensitive solid compounds, have been synthesized by a two-step synthesis involving the reaction of β-lactone with appropriate secondary amines followed by chlorination [7], **1** (liquid compounds) can be easily prepared in high yields by a one-flask preparation from secondary amines and methyl acrylate (Michael reaction) [8], both of which are commercially available.

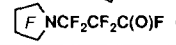
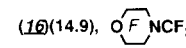
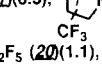


Scheme 1.

Furthermore, it was found that the yield of **2** was improved using **1a** as compared with that from the corresponding acid chloride HCl salt (Table 1). For example, perfluoro-(3-diethylaminopropionyl fluoride (**2a**) was obtained in small yields (6%) by the fluorination of the corresponding compound **3** [6]. However, **2a** was obtained in yields as high as 30% or more by the fluorination of methyl 3-diethylaminopropionate (**1a**) (Run 1 in Table 1; see also Experimental).

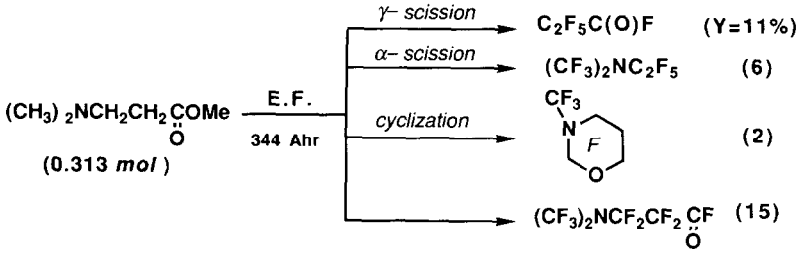
TABLE 1

Results of the fluorination of methyl 3-dialkylaminopropionates

Run	Sample g (mol)	Current passed [Ahr]	Fluorinated products (g)	Products obtained (Yield %)
1	*1a*, 40.9 (0.257)	231	14.7 (33.4)	$C_2F_5C(O)F$ (*4*)(2.7), $(C_2F_5)_2NCF_3$ (*5*)(3.5), $(C_2F_5)_3N$ (*6*)(6.6), $(C_2F_5)_2NCF_2CF_2C(O)F$ (*2a*)(30.1)
2	*1b*, 40.1 (0.214)	279	6.6 (53.9)	$C_3F_7N(CF_3)C_2F_5$ (*7*)(12.7), $(C_3F_7)_2NC_2F_5$ (*8*)(17.5), $(C_3F_7)_2NCF_2CF_2C(O)F$ (*2b*)(25.5)
3	*1c*, 40.7 (0.189)	240	8.4 (32.9)	$(C_4F_9)_2NC_2F_5$ (*11*)(7.1), $(C_4F_9)_2NCF_2CF_2C(O)F$ (*2c*)(13.6),
4	*1d*, 39.5 (0.252)	217	20.7 (20.9)	*9* (16.3),  (*12*)(5.6),  (*13*)(14.4),  (*2d*)(16.5)
5	*1e*, 40.3 (0.233)	164	14.7 (21.4)	$C_2F_5OC_2F_5$ (*14*)(9.8),  (*15*)(3.1),  (*16*)(14.9),  (*2e*)(17.1)
6	*1f*, 41.5 (0.243)	212	15.2 (46.0)	C_5F_{12} (*17*)(8.3),  (*18*)(0.8),  (*19*)(2.5),  (*20*)(1.1),  (*21*)(15.2),  (*22*)(5.1),  (*2f*)(29.7)

Products collected in the −78 °C trap are shown, with cell drainings in parentheses. Products are arranged in order of elution time by GLC (col. A).

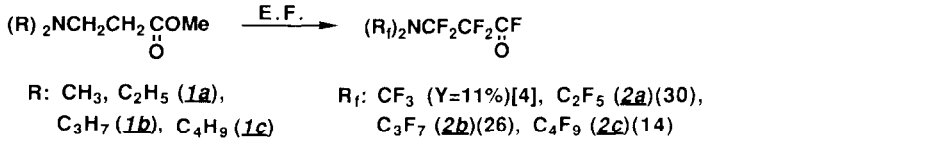
In our previous paper, we have shown that a considerable amount of perfluoropropionyl fluoride (4) was formed as a by-product along with the expected perfluoro-(3-dimethylaminopropionyl fluoride) due to γ-scission of the acid from the fluorination of methyl 3-dimethylaminopropionate [4]. Small amounts of perfluoro-(*N*,*N*-dimethylethylamine) and perfluoro-(3-oxa-*N*-methylpiperidine) were also formed as results of α-scission and cyclization, respectively.



Scheme 2.

However, this pattern of bond scission and cyclization was not the general case for compounds **1** containing a higher aliphatic dialkylamino group and a cyclic amino group. The α-scission occurred increasingly as the carbon number of the dialkylamino group increased (**1a**, **1b** and **1c**), and α-scission rather than γ-scission occurred more in the case of compounds **1** with a cyclic amino group (**1d**, **1e** and **1f**).

Thus, from a series of methyl esters of aliphatic 3-dialkylaminopropionic acid (**1a** to **1c**), corresponding perfluoroacid fluorides (**2a** to **2c**) were obtained in varying yields, as shown below, *viz.*



As for cyclization during electrolysis, it was expected that this side reaction would be greatly minimized in the case of 3-dialkylaminopropionic acid derivatives because of the hindrance towards five-membered ring formation caused by the presence of a nitrogen atom at the γ-position. Thus, it was rational that no appreciable amounts of cyclized products were formed from **1**. The results obtained for **1a** were in sharp contrast to those obtained for isomeric methyl 2-diethylaminopropionate [4], from which no trace of the expected perfluoro-(2-diethylaminopropionyl fluoride) formed during fluorination because of cyclization.

In order to improve the yields of perfluoroacid fluorides by electrochemical fluorination of carboxylic acid derivatives, considerable efforts have been made to suppress cyclization [9]. However, the most effective counter measure is considered to be the introduction of a nitrogen atom at the appropriate position. Because this structural modification of the substrate results not only in the suppression of this side reaction but also in a large increase in the solubility of carboxylic acids in anhydrous hydrogen fluoride (AHF), it is possible to conduct the cell operation smoothly due to the increased electroconductivity compared with carboxylic acids having the same number of carbon atoms.

Thus, compounds such as **1a** to **1f** which have a nitrogen atom at the γ-position are considered to be suitable starting materials for making by electrochemical fluorination perfluoroacid fluorides having C_7 to C_{11} in the chain. Results of the fluorination of methyl 3-dialkylaminoisobutyrates and methyl 3-dialkylamino-*n*-butyrates (both of which contain a nitrogen atom at the γ-position and can be prepared by treating appropriate secondary amines with methyl methacrylate and methyl crotonate respectively) will be published in a subsequent paper.

Perfluoroacid fluorides **2a** to **2f** are versatile intermediates for the preparation of various organofluorine chemicals carrying perfluorodialkyl-

amino groups. For examples, perfluorovinylamines have been synthesized by pyrolysis of perfluorocarboxylic acids derived from **2a** to **2f** [10], as an alternative to the use of the postassium salts of perfluoro-(2-dialkylaminopropionates) [11]. By developing this alternative method, it has become possible to prepare easily higher homologues of aliphatic perfluorovinylamines.

Figure 1 shows the surface tensions of aqueous solutions with various concentrations of sodium salts of perfluoro-(3-dimethylaminopropionic acid) (**23**), perfluoro-(3-diethylaminopropionic acid) (**24**), and perfluoro-(3-di-*n*-propylamino propionic acid) (**25**), together with that of perfluorooctanoic acid (**26**), the ammonium salt of perfluoro-(3-di-*n*-propylaminopropionic acid (**27**) and the potassium salt of perfluoro-(3-di-*n*-butylaminopropionic acid) (**28**). The surface tension of **26** was measured for comparison. It was observed that the extent of the lowering effect depended on the perfluorodialkylamino group, and that **27** and **28** had the ability to lower the surface tensions by 17.1 dyn cm^{-1} at low concentrations (C.M.C./mol l^{-1} estimated from the bending points of the curves were 0.0150 and 0.0037, respectively). Syntheses for other new soft-type fluorosurfactants derived from **2a** to **2d** are underway.

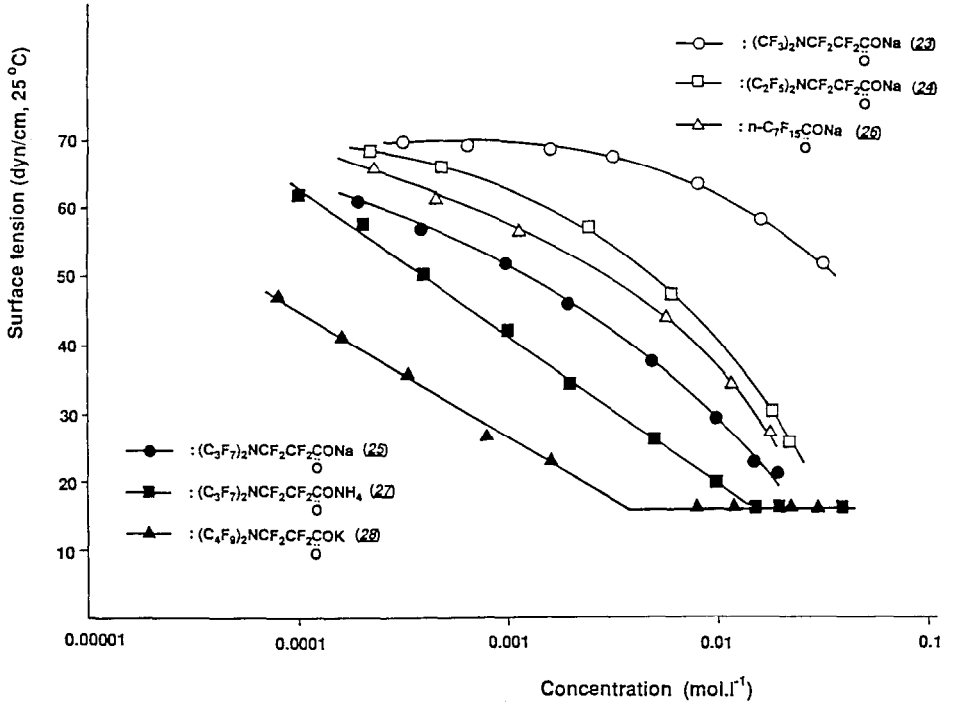


Fig. 1. Surface tensions of salts (K^+, Na^+ and NH_4^+) of several perfluoro-(3-dialkylaminopropionic acids).

Experimental

Reagents

All *N*-containing carboxylic acids were prepared by reaction of appropriate secondary amines and methyl acrylate, as described in the literature [8].

These starting materials had the following boiling points: methyl 3-diethylaminopropionate, b.p. 103.0 to 104.0 °C/48 mmHg; methyl 3-dipropylaminopropionate, b.p. 82.0 to 85.0 °C/8 mmHg; methyl 3-dibutylaminopropionate, b.p. 108.0 to 110.0 °C/7 mmHg (reported: b.p. 108 °C/6 mmHg) [12]; methyl 3-pyrrolidino propionate, 130.0 to 132.0 °C/78 mmHg (reported: b.p. 99 °C/22 mmHg) [13]; methyl 3-morpholinopropionate, 157.0 to 159.0 °C/84 mmHg; methyl 3-piperidinopropionate, 120.0 to 122.5 °C/37 mmHg. Anhydrous hydrogen fluoride (AFH; Daikin Industries Co.) was of purity greater than 99.8%.

Sodium perfluoro-(3-dimethylaminopropionate), which was used for the measurement of surface tension as a comparison with perfluoro-(3-diethylaminopropionate) and perfluoro-(3-dipropylaminopropionate), was prepared from perfluoro-(3-dimethylaminopropionic acid) (b.p. 83 to 87 °C/55 mmHg) [4].

Apparatus

The electrolytic fluorination apparatus and operating procedures were similar to those described previously [4].

Analytical GLC work was carried out with a Shimadzu GC-2C gas chromotograph using stainless steel columns (3 mm diameter) packed with 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane on Chromosorb PAW (6.4 m) (col. A), and 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (6.4 m) (col. B). For semi-preparative work, a GASUKURO LL-75 modified gas chromatograph was used, with stainless steel columns (10 mm diameter) packed with 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy) hexane on Chromosorb PAW (4.9 m) (col. C), and 30% Silicone QF-1 on Chromosorb PAW (4.9 m) (col. D). The carrier gas was helium in all cases.

Infrared spectra were measured on a Hitachi EPI-G3 spectrometer, using a 6-cm gas cell with KBr windows. ^{19}F NMR spectra were measured using CCl_3F as an internal standard, either on a Hitachi R-20B (56.46 MHz) or a Hitachi R-90F (84.68 MHz) spectrometer. Mass spectra were measured on a Shimadzu GC/MS-7000 instrument at 70 eV.

Surface tensions were determined by a du Nöuy type auto-tension meter (Rigosya Model NR-1A). Appropriate salts (Na, NH_4 or K) of perfluoro-(3-dialkylaminopropionic acids) were dissolved in deionized and distilled water to produce solutions of various concentrations (0.000 08 to 0.0150 mol l^{-1}) and were measured at 25 °C.

*Fluorination of methyl 3-diethylaminopropionate (**1a**)*

Sample **1a** (40.9 g, 0.257 mol) was charged into the cell which contained 450 ml electrically purified AHF, and the solution was subjected to fluorination with an anodic current density of 3.5 A dm^{-2}, a cell voltage of 7.2 to 7.4 V and a cell temperature of 7 to 8 °C over a period of 521 min (231 Ahr). At the final stage of the fluorination, the voltage reached 8.0 V.

The effluent gases from the cell were passed over NaF pellets and then condensed in a trap cooled to −78 °C. The gaseous products which did not condense in the −78 °C trap were then bubbled through a fluoropolymer bottle containing water and a gas washing bottle containing an aqueous solution of a mixture of K_2CO_3, KOH and KI, respectively. All products except new ones were identified by comparison of their IR spectra and GLC retention times with those of authentic samples. New compounds were separated from other products by use of semi-preparative GLC, and their structures were determined on the basis of their IR, ^{19}F NMR and mass spectra.

The products (yield, 14.7 g) condensed in the −78 °C trap consisted of: pentafluoropropionyl fluoride (**4**) (1.2 g), perfluoro(diethylmethylamine) (**5**) (2.9 g) perfluoro(triethylamine) (**6**) (3.9 g), perfluoro-(3-diethylaminopropionyl fluoride) (**2b**) (3.0 g) and unidentified compounds (3.7 g). Cell drainings (33.4 g) consisted of **6** (2.5 g), **2a** (27.9 g) and unidentified compounds (3.1 g). The yield of **2a** was 30% based on the sample fed. Optimization of the yield of **2a** was not attempted. However, in another run which was conducted using a larger cell (capacity, 600 ml) under similar conditions, **2a** was obtained in a yield of 35%. The characterization of all perfluoro-(3-dialkylaminopropionyl fluorides) obtained in this experiment, including **2a**, was on the methyl ester.

Methyl perfluoro-(3-diethylaminopropionate) (**29**) was prepared by mixing about 2 g of cell drainings with 1 ml of methanol. The reaction was complete within a few minutes. Then the lower layer of the reaction mixture was subjected to semi-preparative GLC (col. D) to give pure **29**.

Sodium perfluoro-(2-diethylaminopropionate) (**24**), which was used as the sample for the surface tension measurement, was prepared by the reaction of perfluoro-(2-diethylaminopropionic acid) (**35**) with aqueous sodium hydroxide, evaporated to dryness, followed by recrystallization from toluene-*n*-butanol. Compound **35** was prepared by reacting 27.1 g of cell drainings (which contained 21.4 g of **2a**) with 50 ml of water in a 200-ml flask, extracting with ether, drying over $MgSO_4$ and then distilling by adding 3 ml conc. H_2SO_4 to yield 9.0 g **35** (b.p. 104 to 105 °C/44 mmHg).

Perfluoro-(3-diethylaminopropionyl fluoride) (**2a**) [6]: IR (gas): 1888(ms) ν (C=O), 1345(m, sh), 1314(s, sh), 1288(vs), 1246(vs), 1233(s, sh), 1213(ms, sh), 1158(m), 1120(ms), 1108(m), 1075(m), 1000(w), 880(m), 851(m), 761(w), 755(m), 690(w).

Methyl perfluoro-(3-diethylaminopropionate) (**29**) (nc): b.p. 138.5 to 139.0 °C, n_D^{20} 1.3090 and d_4^{20} 1.7077. IR (capillary film): 1789(s) ν (C=O).

TABLE 2

^{19}F NMR spectra

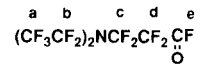
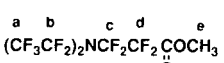
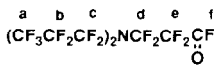
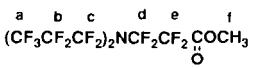
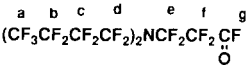
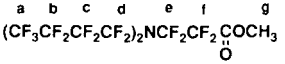
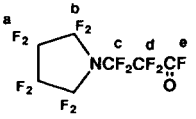
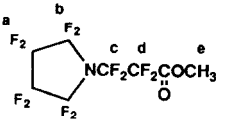
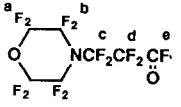
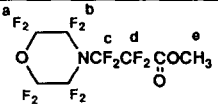
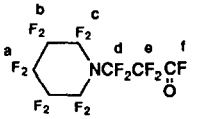
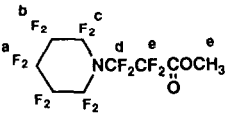
Compd	Formula	Chemical shift [a,b]		J (Hz) [b]
2a		a	-81.9	
		b	-89.7	
		c	-84.8	
		d	-113.5	
		e	24.0	
29		a	-81.9	
		b	-89.4	
		c	-85.5	
		d	-114.6	
		e	δ 3.93	
2b		a	-81.9	
		b	-122.2	
		c	-85.2	
		d	-84.0	
		e	-113.0	
		f	23.9	
30		a	-81.9	
		b	-122.2	
		c,d	-84.0 ~ 85.0	
		e	-114.4	
		f	δ 3.96	
2c		a	-81.3	
		b	-127.0	
		c	-119.4	
		d	-84.8	
		e,f	-83.9 ~ 84.1	
		g	23.9	
31		a	-81.4	
		b	-127.1	
		c	-119.2	
		d,e	-84.0 ~ 84.5	
		f	-114.0	
		g	δ 3.96	
2d		a	-133.0	b-c=11.2
		b	-90.8	b-d=8.9
		c	-93.6	c-e=6.2
		d	-118.8	d-e=7.4
		e	25.9	
32		a	-133.6	b-c=12.4
		b	-90.9	b-d=10.2
		c	-93.6	
		d	-119.4	
		e	δ 3.94	
2e		a	-87.5	
		b,c	-92.6	
		d	-111.9	
		e	26.0	

TABLE 2 (continued)

Compd	Formula	Chemical shift [a,b]	J (Hz) [b]
33		a -87.8 b,c -92.6 d -120.9 e δ 3.96	
21		a -134.7 b -132.3 c,d -91.5 e -120.0 f 25.9	
34		a -134.5 b -132.3 c,d -91.2 e -120.2 f δ 3.77	

[a] ^{19}F Chemical shifts in ppm relative to internal CCl_3F (negative shifts are upfield) and ^{1}H chemical shifts in ppm relative to TMS.
[b] Only obvious chemical shifts and coupling constants are given.

Mass spectra: 392 $[M-F]^+$(3.0), 302 $C_5F_{12}N^+$ (22.2), 214 $C_4F_8N^+$ (11.2), 164 $C_3F_6N^+$ (27.8), 131 $C_3F_5^+$ (25.9), 119 $C_2F_5^+$ (97.7), 114 $C_2F_4N^+$ (15.4), 100 $C_2F_4^+$ (41.4), 81 $C_2F_3^+$ (20.6), 69 CF_3^+ (44.2), 59 $C(O)OMe^+$ (100).

^{19}F NMR data of **2b** and **29** are shown in Table 2.

*Fluorination of methyl 3-di-*n*-propylaminopropionate (**1b**)*

Compound **1b** (40.1 g, 0.214 mol) was fluorinated similarly under the following conditions: 3.5 A dm^{-2}, 6.0 to 6.1 V, 7 to 8 °C, 631 min (279 Ahr). Work-up was as for the fluorination of **1a**. Products collected in the −78 °C trap and cell drainings were subsequently analyzed by GLC (cols. A and B). Thus, the following compounds were obtained; products in the −78 °C trap (6.6 g): perfluoro(methylethyl-*n*-propylamine) (**7**) (2.5 g); perfluoro(di-*n*-propylethylamine) (**8**) (0.5); unidentified compounds (3.6 g); cell drainings (53.9 g): **7** (7.6 g), **8** (17.2 g), perfluoro-(3-di-*n*-propylaminopropionyl fluoride (**2b**) (27.3 g), unidentified compound(s) (1.8 g). The yield of **2b** was 26%. The characterization of **2b** was as for **2a**. Sodium perfluoro-(2-di-*n*-propylaminopropionate) (**25**) was prepared similarly to **24** from perfluoro-(3-di-*n*-propylaminopropionic acid) (**36**). Compound **36** had b.p. 104 to 105 °C/44 mmHg. Ammonium perfluoro-(3-di-*n*-propylaminopropionic acid) (**27**) was prepared by treating **36** with aqueous ammonia to give a yellow liquid, evaporating to dryness at 50 °C and then drying under vacuum at ambient temperature. Compound **27** was obtained as a deliquescent solid.

Methyl perfluoro(di-*n*-propylaminopropionate) (**30**) (nc): b.p. 160 to 162 °C, n_D^{20} 1.3103 and d_4^{20} 1.7607. IR (capillary film): 1789 ν (C=O).

^{19}F NMR data of **2b** and **30** are shown in Table 2.

*Fluorination of methyl 3-di-*n*-butylaminopropionate (**1c**)*

Compound **1c** (40.7 g, 0.187 mol) was fluorinated similarly under the following conditions: 3.5 A dm^{-2}, 6.1 to 6.2 V, 7 to 8 °C, 598 min (249 Ahr). Work-up gave: products in the −78 °C trap (8.4 g), primarily *n*-C_4F_{10} (**9**); cell drainings (32.9 g): perfluoro(di-*n*-butyl methylamine) (**10**) (5.8 g), perfluoro(di-*n*-butylethylamine) (**11**) unidentified compound(s) (4.0 g). The yield of **2c** was 14%.

Potassium perfluoro-(3-di-*n*-butylaminopropionate) (**28**) was prepared similarly from perfluoro-(3-di-*n*-butylaminopropionic acid) (**37**) and aqueous potassium hydroxide solution as for **24**. Compound **37** had a b.p. 137 to 139 °C/55 mmHg.

Methyl perfluoro-(3-di-*n*-butylpropionate) (**31**): b.p. 203 °C, n_D^{20} 1.3139 and d_4^{20} 1.7667. IR (capillary film): 1789(s) ν(C=O).

^{19}F NMR data of **2c** and **31** are shown in Table 2.

*Fluorination of methyl 3-pyrrolidinopropionate (**1d**)*

Compound **1d** (39.5 g, 0.252 mol) was fluorinated similarly under the following conditions: 3.5 A dm^{-2}, 6.1 to 6.2 V, 7 to 8 °C, 598 min (217 Ahr). Work-up gave: products in the −78 °C trap (20.7 g): **9** (7.8 g), perfluoro(*N*-methylpyrrolidine) (**12**) (4.0 g), perfluoro(*N*-ethylpyrrolidine) (**13**) (8.9 g); cell drainings (20.9 g): **13** (3.2 g), perfluoro-(3-pyrrolidinopropionyl fluoride) (**2d**) (15.0 g), unidentified compound(s) (2.7 g). The yield of **2d** was 17% based on the sample fed.

Perfluoro-(3-pyrrolidinopropionyl fluoride) (**2d**): IR (gas): 1886(ms) ν(C=O), 1403(w), 1348(s), 1298(m), 1246(m), 1228(vs), 1185(m), 1172(m), 1120, 1125(m), 1041(m), 978(ms), 882(w), 803(w), 683(w), 557(w), 486(w).

Methyl perfluoro-(3-pyrrolidinopropionate) (**32**) (nc): b.p. 142 to 144 °C, n_D^{20} 1.3182, d_4^{20} 1.6897. IR (capillary film): 1789(ms) ν(C=O). Mass spectra: 314 $C_6F_{12}N^+$ (7.0), 295 $C_6F_{11}N^+$ (5.2), 276 $C_6F_{10}N^+$ (5.5), 264 $C_5F_{10}N^+$ (68.3), 214 $C_4F_8N^+$ (14.8), 159 $C_3F_7^+$ (15.4), 131 $C_3F_5^+$ (28.6), 119 $C_2F_5^+$ (29.2), 114 $C_2F_4N^-$ (17.5), 100 $C_2F_4^+$ (43.4), 81 $C_2F_3^+$ (11.4), 69 CF_3^+ (34.2), 59 $C(O)OMe^+$ (100).

^{19}F NMR data of **2d** and **32** are shown in Table 2.

*Fluorination of methyl 3-morpholinopropionate (**1e**)*

Compound **1e** (40.3 g, 0.233 mol) was fluorinated similarly under the following conditions: 3.5 A dm^{-2}, 6.1 to 6.3 V, 7 to 8 °C, 432 min (164 Ahr). Work-up gave: products in the −78 °C trap (14.7 g): perfluoro(diethyl ether) (**14**) (5.8 g), perfluoro(*N*-methylmorpholine) (**15**) (3.1 g), perfluoro(*N*-ethylmorpholine) (**16**) (14.9 g), perfluoro(3-morpholinopropionyl fluoride) (**2e**) (15.0 g). The yield of **2e** was 17%.

Perfluoro-(3-morpholinopropionyl fluoride) (**2e**) (nc): IR (gas): 1886(ms) ν(C=O), 1347(m), 1312(vs), 1296(s), 1226 to 1236(s to vs), 1214(s, sh), 1196(s, sh), 1183(vs), 1153(s), 1121(m), 1104(m), 1029(m), 996(w), 931(ms), 801(w), 657(w), 626(w).

Methyl perfluoro-(3-morpholinopropionate) (**33**) (nc): b.p. 144 to 145 °C, n_D^{20} 1.3197, d_4^{20} 1.7127. IR (capillary film): 1778(ms) ν(C=O).

^{19}F NMR data of **2e** and **33** are shown in Table 2.

Fluorination of methyl 3-piperidinopropionate (1f)

Compound **1f** (41.5 g, 0.243 mol) was fluorinated similarly under the following conditions: 3.5 A dm^{-2}, 7.5 to 7.6 V, 7 to 8 °C, 536 min (212 Ahr). Work-up gave: products in the −78 °C trap (15.2 g): perfluoropentane (**17**) (5.8 g), perfluoro(*N*-methylmethylpyrrolidine) (**18**) (0.6 g), perfluoro(*N*-methylpiperidine) (**19**) (2.0 g), perfluoro(*N*-ethylmethylpyrrolidine) (**20**), perfluoro(*N*-ethylpiperidine) (**21**) (4.1 g), unidentified compound(s) (2.3 g); cell drainings (46.0 g): **20** (0.5 g), **21** (9.6 g), perfluoro-[3-(methylpyrrolidino)propionyl fluoride] (**22**) (5.1 g), perfluoro-(3-piperidinopropionyl fluoride) (**2f**) (29.6 g). The yield of **2f** was 30%.

Perfluoro-(3-piperidinopropionyl fluoride) (**2f**) (nc): IR (gas): 1886(ms) ν(C=O), 1372(w), 1348(w), 1328(s), 1275(m), 1231(w), 1213(vs), 1192(ms), 1169(w), 1138(m), 1110 to 1120(w), 1071(w), 1030(ms), 993(w), 976(ms), 851(w), 792 to 800(w).

Methyl perfluoro-(3-piperidinopropionate) (**34**): b.p. 163 to 165 °C, n_D^{20} 1.3217, d_4^{20} 1.7462. IR (capillary film): 1601 ν(C=O).

^{19}F NMR of **2f** and **34** are shown in Table 2.

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