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THE ELECTROCHEMICAL FLUORINATION OF NITROGEN-CONTAINING CARBOXYLIC ACIDS. FLUORINATION OF DIMETHYLAMINO- OR DIETHYLAMINO-SUBSTITUTED CARBOXYLIC ACID DERIVATIVES

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SUMMARY

The electrochemical fluorination of six derivatives of dimethylamino- or diethylamino-substituted carboxylic acids has been conducted. As the main fluorination products, cyclized and cleaved products as well as the desired N-containing perfluoroacid fluorides were formed, and their ratios depended on the chain length and the structure of the starting carboxylic acids, and the nature of the dialkylamino group. Through this work, perfluoro(dimethylamino-acetyl fluoride), perfluoro(diethylamino-acetyl fluoride), perfluoro(2-dimethylamino-propionyl fluoride), perfluoro(2-dimethylamino-butyryl fluoride) and perfluoro(3-dimethylamino-propionyl fluoride) were prepared. Except for perfluoro(dimethylamino-acetyl fluoride), these acid fluorides were new compounds. The physical properties of new compounds obtained including these acid fluorides are reported together with their spectral (^{19}F nmr, Mass and IR) data.

INTRODUCTION

A great many papers have described the preparation of perfluorocarboxylic acids, because they are fundamental and important starting compounds for fluoro-organic synthesis [1]. Four types of methods have been generally employed for the

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preparation of these compounds: (1) electrochemical fluorination of alkanoyl chlorides or fluorides [2]. (2) from iodoperfluoroalkanes by reaction, with oleum, chloro- or fluorosulfonic acids [3], with Rongalite-$NaHCO_3$ [4], by electrolysis in the presence of CO_2 [5], or by enzyme reaction [6]. (3) oxydation of ω,ω,ω - trichloroperfluoroalkanes with oxygen under irradiation [7], or with oleum [8]. (4) oxidation of fluoroolefins [9].

The electrochemical fluorination is of importance methodologically, because not only perfluorocarboxylic acid fluorides themselves but also analogues containing a heteroatom (N, O or $-SF_4-$) can be prepared in a simple operation in reasonable yields from the corresponding alkanoyl chlorides or fluorides, or preferably from their methyl esters [10].

While amino-acids are receiving increased attention because they are key constituents of natural products having versatile uses in the biological and pharmaceutical fields, the synthesis of their perfluorinated analogues, that is, nitrogen-containing perfluorocarboxylic acids, have been rarely investigated except that of perfluoro(dimethylamino-acetyl fluoride) [11], perfluoro[2-(N,N-difluoroamino)propionyl fluoride] [12] and perfluoro(3-dialkylamino-propionyl fluorides) [13].

Though the chemical behavior of the nitrogen-containing perfluorocarboxylic acids is not similar to that of hydrocarbon-type amino-acids at all, these compounds are of considerable interest as new materials for versatile uses such as monomers, surface active agents, and in the specific case where a chiral carbon is contained, as optically-active compounds by use of their bulky perfluorodialkylamino group.

As a part of our work with these objectives, we have synthesized several kinds of nitrogen-containing perfluorocarboxylic acids as starting materials for making fluoroolefins bearing a bulky perfluoro-dialkylamino-pendant group.

In this paper, we report the results of the fluorination of the following six aliphatic N,N-dialkylamino-substituted carboxylic acid derivatives. Though the electrochemical fluorination of methyl dimethylamino-acetate (1) is known [11], it was included in our work for comparison purposes:

$(CH_3)_2NCH_2C(O)OMe$ (1), $(C_2H_5)_2NCH_2C(O)OMe$ (2),
$(CH_3)_2NCH(CH_3)C(O)X$ [X=OMe (3a), OEt (3b), $N(CH_3)_2$ (3c)],
$(C_2H_5)_2NCH(CH_3)C(O)OMe$ (4),
$(CH_3)_2NCH(C_2H_5)C(O)OMe$ (5),
$(CH_3)_2NCH_2CH_2C(O)OMe$ (6)

RESULTS AND DISCUSSION

Analysis of the fluorination products from 1-6

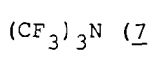
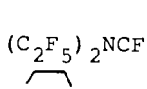
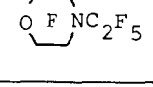
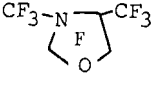
All starting materials were fluorinated in the form of methyl esters, which have been known to undergo fluorination at lower and more stable voltages than corresponding acid chlorides [10]. Conveniently, they are accessible in high yields by the reaction of appropriate methyl esters of bromo- or chloro-substituted carboxylic acids with corresponding secondary amines. The results of the fluorination of 1-6 are summarized in Table 1.

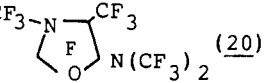
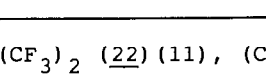
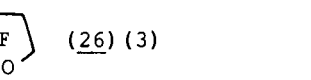
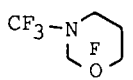
It has been reported [11] that the fluorination of 1 suffers from a difficulty associated with the cell operation: none of the desired perfluoroacid fluoride or cyclized product was said to be formed unless the cell voltage was maintained at lower than 5.1 V strictly. However, we found that all starting materials including 1 underwent smooth electrolysis without any such difficulty. For example, from 1, perfluoro(dimethylamino-acetyl fluoride)(9) was obtained in a yield of 20%; respectable for a perfluoroacid fluoride by the electrochemical process. Considerable amounts of perfluoro(trimethylamine)(7) and perfluoro(3-methyloxazolidine)(8) were produced also.

Generally, the fluorination products obtained in the present study could be classified into three groups: degradation products, cyclization product(s), and the expected perfluoroacid fluoride. Their formation ratios depended on the chain length and the structure of the parent carboxylic acid. Obviously, formation of the first two by-product types was the main reason for the suppression of the yield of the desired perfluoroacid fluoride. The production of cyclized compounds is

TABLE 1

Results of the fluorination of N,N-dialkylamino-substituted carboxylic acid derivatives

Run	Sample g (mol)	Electricity passed (Ahr)	Fluorinated compds obtained (g)	Products obtained (Yield %)[b]
1	1, 40.6 (0.347)	250	30.6[a]	$(CF_3)_3N$ (7) (7),  (8) (8), $(CF_3)_2NCF_2C(O)F$ (9) (20)
2	2, 41.1 (0.284)	256	21.1 (11.1)	$(C_2F_5)_2NCF_3$ (10) (5),  (11) (2),  (12) (7), $(C_2F_5)_2NCF_2C(O)F$ (13) (10)
3	3a, 39.7 (0.303)	240	53.2	$C_2F_5N(CF_3)_2$ (14) (15), $(CF_3)_2NCHF_2$ (15) (3)  (16) (4), $C_2F_5NCHF_2(CF_3)$ (17) (4) $(CF_3)_2NCF(CF_3)C(O)F$ (18) (29)
4	3b, 40.9 (0.303)	256	35.4 (2.6)	14 (11), 15 (2), 16 (3), 17 (3), 18 (21)

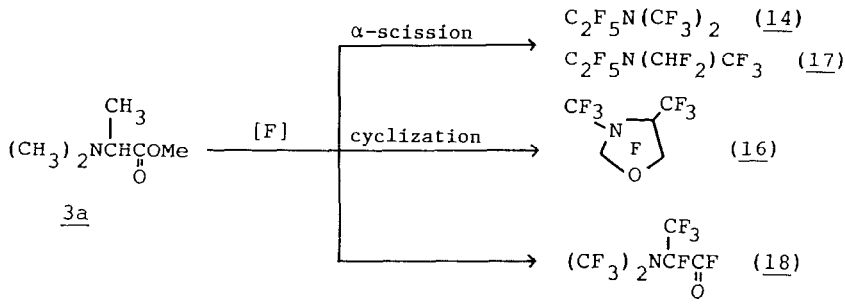
5	3c, 40.7 (0.283)	263	34.6 (4.4)	14 (11), 15 (1), $(CF_3)_2NC(O)F$ (19)(11), 16 (2), 17 (4), 18 (13),  (20) (2)
6	4, 26.7 (0.168)	193	13.2 (4.8)	14 (2), 10 (3), $(C_2F_5)_3N$ (21)(8)
7	5, 40.8 (0.281)	258	35.5 (7.0)	$n\text{-}C_3F_7N(CF_3)_2$ (22)(11), $(CF_3)_2N(CF_2)_2OCF_3$ (23) (2),  (24)(3), $(CF_3)_2NCF(C_2F_5)C(O)F$ (25)(9),  (26)(3)
8	6, 41.5 (0.317)	244	32.8	$C_2F_5C(O)F$ (27)(11), 7 (2), 14 (6), 17 (1.2),  (28)(2), $(CF_3)_2NCF_2CF_2C(O)F$ (29)(15)

a Product collected in the -78 °C trap, and cell drainings in () are shown respectively.

b Products are arranged in order of elution time by GLC (Col. A).

one of the unavoidable competing reactions in the fluorination of all carboxylic acid derivatives which contain sufficient carbon atoms to form a five- or a six-membered ring. Though the 5-membered oxazolidine compounds (8) was formed from 1, 6-membered morpholines (11 and 12) were obtained from 2 as the cyclization products.

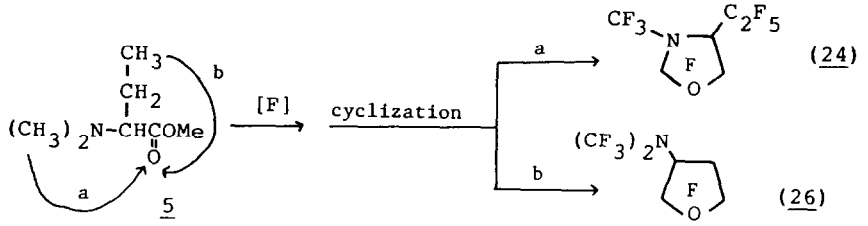
The formation of cleaved products as a result of the scission of a C-C bond (α-scission from carbonyl group) was the dominant factor for 3a on the yield of the expected perfluoroacid fluorides (18), though all three types of compounds were obtained as in the fluorination of 1.



Scheme 1.

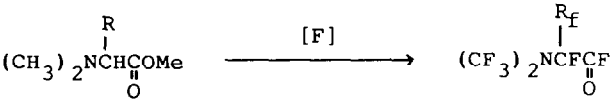
α-Scission predominated in the case of an alanine derivative having a diethylamino-group (4). The GLC analysis of the cell drainings from 4 revealed that they consisted of a complex mixture of 5 components, considered to be cyclization products on the basis of their GLC retention times. The corresponding perfluoroacid fluoride, perfluoro(2-diethylamino-propionyl fluoride)[14], was not found among them.

Fluorination of an amino-acid derivative (5) possessing an ethyl and a dimethylamino group at the α-position of acetic acid offers two likely modes of cyclization; (1) formation of an oxazolidine ring by use of the dimethylamino group (Path a) and (2) formation of an oxolane ring by use of the ethyl group (Path b). As expected, two kinds of cyclization products (24 and 26) were formed from 5 almost in the same ratio, together with products of α-scission (22) and the acid fluoride (25).



Scheme 2.

Thus, from the series of α-(dimethylamino)-substituted carboxylic acid derivatives, 1, 3a and 5, the corresponding perfluoroacid fluorides were obtained in varying yields:

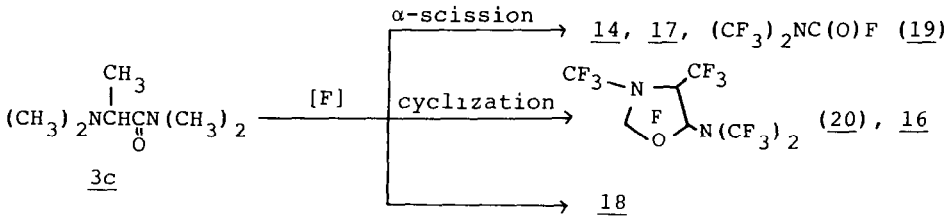


R: H(1), CH_3(3a), C_2H_5 (5)

R_f: F(9) (Y=20%), CF_3(18) (Y=29%), C_2F_5(25) (Y=9%)

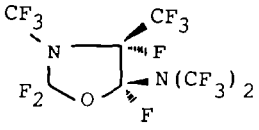
Next, we investigated the fluorination of two other derivatives [ethyl ester (3b) and N,N-dimethylamide (3c)] of 2-dimethylamino-propionic acid to study the effects of these derivatives on the yield of the desired perfluoroacid fluoride (18). From these starting materials, lower yields of 18 (21% from 3b and 13% from 3c, respectively) were obtained compared with that (29%) from methyl ester (3a).

Although the ester linkage of 3a and 3b was destroyed completely during the fluorination, which gave carbonyl fluoride or trifluoroacetyl fluoride together with 18 respectively, the amide linkage of 3c converted its -C(O)N< bond into -C(-O-)N< in a cyclization product, perfluoro(3,4-dimethyl-5-dimethylamino-oxazolidine) (20), as shown in Scheme 3. Young et al. reported the synthesis of perfluoro(N,N-dimethylacetamide) and perfluoro-(tetramethylurea), both of which contain -C(O)N< bonds, by electrochemical fluorination [15], and also the formation of a cyclized product, perfluoro(3-methyl-5-dimethylamino-oxazolidine), from the fluorination of N,N-dimethylaminoacetyl N,N-dimethylamide [11].

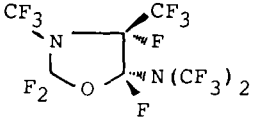


Scheme 3.

Compound 20 is a mixture of two stereo-isomers, and was separated by GLC (ratio 1 : 0.2~0.3). It was difficult to elucidate unambigously their stereochemistry by ^{19}F nmr. However, the major component was assigned as the trans-isomer. Because it was considered that the formation of the trans-form would be more facile than the cis one because the steric repulsion between two vicinal substituents would be minimized in the case of the trans-form.



Cis-20



Trans-20

In the fluorination of methyl 3-dimethylamino-propionate (6), which is an isomer of 3a, a considerable amount of pentafluoro-propionyl fluoride (27) was formed as a result of scission of the C-N bond (γ-scission): the amount was almost twice that of perfluoro(N,N-dimethyl ethylamine) (14) formed, which implies that the γ-scission as well as the α-scission from the carbonyl group took place simultaneously.

Two different modes of fragmentation were observed in the fluorination of amines of the type of R-$N(CH_3)_2$ depending on the nature of the alkyl (R) group: α-scission (from amine) occurred extensively when R was an aliphatic straight-chain alkyl group, particularly a higher one, while β-scission resulted when R was secondary or tertiary [16]. Taking into consideration that 6

is an amine of the type of $R\text{-}N(CH_3)_2$ having a straight chain alkyl group, $R = -(CH_2)_2C(O)Me$, it is understandable that it obeyed the above-mentioned empirical rule for the bond scission.

The effect by a solute-concentration and a solute-temperature

In the electrochemical fluorination of tertiary amines, several examples are known where a small change in the initial concentration of the substrate in anhydrous hydrogen fluoride affects remarkably the yield of the product, depending also on the structures of the amines [16]. The higher the concentration of the substrate, the more the yield is improved [substrate-concentration effect]. Accordingly, the fluorination of (3a) was conducted under several conditions by changing the solute-concentration and by lowering the temperature of the cooling jacket surrounding the cell from 0 °C to -20 °C, respectively. The results are summarized in Table 2.

The solute-concentration effect was observed for 3a: the yield of 18 increased by ca. 10% by just increasing the initial solute-concentration from 6.3 wt% to 8.1 wt%, which resulted in suppressing the formation both of cleaved products and the cyclization product relatively [Run 2]. The effect was not observed beyond the concentration of 10.0 wt% [Run 3].

On the other hand, contrary to our expectation, lowering the solute-temperature did not moderate the reaction by controlling the heat-evolution more effectively [Run 4]. Instead an adverse effect resulted in the formation of increased amounts of cleaved products. With circulation of brine at -20 °C, the thermometer adjacent to the cell wall indicated temperatures of 2～3 °C. It seemed that the cooling of the solution through the jacket without the help of mechanical agitation enhanced the temperature gradient between the electrodes and the inner cell wall. Therefore, the smooth convection of the liquid was disturbed by the increased viscosity.

TABLE 2

Fluorination of 3a under various concentrations and at low temperature

Run	Sample conc (Wt%)	Jacket temp (°C)	Solute temp (°C)	Electricity passed (Ahr)	Product (g)	Yield of 18 (%)	Ratio[a] A	Ratio[a] B
1	6.3[c]	0	7 ~ 9	231	27.2	18.0	0.700	0.139
2[b]	8.1	0	7 ~ 9	240	53.2	28.9	0.651	0.125
3	10.0[d]	0	7 ~ 9	287	70.0	29.7	0.693	0.120
4	8.2[e]	-20	2 ~ 3	244	38.8	19.3	0.773	0.124

a Ratios of A and B were calculated for the evaluation both of the degree of the α-scission of 3a and the cyclization during electrochemical fluorination, respectively: A = yields of cleaved products (14 and 17) / yield of 18; B = yield of cyclization product (16) / yield of 18.

b This datum is duplicated with that given in Table 1.

c 3a (30.4 g) was fed.

d 3a (50.1 g) was fed.

e 3a (40.5 g) was fed.

EXPERIMENTAL

Reagents

Except methyl diethylamino-acetate, all N-containing carboxylic acids were prepared by reactions of appropriate esters of chloro- or bromo-substituted carboxylic acids with a dialkylamine (dimethylamine and diethylamine) [17]. Methyl diethylamino-acetate [Tokyo Kasei Co.] was used as received.

These starting materials had following boiling points: methyl dimethylamino-acetate, bp 86～89 °C/149 mmHg (reported: bp 50 °C/25 mmHg)[11], methyl 2-(dimethylamino)-propionate, bp 90～91 °C/139 mmHg, ethyl 2-(dimethylamino)-propionate, bp 106～107 °C/142 mmHg (reported: bp 154～157 °C/759 mmHg)[17], N,N-dimethylamide of 2-(dimethylamino)-propionic acid, bp 136～137 °C/100 mmHg (reported bp 83～84 °C/12 mmHg)[18], methyl 2-(diethylamino)-propionate, bp 106～108 °C/102 mmHg, methyl 2-(dimethylamino)-butyrate, bp 99～100 °C/116 mmHg, methyl 3-(dimethylamino)-propionate, bp 104～105 °C/148 mmHg (reported: bp 152～154 °C)[19]. Anhydrous hydrogen fluoride (AHF)(Daikin Industries Co.) was better than 99.8% pure.

Apparatus

The electrolytic fluorination apparatus and operating procedures were similar to those described previously [16].

Analytical GLC work was carried out with a Shimadzu GC-2C gas chromatograph using stainless columns (3 mm dia) 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 Shimadzu GC-1C gas chromatograph was used employing stainless columns (10 mm dia) packed with 30% 1,6-bis-(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosrob PAW (4.9 m)(Col. C), and 30% 1,6-bis(1,1,7-trihydroperfluoroheptyloxy)hexane 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 on a Hitachi R-20B high resolution spectrometer operating at 56.46 MHz using CCl_3F as an internal standard. Mass spectra were measured on a Shimadzu GC/MS-7000 instrument at 70 eV.

Fluorination of methyl dimethylamino-acetate (1)

Sample 1 (40.6 g, 0.347 mol) was charged into the cell which contained 450 ml electrically purified anhydrous hydrogen fluoride, and the solution was subjected to fluorination with an anodic current density of 3.5 A/dm^2, a cell voltage of 5.7～5.8 V, and cell temperature of 7～8 °C over a period of 581 min (250 Ahr).

The effluent gases from the cell were passed over NaF pellets and then condensed in a trap cooled at -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 bottles containing aq. solution of K_2SO_3, KOH and KI. All products except new ones were identified by comparison of their infrared 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 infrared, ^{19}F nmr and mass spectra.

The products (compound number, g Yield)(30.6 g) condensed in the -78 °C trap consisted of perfluoro(trimethylamine)(7) (5.4), perfluoro(3-methyloxazolidine)(8)[11,20](7.9), perfluoro-(dimethylamino-acetyl fluoride)(9)[11](19.5) and unidentified (1.6). The yield of 9 was 20% based on the sample fed. Among these products, 8 and 9 were isolated from other products by GLC (Col. C and D) and were characterized spectroscopically.

Perfluoro(3-methyloxazolidine)(8): IR (gas): 1418 (w), 1363 (s), 1323 (ms), 1288 (ms), 1235 (vs), 1085 (m), 1018 (m), 918 (m), 798 (w), 753 (w), 700 (w).

Perfluoro(dimethylamino-acetyl fluoride)(9): IR (gas): 1898 (s) ν(C=O), 1450 (w), 1350~1360 (vs), 1315 (sh,ms), 1275 (s), 1227 (vs), 1092 (ms), 998 (s), 923 (ms), 815 (w), 782 (w), 768 (w), 733 (w), 700 (w).

^{19}F nmr data of 8 and 9 are shown in Table 3.

Fluorination of methyl diethylamino-acetate (2)

2 (41.1 g, 0.284 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.1~6.3 V, 7~8 °C, 612 min (256 Ahr).

Work-up was as for the fluorination of 1. Products collected in the -78 °C trap and cell drainings were subsequently analyzed by GLC (Col. A and B). Thus, the following compounds were obtained; products in the -78 °C trap (21.1 g) perfluoro(N,N-diethylmethylamine)(10)(4.6), perfluoro(N-methylmorpholine)(11)(1.4), perfluoro(N-ethylmorpholine)(12)(4.2), perfluoro(diethylamino-acetyl fluoride)(13)(5.3), unidentified (5.6). Cell drainings (11.1 g) 11 (11.1 g), 12 (2.3), 13 (4.8), unidentified (3.9) The yield of 13 was 10% based on the sample fed.

Perfluoro(diethylamino-acetyl fluoride)(13)(nc) had bp 71~73 °C. $n_D^{20} < 1.28$ and d_4^{20} 1.7146. IR (gas): 1895 (s) ν(C=O), 1370 (m), 1310 (s), 1287 (vs), 1240 (vs), 1210 (ms,s), 1154 (s), 1108 (vs), 1053 (m), 881 (s), 777 (w), 763 (w), 743 (s), 703 (m). Mass: 313 $[M-COF]^+$ (5.5), 280 $C_5F_{10}NO^+$ (2.6), 214 $C_4F_8N^+$ (5.0), 164 $C_3F_6N^+$ (29.2), 119 $C_2F_5^+$ (100), 114 $C_2F_4N^+$ (21.6), 100 $C_2F_4^+$ (6.8), 97 $C_2F_3O^+$ (24.9), 69 CF_3^+ (68.4).

^{19}F nmr data of 13 is shown in Table 3.

Fluorination of methyl 2-dimethyl-propionate (3a)

3a (39.7 g, 0.303 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 6.0~6.3 V, 7~8 °C, 555 min (240 Ahr). Work-up of the products (53.2 g from -78 °C trap) as for the fluorination of 1 gave; perfluoro(N,N-dimethylethylamine)(14)(12.3), bis(trifluoromethyl)difluoromethylamine (15)(1.6),

perfluoro(3,4-dimethyloxazolidine) (16) (3.3), N-trifluoromethyl-N-difluoromethylpentafluoroethylamine (17) (2.9), perfluoro(2-dimethylamino-propionyl fluoride) (18) (26.2), unidentified (6.9). The yield of 18 was 29% based on the sample fed. The oxazolidine (16) has been synthesized by the reaction of 2-(trifluoromethyl-3,3-difluorooxaziridine with perfluoropropeneoxide in a low yield recently [20]. Among these products, 16 and 18 were isolated from other products by GLC (Col. B and C) and were characterized spectroscopically.

Perfluoro(3,4-dimethyloxazolidine) (16) had bp 40.5～41.5 °C. IR (gas): 1393 (ms), 1319 (vs), 1305 (s,sh), 1280 (s), 1263 (vs), 1236 (ms), 1219 (ms), 1180 (m), 1145 (w), 1100 (m), 1033 (m), 975 (m), 900 (ms), 760 (w), 737 (m). Mass: 280 $[M-F]^+$ (2.2), 252 $C_4F_{10}N^+$ (2.3), 231 $C_5F_9^+$ (8.4), 214 $C_4F_8N^+$ (13.6), 164 $C_3F_6N^+$ (49.9), 114 $C_2F_4N^+$ (41.2), 69 CF_3^+ (100).

Perfluoro(2-dimethylamino-propionyl fluoride) (18) (nc) had bp 43.5～44.0 °C, $n_D^{20} < 1.28$, d_4^{20} 1.6735. IR (gas): 1899 (m,sh) and 1886 (ms) ν(C=O), 1356 (s), 1312 (ms), 1289 (ms,sh), 1266 (vs), 1242 (vs), 1226 (vs), 1184 (m), 1164 (m), 1099 (m), 1025 (m), 999 (w), 976 (w), 938 (w), 904 (m). Mass: 252 $[M-COF]^+$ (8.3), 231 $C_5F_9^+$ (4.3), 164 $C_3F_6N^+$ (34.0), 114 $C_2F_4N^+$ (15.3), 69 CF_3^+ (100).

^{19}F nmr data of 16 and 18 are shown in Table 3.

Fluorination of ethyl 2-dimethylamino-propionate (3b)

3b (40.9 g, 0.282 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.9～6.0 V, 7～8 °C, 590 min (256 Ahr). The products weighed 35.4 g (-78 °C trap) and 2.6 g (cell drainings). Work-up as for the fluorination of 3a gave, from the -78 °C trap, 14 (8.3), 15 (1.3), 16 (2.3), 17 (2.2), 18 (16.8), unidentified (4.5). From the cell drainings 18 (0.5), unidentified (2.1). The yield of 18 was 21% based on the sample fed.

Fluorination of dimethylamide of 2-dimethylamino-propionic acid (3c)

3c (40.7 g, 0.283 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.8～5.9 V, 7～8 °C, 615 min (263 Ahr). After the usual work-up, the following compounds were obtained; product in the -78 °C trap (34.6 g) 14 (8.0), 15 (0.7), perfluoro(N,N-dimethylcarbamoyl fluoride) (19) (5.9), 16 (1.4), 17 (2.8), 18 (11.1), trans-perfluoro(3,4-dimethyl-5-dimethylamino-oxazolidine) (20) (1.2), cis-20 (0.3), unidentified (3.3). Cell drainings (4.4 g) trans-20 (3.5), cis-20 (0.9). The yield of 18 was 13% based on the sample fed. Among these products, trans- and cis-20 were isolated by GLC (Col.D) and their structure was determined by studying the ^{19}F nmr.

Trans-perfluoro(3,4-dimethyl-5-dimethylamino-oxazolidine) (20) had bp 97.0～98.5 °C, n_D^{20}1.2866, and d_4^{20}1.8099. IR (gas): 1343 (vs), 1310 (ms), 1253 (ms,sh), 1240 (s), 1224 (s), 1166 (w), 1100 (w), 1026 (w), 991 (m), 969 (w), 840 (w), 791 (w), 757 (w), 735 (w). Mass: 413 $[M-F]^+$ (1.2), 347 $C_6F_{13}N_2^+$ (5.0), 325 $C_6F_{11}N_2O^+$ (5.8), $[M-N(CF_3)_2]^+$(15.6), 259 $C_4F_9N_2^+$(9.1), 233 $C_4F_9N^+$(30.0), 214 $C_4F_8N^+$(9.5), 164 $C_3F_6N^+$ (100), 145 $C_3F_5N^+$ (10.2), 114 $C_2F_4N^+$ (28.8), 69 CF_3^+ (90.0).

Cis-20 had bp 99.0～100.5 °C. IR (gas): 1388 (m,sh), 1355 (s), 1318～1328 (vs), 1250 (s), 1225 (s), 1178 (m), 1118 (w), 1096 (w), 1037 (ms), 985 (ms), 980 (w), 925 (w), 845 (m), 767 (w), 752 (w), 721 (m). Its mass spectral data were almost the same as those of trans-20.

^{19}F nmr spectra of trans-20 and cis-20 are shown in Table 3

Fluorination of methyl 2-diethylamino-propionate (4)

4 (26.7 g, 0.168 mol) was fluorinated similarly under the following conditions, 3.5 A/dm^2, 5.9～6.1 V, 7～9 °C, 437 min (193 Ahr). The products weighed 13.2 g (-78 °C trap) and 4.8 g (cell drainings). Perfluoro(triethylamine) was the major flu-

orination product (Y=8%). Several compounds having a similar GLC retention time to that of authentic perfluoro(2-diethylamino-propionyl fluoride) [14] (Col. A) were checked by comparing their IR data with authentic ones. However, the identification of perfluoro(2-diethylamino-propionyl fluoride), if formed, was not confirmed. So, further investigation on the structure of these compounds was not conducted.

Fluorination of methyl 2-dimethylamino-butyrate (5)

5 (40.8 g, 0.281 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 5.9~6.1 V, 7~8 °C, 591 min (258 Ahr). Work-up gave; product in the -78 °C trap (35.5 g) perfluoro(N,N-dimethyl-n-propylamine) (22) (9.9), perfluoro(3-dimethylamino-propyl methylether) (23) (1.5), perfluoro(3-methyl-4-ethyloxazolidine) (24) (2.7), perfluoro(2-dimethylamino-butyryl fluoride) (25) (6.7), perfluoro(3-dimethylamino-oxolane) (26) (2.0), unidentified (12.7). Cell drainings (7.0 g), 23 (0.5), 24 (0.6), 25 (2.0), 26 (0.7), unidentified (3.2). The yield of 25 was 9%.

Perfluoro(3-dimethylamino-propyl methylether) (23) (nc) had bp 69.0~70.0 °C. IR (gas): 1339~1354 (vs), 1289 (s), 1229~1249 (vs), 1159 (vs), 1040 (w), 998 (s), 916 (w), 879 (w), 856 (ms), 822 (m), 767 (ms), 736 (m). Mass: 214 $C_4F_8N^+$(3.7), 202 $C_3F_8N^+$(6.8), 169 $C_3F_7^+$(5.5), 164 $C_3F_6N^+$(2.8), 135 $C_2F_5O^+$(3.7), 119 $C_2F_5^+$(5.1), 114 $C_2F_4N^+$(20.1), 69 CF_3^+(100).

Perfluoro(3-methyl-4-ethyloxazolidine) (24) (nc) had bp 63.0~63.5 °C, $n_D^{20} < 1.28$ and d_4^{20}1.7352. IR (gas): 1379 (s), 1331 (s), 1285~1300 (vs), 1225~1255 (vs), 1169 (s), 1150 (ms), 1102 (m), 1060 (w), 1023 (ms), 958 (ms), 937 (w), 853 (s), 741 (s). Mass: 330 $[M-F]^+$(3.6), 264 $C_5F_{10}N^+$(9.9), 231 $C_5F_9^+$(8.1), 214 $C_4F_8N^+$(15.6), 176 $C_4F_6N^+$(4.6), 164 $C_3F_6N^+$(30.2), 145 $C_3F_5N^+$(5.2), 119 $C_2F_5^+$(5.4), 114 $C_2F_4N^+$(34.2), 100 $C_2F_4^+$(5.4), 95 $C_2F_3N^+$(4.4), 69 CF_3^+(100).

Perfluoro(2-dimethylamino-butyryl fluoride) (25) (nc) had bp 68.0~69.0 °C, $n_D^{20} < 1.28$, d_4^{20} 1.7172. IR (gas): 1888 (ms) ν(C=O), 1360 (vs), 1348 (vs), 1318 (s), 1250 (vs), 1228 (vs), 1175 (m), 1157 (m), 1122 (w), 1083 (w), 997 (ms), 950 (w), 883 (m), 860 (m), 744 (m), 693 (w). Mass: 302 $[M-COF]^+$ (2.6), 230 $C_4F_8NO^+$ (4.1), 214 $C_4F_8N^+$ (11.5), 114 $C_2F_4N^+$ (10.3), 100 $C_2F_4^+$ (4.1), 69 CF_3^+ (100).

Perfluoro(3-dimethylamino-oxolane) (26) (nc) had bp 74.0~75.5 °C. n_D^{20} 1.2869. d_4^{20} 1.7705. IR (gas): 1360 (vs), 1319 (m), 1255~1270 (vs), 1220~1230 (vs), 1150 (ms), 1128 (s), 1087 (m), 1028 (w), 1011 (w), 938 (w), 853 (s), 807 (w), 767 (m), 713 (w). Mass: 330 $[M-F]^+$ (1.4), 283 $C_5F_{11}N^+$ (1.9), 214 $C_4F_8N^+$ (12.1), 195 $C_4F_7N^+$ (6.7), 150 $C_3F_6^+$ (5.9), 145 $C_3F_5N^+$ (13.4), 131 $C_3F_5^+$ (3.6), 114 $C_2F_4N^+$ (5.5), 100 $C_2F_4^+$ (14.6), 69 CF_3^+ (100).

^{19}F nmr spectra of 23, 24, 25 and 26 are shown in Table 3.

Fluorination of methyl 3-dimethylamino-propionate (6)

6 (41.5 g, 0.317 mol) was fluorinated similarly under the following conditions; 3.5 A/dm^2, 6.0~6.1 V, 7~8 °C, 547 min (244 Ahr). The amounts of the products were 32.8 g (-78 °C trap) The following compounds were obtained; 27 (5.6), 7 (1.3), 14 (5.2), 17 (1.0), perfluoro(3-methyl-3-aza-oxane) (28) (1.7), perfluoro(3-dimethylamino-propionyl fluoride) (29) (13.9), unidentified (4.1). The yield of 29 was 15%.

Perfluoro(3-methyl-3-aza-oxane) (28) (nc) had bp 48.5~49.5 °C. IR (gas): 1438 (w), 1369 (vs), 1345 (vs), 1314 (s), 1274 (s), 1217~1242 (s~vs), 1203 (s), 1168 (s), 1130 (s), 1003 (s), 901 (s), 867 (w), 756 (w), 727 (w), 700 (w), 637 (w). Mass: 280 $[M-F]^+$ (2.2), 214 $C_4F_8N^+$ (18.6), 192 $C_4F_6NO^+$ (7.0), 164 $C_3F_6N^+$ (10.9), 119 $C_2F_5^+$ (8.0), 114 $C_2F_4N^+$ (20.9), 100 $C_2F_4^+$ (100), 69 CF_3^+ (55.2).

Perfluoro(3-dimethylamino-propionyl fluoride) (29) (nc) had bp 52.5~53.0 °C. $n_D^{20} < 1.28$ and d_4^{20} 1.6678. IR (gas): 1888 (s) ν(C=O), 1359~1364 (vs), 1341 (vs), 1230 (vs), 1177 (m), 1325

(s), 1021 (w), 1000 (ms), 772 (w), 737 (m), 699 (w). Mass: 202 $C_3F_8N^+$(13.3), 164 $C_3F_6N^+$(7.4), 119 $C_2F_5^+$(22.5), 114 $C_2F_4N^+$(34.3), 100 $C_2F_4^+$(7.1), 69 CF_3^+(100).

^{19}F nmr spectra of 28 and 29 are shown in Table 3.

To check the effect of solute concentration and solute temperature in the fluorination of 3a, several experiments were conducted as shown in Table 2; that using a low solute temperature (-20 °C) will be described.

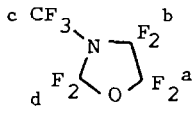
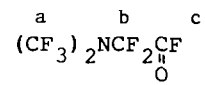
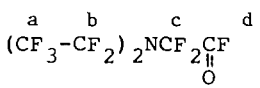
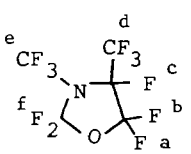
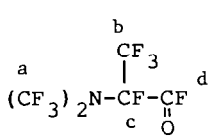
Fluorination of 3a at a low temperature

3a (40.5 g, 0.309 mol) was fluorinated as before except that brine (-20 °C) was circulated instead of ice-water through the jacket of the cylindrical cell for cooling during the electrolysis [condition: 3.5 A/dm^2, 6.0～6.1 V, 581 min (244 Ahr)]. The thermometer, being located about 10 mm from the cooling jacket indicated temperatures of 2～3 °C. The product (38.8 g, -78 °C trap) worked up as for Run 3 in Table 1, gave; 14 (9.6), 15 (1.4), 16 (2.8), 17 (2.8) and 18 (17.9). The yield of 18 was 19%. The residual AHF in the cell was ocher-colored, and small quantities of yellow oily materials were present on the surface of it. This was in contrast to the case of the fluorination of 3a under the circulation of ice-water, where the residual AHF was transparent and clear.

Several perfluoroacid fluorides (9, 18 and 29) were converted into their corresponding methyl esters for further characterization. These results and the oligomerization reactions using these perfluoroacid fluorides with perfluoropropeneoxide will be described in due course.

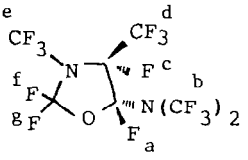
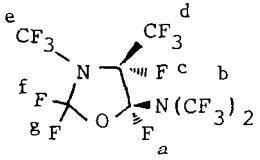
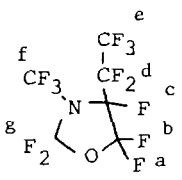
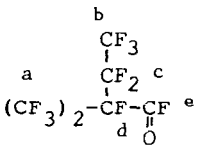
TABLE 3

^{19}F nmr data of 8, 9, 13, 16, 18, trans-20, cis-20, 23, 24, 25 26, 28 and 29

Compd	Formula		Chemical Shift[a,b]	J (Hz)[b]
8		a	-86.4	
		b	-93.3	
		c	-57.3	
		d	-58.1	
9		a	-54.3	a-b=10.2
		b	-83.3	
		c	+12.5	
13		a	-82.9	
		b	-91.3	
		c	-82.9	
		d	+12.2	
16		a	-87.4	a-b=139
		b	-80.1	
		c	-140.0	
		d	-77.1	
		e	-56.3	
		f	-57.5	
18		a	-53.0	a-b=7.6
		b	-76.0	a-c=7.6
		c	-141.3	b-d=6.2
		d	+22.3	c-d=16.1

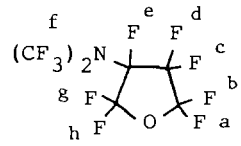
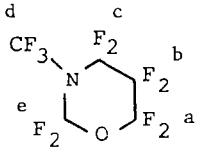
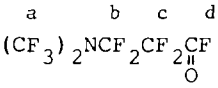
(continued)

TABLE 3 (cont.)

trans-20		a	-81.4	f-g=100
		b	-54.1	
		c	-152.5	
		d	-80.7	
		e	-55.6	
		f	-60.5] J_{AB}	
		g	-54.3]	
cis-20		a	-94.9	f-g=90
		b	-52.9	
		c	-133.3	
		d	-76.1	
		e	-55.7	
		f	-60.1] J_{AB}	
		g	-52.2]	
23	$(CF_3)_2NCF_2CF_2CF_2OCF_3$ (a b c d e)	a	-53.1	a-b≈15.5
		b	-91.3	a-c≈8.2
		c	-125.8	d-e≈15.2
		d	-86.2	
		e	-56.1	
24		a	-94.1] J_{AB}	a-b=136
		b	-99.8]	
		c	-136.1	
		d	-120.1	
		e	-80.4	
		f	-54.9	
		g	-57.2	
25		a	-51.1	b-d=13.3
		b	-80.1	
		c	-120.4	
		d	-151.4	
		e	+21.6	

(continued)

TABLE 3 (cont.)

26		a	-106.0	a-b=134
		b	-94.0	c-d=253
		c	-140.0	g-h=134
		d	-131.4	
		e	-135.9	
		f	-53.1	
		g	-85.0	
		h	-96.0	
28		a	-88.6	c-d=13.0
		b	-132.2	d-e=13.0
		c	-95.4	
		d	-53.9	
		e	-51.1	
29		a	-53.1	a-b=15.2
		b	-91.6	a-c=15.2
		c	-117.6	b-d=5.7
		d	+23.7	

a ^{19}F chemical shift in ppm relative to internal CCl_3F in CCl_4.
b Only evident chemical shifts and coupling constants are given.

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