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# ELECTROCHEMICAL FLUORINATION OF CHLORINE-CONTAINING AMINES*

KOTA OMORI,** SHUNJI NAGASE, HAJIME BABA, KAZUO KODAIRA and TAKASHI ABE

Government Industrial Research Institute, Nagoya, Hirate-machi,
Kita-ku, Nagoya 462 (Japan)

## SUMMARY

The electrochemical fluorination of chlorine-containing alkylamines has been studied. It was found that, in general, the carbon-chlorine bond in the alkylamines is retained during electrochemical fluorination in anhydrous hydrogen fluoride, yielding chlorine-containing polyfluoroalkylamines. Perfluoroalkylamines and fluorocarbons were also produced.

By the use of this method, several new chloropolyfluoroamines such as $(CF_3)_2NCF_2CClF_2$, $(C_2F_5)_2NCF_2CClF_2$, $(CF_3)(C_2F_5)N$-$CF_2CClF_2$, $(CClF_2CF_2)_2NCF_3$, $(CClF_2CF_2)_2NC_2F_5$, $(C_2F_5)(CClF_2CF_2)NF$, $(CClF_2CF_2)_2NF$, $(CF_3)_2NCF_2CF_2CClF_2$, $\overline{CF_2(CF_2)_3N}CF_2CClF_2$, and $\overline{CF_2CF_2OC_2F_4N}CF_2CClF_2$ have been isolated and characterized.

## INTRODUCTION

In a previous paper [1], we have shown that the electrochemical fluorination of certain chlorinated ethers yields chlorine-containing polyfluoroethers, that is, the carbon-chlorine bond in the ethers is retained during the electrochemical fluorination.

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** Present address: Research Laboratories, Tohoku Hiryo Co., Ltd., Barajima, Akita 010, Japan.

The present work was undertaken to examine the behavior of chlorine-containing alkylamines in the electrochemical fluorination, and several tertiary and secondary alkylamines including cyclic ones having a chlorine atom were subjected to the fluorination. These were expected to yield the corresponding polyfluorinated tertiary or secondary amines containing the chlorine atom.

## RESULTS AND DISCUSSION

Chlorine atoms attached to certain types of organic molecules are known to be retained during electrochemical fluorination; for example, chlorinated ethers [1] and chlorinated benzenes [2] yielded chloropolyfluoroethers and chloropolyfluorocyclohexanes.

This report describes the results of a study of the electrochemical fluorination of chlorinated alkylamines, and the following amines were included in the present investigation: 2-chloro-N,N-dimethylethyl, 2-chloro-N,N-diethylethyl, 2,2'-dichloro-N-methyldiethyl, 2,2',2"-trichlorotriethyl (I), 2,2'-dichlorodiethyl, 2-chloro-N,N-dimethylpropyl (II), 3-chloro-N,N-dimethylpropyl (III), 3-chloro-N,N,2-trimethylpropylamine (IV), and 1-(2-chloroethyl)pyrrolidine (V), and 4-(2-chloroethyl) morpholine. Amines have often been subjected to the electrochemical fluorination but no work has yet been reported on chlorinated amines.

The electrochemical fluorination was performed in the usual manner. The crude product was separated into portions by rectification, and each of these portions was further resolved into their components by gas chromatography. Although the yields were generally low (2 - 19%), these amines afforded expected chlorine-containing polyfluorinated tertiary or secondary amines. They were accompanied by perfluoroamines as well as fluorocarbons and nitrogen trifluoride, which were formed by extensive degradation due to the scission of carbon-carbon and carbon-nitrogen bonds during the fluorination.

The chlorine-containing new amines prepared and isolated during the course of the work include 2-chloro-1,1,2,2-tetrafluoro-N,N-bis(trifluoromethyl)ethyl (VI), 2-chloro-1,1,2,2-

tetrafluoro-N,N-bis(pentafluoroethyl)ethyl (VII), 2-chloro-1,1,2,2-tetrafluoro-N-pentafluoroethyl-N-trifluoromethylethyl (VIII), 2,2'-dichloro-1,1,1',1',2,2,2',2'-octafluoro-N-trifluoromethyldiethyl (IX), 2,2'-dichloro-1,1,1',1',2,2,2',2'-octafluoro-N-pentafluoroethyldiethyl (X), 2-chloro-1,1,2,2-tetrafluoro-N-fluoro-N-pentafluoroethylethyl (XI), 2,2'-dichloro-1,1,1',1',2,2,2',2'-octafluoro-N-fluorodiethyl (XII), and 3-chloro-1,1,2,2,3,3-hexafluoro-N,N-bis(trifluoromethyl)-propylamine (XIII), 2,2,3,3,4,4,5,5-octafluoro-1-(2-chloro-1,1,2,2-tetrafluoroethyl)pyrrolidine (XIV), and 2,2,3,3,5,5,-6,6-octafluoro-4-(2-chloro-1,1,2,2-tetrafluoroethyl)morpholine (XV), and their yields and simpler physical constants are shown in Table 1.

The compound (I) did not afford the anticipated corresponding trichloro-compound. Mono- and dichloro-compounds as well as perfluoroamines were produced as follows:

$$(CH_2ClCH_2)_3N \longrightarrow (C_2F_5)_3N(8.6\%),\ (CF_3)(C_2F_5)NCF_2CClF_2\ (VIII)(2.2\%),\ (C_2F_5)_2NCF_2CClF_2(VII)(2.0\%),\ (CClF_2CF_2)_2NC_2F_5(X)(1.8\%)$$

The electrochemical fluorination of (II) yielded (XIII) as well as expected 2-chloro-1,1,2,3,3,3-hexafluoro-N,N-bis(trifluoromethyl)propylamine (XVI) [3]. Chlorine-migration took place in this fluorination.

Similar rearrangement was also observed in the electrochemical fluorination of (III): (XVI) as well as (XIII) were formed. The isomerization reaction accompanying the electrochemical fluorination has been often reported, usually by the migration of a methyl or a ethyl group [4].

The structures of these compounds were established by means of their $^{19}F$ NMR, mass, and IR spectra as well as by elemental analysis. The chemical shifts and evident coupling constants obtained by the first order analysis are presented. The chemical shifts ($\delta$ ppm, relative to external trifluoroacetic acid) are in the ranges indicated below: $CF_3\text{-}C\text{-}N$, 3 to 7; $CF_2\text{-}N{<}^{C}_{C}$, 8 to 17; $CF_2\text{-}N{<}^{F}_{C}$; 29 to 32; F-N, 14 to 15;

TABLE 1

Chloropolyfluoroamines

| Starting material | Cl-F compound | Yield (%) | B.p.[a] (°C) | $n_D^{20}$ |
|---|---|---|---|---|
| $(CH_3)_2NCH_2CH_2Cl$ | $(CF_3)_2NCF_2CClF_2$(VI) | 4.8 | 47.6 | $<1.28$ |
| $(C_2H_5)_2NCH_2CH_2Cl$ | $(C_2F_5)_2NCF_2CClF_2$(VII) | 12.3 | 96.0 | 1.2913 |
| $(CH_2ClCH_2)_2NCH_3$ | (VI) | 3.6 | | |
| | $(CF_3)(C_2F_5)NCF_2$-$CClF_2$(VIII) | 12.9 | 73.3 | 1.2842 |
| | $(CClF_2CF_2)_2NCF_3$ | 6.8 | 103.1 | 1.3152 |
| $(CH_2ClCH_2)_3N$ | (VII) | 2.0 | | |
| | (VIII) | 2.2 | | |
| | $(CClF_2CF_2)_2NC_2F_5$ | 1.8 | 122.6 | 1.3184 |
| $(CH_2ClCH_2)_2NH$ | $(C_2F_5)(CClF_2CF_2)NF$ | 4.4 | 53.2 | $<1.28$ |
| | $(CClF_2CF_2)_2NF$ | 2.1 | 83.7 | 1.3115 |
| $(CH_3)_2NCH_2CHClCH_3$ | $(CF_3)_2NCF_2CClFCF_3$(XVI)[b] | 6.4 | 72.6 | 1.2828 |
| | $(CF_3)_2NCF_2CF_2CClF_2$(XIII) | 14.6 | 73.6 | 1.2820 |
| $(CH_3)_2NCH_2CH_2CH_2Cl$ | (XVI) | 4.0 | | |
| | (XIII) | 3.5 | | |
| $\overline{CH_2(CH_2)_3N}CH_2CH_2Cl$ | $\overline{CF_2(CF_2)_3N}CF_2CClF_2$ | 19.2 | 89.1 | 1.3002 |
| $\overline{CH_2CH_2OC_2H_4N}$-$CH_2CH_2Cl$ | $\overline{CF_2CF_2OC_2F_4N}CF_2CClF_2$ | 4.9 | 99.4 | 1.3033 |

[a] Recorded at atmospheric pressure and uncorrected.

[b] Reported in Ref.[3].

$CF_2Cl$-C, -5 to -11; C-$CF_2$-C-N, 43. These are in the regions expected [5, 6].

The mass spectra of these compounds with a beam energy of 70 eV are sufficiently distinctive to permit an identification of the molecule with consistent fragmentation patterns. The molecular ion peaks were undetectable but [M - F] ion peaks were always observed.

The chlorine-migration was also found in the electrochemical fluorination of (IV). 3-Chloro-1,1,2,3,3-pentafluoro-N,N,2-tris(trifluoromethyl)propylamine (XVII) which has not been reported previously, was obtained as an approximately 1 : 1 mixture with its isomer, 2-chloro-1,1,3,3,3-pentafluoro-N,N,3-tris(trifluoromethyl)propylamine (XVIII) (according to $^{19}F$ NMR spectroscopy), but separation of the mixture into individual components by gas chromatography was not achieved. The $^{19}F$ NMR data are as follows: $(CF_3{}^a)_2NCF_2{}^bCF^c(CF_3{}^d)CF_2{}^eCl$ (XVII), -23.9 ($CF_3{}^a$), +6.0 ($CF_2{}^b$), +95.8 ($CF^c$), -5.0 ($CF_3{}^d$), -16.2 ppm ($CF_2{}^e$); $J_{ac}$ = 17.7, $J_{ab}$ = 14.4, $J_{ae}$ = 3.0, $J_{ad}$ = 2.6 Hz. $(CF_3{}^a)_2NCF_2{}^bCCl(CF_3{}^c)_2$ (XVIII), -24.7 ($CF_3{}^a$), -1.2 ($CF_2{}^b$), -8.4 ppm ($CF_3{}^c$); $J_{ab}$ = 16.2, $J_{ac}$ = 3.2, $J_{cb}$ = 12.8 Hz.

Among the amines examined, the best yield was observed in the electrochemical fluorination of (V) which afforded the corresponding polyfluorinated cyclic amine containing chlorine atom in 19.2% yield, as well as perfluoro(1-ethylpyrrolidine) [4] (41.6%).

In addition to these chloropolyfluoroamines, the following fluorinated amines, which have not been listed in the literature, were isolated and fully characterized; perfluoro-N,N-dimethylpropylamine (XIX) from (II) and (III), and perfluoro-N,N-dimethylbutylamine (XX) (by rearrangement), perfluoro-N,N,2-trimethylpropylamine (XXI), and 2-trifluoromethyl-1,1,-3,3,3-pentafluoro-N,N-bis(trifluoromethyl)propylamine (XXII) from (IV).

## EXPERIMENTAL

The electrolytic cell used was similar to the one described previously [1]. Analytical gas chromatography was carried out with a Shimadzu GC-4A chromatograph using a 3 m x 3 mm stainless-steel column packed with silica gel (60 - 80 mesh) (Col. A) and a 4 m x 3 mm column packed with Porapak-Q for lower boiling materials, and 15% of Silicone DC QF-1 on Chromosorb P-AW (60 - 80 mesh) (Col. B) and 15% of Silicone KF-96 on Chromosorb P-AW for higher boiling materials. For semi-preparative work, a Varian Aerograph 700 chromatograph was used with a 20 ft x 3/8 in aluminum column packed with 15% Silicone KF-96 on Chromosorb P-AW. The carrier gas was helium in all cases.

IR spectra were measured on a Hitachi EPI-G3 spectrometer using a gas cell equipped with KBr windows, and mass spectra on a Hitachi RMU-7 instrument at 70 eV. $^{19}$F NMR spectra were measured with a Hitachi R-20B spectrometer at 56.4 MHz. The chemical shifts are given in $\delta$ ppm from external trifluoroacetic acid.

The amines were added into the electrolytic cell in the form of hydrochloride. 2-Chloro-N,N-dimethylethylamine.HCl and 2-chloro-N,N-diethylethylamine.HCl were purchased from Tokyo Kasei Kogyo Co., and others from Aldrich Chemical Co.

## Fluorination of 2-chloro-N,N-dimethylethylamine

2-Chloro-N,N-dimethylethylamine.HCl (25.0 g, 0.174 mol) was dissolved into electrically purified anhydrous hydrogen fluoride (450 cm$^3$), and the resulting solution was electrolyzed over a period of 330 min (136 A h) with an anodic current density of 3.3 A dm$^{-2}$ (effective surface areas of the anodes and cathodes were each 7.5 dm$^2$), a cell voltage of 6.0 - 7.0 V, and a cell temperature of 10 - 13$^{\circ}$C. Helium (50 cm$^3$ min$^{-1}$) was introduced through the bubbler fitted in the bottom of the cell.

The gaseous products evolving from the cell were passed through a sodium fluoride tube, gas-washing bottles filled with a 10% aqueous solution of potassium sulfite containing a small amount of potassium iodide, and then led to a series of cold traps immersed in ice and in liquid nitrogen. All the products were sufficiently volatile under the conditions used so they moved with hydrogen and helium from the cell into these traps.

The products collected in the traps were combined and then separated into four fractions by rectification. Each fraction was then subjected to gas chromatographic analysis (compositions were calculated on the basis of chromatographic peak areas, assuming, as usual, equal weight sensitivities for all components); (i) -128°C to -126°C, 21.6 g (Col. A, ambient temperature); (ii) -90°C to -75°C, 19.1 g (Col. A, 80°C); (iii) -16°C to 0°C, 6.4 g (Col. A, 80°C); (iv) above 0°C, 9.0 g (Col. B, 50°C). The following compounds were found: $CF_4$ (17.0 g), $NF_3$ (4.7 g), $C_2F_6$ (3.9 g), $CHF_3$ (9.7 g), $CClF_3$ (1.3 g), $C_2ClF_5$ (2.7 g), $(CF_3)_3N$ (2.9 g), $(CF_3)_2NC_2F_5$ (3.6 g, 7.7% yield), $(CF_3)_2NCF_2CClF_2$ (VI) (2.4 g, 4.8% yield), and unidentified compounds (mostly complex mixtures, 7.9 g).

(VI) had b.p. 47.6°C (measured with a Mettler FP1 instrument) and $n_D^{20} < 1.28$. IR: 1353 (vs), 1333 (s), 1281 (w), 1263 (m), 1224 (vs), 1192 (m), 1166 (m), 1119 (m), 1015 (w, sh), 990 (m), 883 (w), 839 (m), 761 (m), 727 (w), 690 (w), 652 (w), 550 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $(CF_3^{a})_2NCF_2^{b}CF_2^{c}Cl$, -23.8 $(CF_3^{a})$, +16.0 $(CF_2^{b})$, -5.8 ppm $(CF_2^{c})$; $J_{ab}$ = 16.1, $J_{ac}$ = 8.2, $J_{bc} \leq 1.7$ Hz. The mass spectrum had peaks at 268 [M - F], 252 [M - Cl], 202 $[C_3F_8N]$, and 164 $[C_3F_6N]$. (The chlorine isotope ratios were consistent with ion assignments but the $Cl^{37}$ ions have been omitted). Found: C, 16.49; F, 66.0%. $C_4ClF_{10}N$ requires C, 16.71; F, 66.1%.

## Fluorination of 2-chloro-N,N-diethylethylamine

2-Chloro-N,N-diethylethylamine.HCl (25.0 g, 0.146 mol) was fluorinated with the similar procedures to those described above under the following conditions; 6.0 V, 3.2 A $dm^{-2}$, 6.5°C, 140 A h (350 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (16.9 g), $(CF_3)_2NC_2F_5$ (0.4 g), $(C_2F_5)_2NCF_3$ (3.6 g), $(C_2F_5)_3N$ (14.1 g, 26.0%), $(C_2F_5)_2NCF_2CClF_2$ (VII) (7.0 g, 12.3%) and others (6.0 g).

(VII) had b.p. 96.0°C and $n_D^{20}$ 1.2913. IR: 1338 (m), 1300 (vs, sh), 1286 (vs), 1272 (s, sh), 1242 (vs), 1232 (s, sh), 1201 (m), 1187 (m), 1159 (s), 1120 (s), 1105 (s), 1076 (m), 980 (m), 883 (m), 854 (w), 818 (s), 759 (m), 746 (m), 697 (w), 672 (w), 557 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $(CF_3{}^aCF_2{}^b)_2NCF_2{}^cCF_2{}^dCl$, +4.0 ($CF_3{}^a$), +11.6 ($CF_2{}^b$), +8.7 ($CF_2{}^c$), -9.1 ppm ($CF_2{}^d$); $J_{ac}$ = 8.8, $J_{ab}$ = 6.0, $J_{ad}$ = 3.0, $J_{db}$ = 13.9 Hz. The mass spectrum had peaks at 368 [M - F], 352 [M - Cl], 318 [$C_5ClF_{11}N$], and 302 [$C_5F_{12}N$]. Found: C, 18.54; F, 68.2%. $C_6ClF_{14}N$ requires C, 18.60; F, 68.6%.

## Fluorination of 2,2'-dichloro-N-methyldiethylamine

2,2'-Dichloro-N-methyldiethylamine.HCl (25.0 g, 0.131 mol) was fluorinated: 3.2 A $dm^{-2}$, 6.2 V, 5 - 6°C, 120 A h (300 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (23.0 g), $(CF_3)_3N$ (0.6 g), $(CF_3)_2NC_2F_5$ (1.4 g), $(C_2F_5)_2NCF_3$ (7.2 g, 17.0%), (VI) (1.3 g, 3.6%), $(CF_3)(C_2F_5)NCF_2CClF_2$ (VIII) (5.7 g, 12.9%), $(CClF_2CF_2)_2NCF_3$ (IX) (3.2 g, 6.8%), and others (4.5 g).

(VIII) had b.p. 73.3°C and $n_D^{20}$ 1.2842. IR: 1341 (s), 1318 (vs), 1273 (m), 1245 (vs), 1234 (s, sh), 1204 (s), 1187 (s), 1158 (m), 1124 (s), 1096 (s), 1011 (w), 995 (w), 931 (m), 862 (m), 828 (s), 763 (m), 742 (m), 698 (w), 669 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $(CF_3{}^a)(CF_3{}^bCF_2{}^c)NCF_2{}^dCF_2{}^eCl$, -26.2 ($CF_3{}^a$), +6.8 ($CF_3{}^b$), +15.7 ($CF_2{}^c$), +12.5 ($CF_2{}^d$), -7.2 ppm ($CF_2{}^e$); $J_{ad}$ = 16.1, $J_{ac}$ = 15.6, $J_{ae}$ = 9.6, $J_{ab}$ = 7.4, $J_{bd}$ = 8.5, $J_{ec}$ = 13.0, $J_{ea}$ = 9.6 Hz. The mass spectrum had peaks at 318 [M - F], 302 [M - Cl], 268 [$C_4ClF_9N$], and 252 [$C_4F_{10}N$]. Found: C, 17.84; F, 67.3%. $C_5ClF_{12}N$ requires C, 17.79; F, 67.6%.

(IX) had b.p. 103.1°C and $n_D^{20}$ 1.3152. IR: 1340 (vs), 1314 (vs), 1271 (m), 1230 (m), 1208 (s), 1187 (s), 1174 (m, sh), 1155 (m), 1122 (s), 1114 (m, sh), 1019 (m), 994 (m), 907 (m), 872 (m), 814 (s), 798 (s), 747 (m), 692 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $CF_3{}^aN(CF_2{}^bCF_2{}^cCl)_2$, -27.0 ($CF_3{}^a$), +11.3 ($CF_2{}^b$), -8.2 ($CF_2{}^c$); $J_{ab}$ = 15.9, $J_{ac}$ = 10.6, $J_{cb}$ = 6.4 Hz. The mass spectrum had peaks at 334 [M - F], 268 [$C_4ClF_9N$], 246 [$C_4Cl_2F_5N$], and 230 [$C_4ClF_7N$]. Found: C, 16.56; F, 59.3%. $C_5Cl_2F_{11}N$ requires C, 16.97; F, 59.1%.

## Fluorination of 2,2',2"-trichlorotriethylamine (I)

(I).HCl (25.0 g, 0.105 mol) was fluorinated in the presence of a conductivity additive, sodium fluoride (5.0 g); 2.9 - 3.2 A dm$^{-2}$, 6.4 - 7.0 V, 7 - 9°C, 128 A h (330 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (11.9 g), $(CF_3)_2NC_2F_5$ (0.3 g), $(C_2F_5)_2NCF_3$ (1.2 g), $(C_2F_5)_3N$ (3.4 g, 8.6%), (VIII) (0.8 g, 2.2%), (VII) (0.8 g, 2.0%), $(CClF_2CF_2)_2NC_2F_5$ (X) (0.8 g, 1.8%), and others (7.8 g). The cell content was carefully examined, but no polyfluorinated amines containing three chlorine atoms were found.

(X) had b.p. 122.6°C and $n_D^{20}$ 1.3184. IR: 1335 (m, sh), 1309 (vs), 1287 (vs), 1262 (s), 1240 (vs), 1198 (s, sh), 1186 (s), 1159 (s), 1120 (s), 1110 (s, sh), 1082 (s), 1000 (m), 957 (m), 859 (m), 838 (m), 808 (s, sh), 794 (s), 750 (m), 686 (w, sh) cm$^{-1}$. $^{19}F$ NMR (neat): $CF_3^aCF_2^bN(CF_2^cCF_2^dCl)_2$, +2.7 ($CF_3^a$), +10.2 ($CF_2^b$), +7.6 ($CF_2^c$), -10.5 ppm ($CF_2^d$). The mass spectrum had peaks at 384 [M - F], 334 [$C_5Cl_2F_{10}N$], 318 [$C_5ClF_{11}N$], and 246 [$C_4Cl_2F_6N$]. Found: C, 17.80; F, 61.6%. $C_6Cl_2F_{13}N$ requires C, 17.84; F, 61.1%.

## Fluorination of 2,2'-dichlorodiethylamine

2,2'-Dichlorodiethylamine.HCl (25.0 g, 0.140 mol) was fluorinated; 3.3 A dm$^{-2}$, 5.9 - 6.2 V, 8 - 10°C, 125 A h (300 min). In this fluorination, the gas-washing bottles contained a 10% aqueous solution of potassium hydroxide. The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (31.2 g), $(C_2F_5)_2NF$ (1.2 g, 3.1%), $(C_2F_5)(CClF_2CF_2)NF$ (XI) (1.8 g, 4.4%), $(CClF_2CF_2)_2NF$ (XII) (0.9 g, 2.1%), and others (3.8 g).

(XI) had b.p. 53.2°C and $n_D^{20} < 1.28$. IR: 1371 (w), 1302 (m), 1250 (vs), 1239 (vs, sh), 1203 (s, sh), 1189 (vs), 1128 (m, sh), 1117 (s), 1094 (s), 1030 (m), 975 (m), 964 (m, sh), 805 (w), 784 (w), 751 (w), 721 (w), 676 (w), 625 (w), 543 (w) cm$^{-1}$. $^{19}F$ NMR (neat): $(CF_3^aCF_2^b)(F^c)NCF_2^dCF_2^eCl$, +6.5 ($CF_3^a$), +32.0 ($CF_2^b$), +15.0 ($F^c$), +30.4 ($CF_2^d$), -6.5 ppm ($CF_2^e$); $J_{ac}$ = 15.9, $J_{ad}$ = 1.6, $J_{ab}$ = 0.9, $J_{ec}$ = 19.5, $J_{eb}$ = 2.7, $J_{ed}$ = 1.8 Hz. The mass spectrum had peaks at 268 [M - F], 252 [M - Cl], 230 [$C_4ClF_7N$], and 202 [$C_3F_8N$]. Found: C, 16.92; F, 65.8%. $C_4ClF_{10}N$ requires C, 16.71; F, 66.1%.

(XII) had b.p. 83.7°C and $n_D^{20}$ 1.3115. IR: 1326 (w), 1291 (w), 1239 (s), 1194 (vs), 1185 (vs, sh), 1125 (m, sh), 1115 (m), 1032 (w), 1002 (m, sh), 991 (m), 967 (w), 942 (w), 811 (w), 791 (w), 769 (w), 722 (w), 655 (w), 630 (w) cm$^{-1}$. $^{19}$F NMR (neat): $F^aN(CF_2^bCF_2^cCl)_2$, +13.5 ($F^a$), +29.0 ($CF_2^b$), -7.6 ppm ($CF_2^c$); $J_{ba}$ = 22.6, $J_{ca}$ = 20.0 Hz. The mass spectrum had peaks at 284 [M - F], 268 [M - Cl], 218 [$C_3ClF_7N$], and 180 [$C_3ClF_5N$]. Found: C, 15.43; F, 56.4%. $C_4Cl_2F_9N$ requires C, 15.81; F, 56.3%.

### Fluorination of 2-chloro-N,N-dimethylpropylamine (II)

(II).HCl (25.0 g, 0.159 mol) was fluorinated; 3.3 A dm$^{-2}$, 6.6 V, 8°C, 136 A h (330 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (31.0 g), $(CF_3)_3N$ (2.2 g), $C_2F_5CClF_2$ + $(CF_3)_2CClF$ (2.3 g), $(CF_3)_2NC_3F_7$ (XIX) (5.6 g, 11.0%), $(CF_3)_2NCF_2CClFCF_3$ (XVI) (3.5 g, 6.4%), $(CF_3)_2NCF_2CF_2CClF_2$ (XIII) (7.8 g, 14.6%), and others (0.8 g).

(XIX) had b.p. 46.6°C and $n_D^{20} < 1.28$. IR: 1362 (s, sh), 1353 (vs), 1332 (s), 1294 (w), 1265 (m), 1236 (vs), 1222 (s, sh), 1213 (s, sh), 1170 (m), 1138 (m), 1040 (w), 998 (s), 896 (w), 864 (s), 746 (m), 735 (m, sh) cm$^{-1}$. $^{19}$F NMR (neat): $(CF_3^a)_2NCF_2^bCF_2^cCF_3^d$, -23.4 ($CF_3^a$), +15.0 ($CF_2^b$), +49.5 ($CF_2^c$), +5.7 ppm ($CF_3^d$); $J_{ab}$ = 15.8, $J_{ac}$ = 8.2, $J_{bd}$ = 10.4 Hz. The mass spectrum had peaks at 302 [M - F], 214 [$C_4F_8N$], 202 [$C_3F_8N$], and 169 [$C_3F_7$]. Found: C, 18.33; F, 76.6%. $C_5F_{13}N$ requires C, 18.70; F, 76.9%.

(XVI), b.p. 72.6°C (lit. value [3]; 74°C), $n_D^{20}$ 1.2828, was identified by a comparison of its IR and NMR spectra with those reported [3]. (XIII) had b.p. 73.6°C, $n_D^{20}$ 1.2820. IR: 1356 (vs), 1336 (vs), 1245 (s, sh), 1226 (vs), 1181 (m), 1154 (w), 1137 (m), 1082 (w), 1069 (m), 996 (s), 962 (w), 844 (m), 799 (m), 765 (m, sh), 759 (m), 733 (m), 710 (w), 642 (w), 548 (w) cm$^{-1}$. $^{19}$F NMR (neat): $(CF_3^a)_2NCF_2^bCF_2^cCF_2^dCl$, -24.0 ($CF_3^a$), +12.7 ($CF_2^b$), +42.8 ($CF_2^c$), -8.1 ppm ($CF_2^d$); $J_{ab}$ = 15.6, $J_{ac}$ = 8.4, $J_{bd}$ = 14.1 Hz. The mass spectrum had peaks at 318 [M - F], 302 [M - Cl], 202 [$C_3F_8N$], and 185 [$C_3ClF_6$]. Found: C, 17.95; F, 67.1%. $C_5ClF_{12}N$ requires C, 17.79; F, 67.6%.

## Fluorination of 3-chloro-N,N-dimethylpropylamine (III)

(III).HCl (25.0 g, 0.159 mol) was fluorinated; 3.3 A $dm^{-2}$, 6.0 - 6.4 V, 8 - 10°C, 136 A h (330 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (26.4 g), $(CF_3)_3N$ (1.0 g), $(CF_3)_2CHF$ (0.6 g), $(CF_3)_2CH_2$ (0.8 g), (XIX) (10.4 g, 20.3%), (XVI) (2.1 g, 4.0%), (XIII) (1.9 g, 3.5%), and others (4.7 g).

## Fluorination of 3-chloro-N,N,2-trimethylpropylamine (IV)

(IV).HCl (25.0 g, 0.146 mol) was fluorinated; 3.6 - 3.7 A $dm^{-2}$, 5.8 - 6.6 V, 11 - 12°C, 155 A h (340 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (22.0 g), $C_3F_8$ (3.1 g), $(CF_3)_3N$ (0.5 g), $CF_3(CF_2)_2CF_3$ + $(CF_3)_3CF$ (4.4 g), $(CF_3)_3CH$ (1.3 g), $(CF_3)_2NCF_2(CF_2)_2CF_3$ (XX) (2.3 g, 4.1%), $(CF_3)_2NCF_2CF(CF_3)_2$ (XXI) (3.0 g, 5.6%), $(CF_3)_2NCF_2CH(CF_3)_2$ (XXII) (0.9 g, 1.8%), $(CF_3)_2NCF_2CF(CF_3)CF_2Cl$ (XVII) + $(CF_3)_2N$-$CF_2CCl(CF_3)_2$ (XVIII) (3.3 g, 5.9%), and others (13.9 g).

(XX) had b.p. 72.4°C and $n_D^{20} < 1.28$. IR: 1355 (vs), 1336 (s), 1307 (m, sh), 1250 (s), 1230 (s), 1202 (m, sh), 1172 (m), 1148 (m), 1100 (w), 1076 (w), 995 (m), 862 (w), 848 (w), 821 (m), 768 (w), 746 (w, sh), 727 (m), 655 (w), 641 (w, sh), 585 (w), 532 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $(CF_3^{a})_2N$-$CF_2^{b}CF_2^{c}CF_2^{d}CF_3^{e}$, -23.4 ($CF_3^{a}$), +13.8 ($CF_2^{b}$), +45.9 ($CF_2^{c}$), +50.5 ($CF_2^{d}$), 5.3 ppm ($CF_3^{e}$); $J_{ab}$ = 15.6, $J_{ac}$ = 8.1, $J_{ec}$ = 10.4, $J_{eb}$ = 2.4, $J_{db}$ = 15.2 Hz. The mass spectrum had peaks at 352 [M - F], 262 [$C_4F_{10}N$], 219 [$C_4F_9$], and 202 [$C_3F_8N$]. Found: C, 19.01; F, 76.1%. $C_6F_{15}N$ requires C, 19.42; F, 76.8%.

(XXI) had b.p. 72.3°C and $n_D^{20} < 1.28$. IR: 1351 (vs), 1342 (vs), 1312 (s), 1301 (m, sh), 1279 (s, sh), 1261 (vs), 1228 (s), 1212 (m, sh), 1204 (m), 1190 (m), 1162 (m), 1144 (m), 1014 (w), 991 (s), 861 (m), 770 (w), 749 (m), 730 (m), 680 (w), 539 (w) $cm^{-1}$. $^{19}F$ NMR (neat): $(CF_3^{a})_2NCF_2^{b}CF^{c}(CF_3^{d})_2$,

-23.0 ($CF_3^a$), +7.9 ($CF_2^b$), +105.9 ($CF^c$), -2.9 ppm ($CF_3^d$); $J_{ac}$, $J_{ab}$ = 14, 17, $J_{ad}$ = 2.3, $J_{bc}$ = 5.9, $J_{db}$ = 11.3, $J_{dc}$ = 6.5, $J_{da}$ = 2.3 Hz. The mass spectrum had peaks at 352 [M - F], 333 [$C_6F_{13}N$], 314 [$C_6F_{12}N$], and 264 [$C_5F_{10}N$]. Found: C, 19.51; F, 76.9%. $C_6F_{15}N$ requires C, 19.42; F, 76.8%.

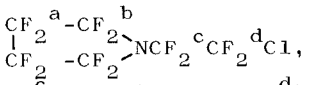
(XXII) had b.p. 76.4°C and $n_D^{20} < 1.28$. IR: 1356 (s), 1344 (vs), 1330 (vs), 1290 (m), 1275 (m), 1253 (s), 1223 (m), 1201 (m, sh), 1184 (w, sh), 1169 (w), 1114 (m), 1086 (w), 990 (m), 919 (w), 866 (w), 845 (w, sh), 834 (w), 766 (w), 737 (w), 723 (w), 675 (w), 539 (w) $cm^{-1}$. $^{19}F$ NMR ($CCl_4$): $(CF_3^a)_2NCF_2^b$-$CH(CF_3^c)_2$, -24.3 ($CF_3^a$), +1.5 ($CF_2^b$), -14.9 ppm ($CF_3^c$); $J_{ab}$ = 12.1, $J_{ac}$ = 1.5, $J_{cb}$ = 10.9, $J_{F^cH}$ = 7.2 Hz. $^1H$ NMR ($CCl_4$; Hitachi R-22 spectrometer, 90 MHz, TMS internal): 3.8 ppm; $J_{HF^b}$ = 12.8, $J_{HF^c}$ = 7.2 Hz. The mass spectrum had peaks at 353 [M], 333 [$C_6F_{13}N$], 314 [$C_6F_{12}N$], and 264 [$C_5F_{10}N$]. Found: C, 20.19; H, 0.31; F, 75.5%. $C_6HF_{14}N$ requires C, 20.41; H, 0.29; F, 75.3%.

(XVII) and (XVIII) were obtained as an approximately 1 : 1 mixture which was analyzed by $^{19}F$ NMR spectroscopy. The mass spectrum of the mixture had peaks at 368 [M - F], 352 [M - Cl], 330 [$C_6ClF_{11}N$], and 314 [$C_6F_{12}N$].

## Fluorination of 1-(2-chloroethyl)pyrrolidine (V)

(V).HCl (25.0 g, 0.144 mol) was fluorinated; 3.3 A $dm^{-2}$, 6.2 V, 5 - 6°C, 128 A h (310 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (2.5 g), $\overline{CF_2(CF_2)_3N}C_2F_5$ [4] (20.0 g, 41.6%), $\overline{CF_2(CF_2)_3N}CF_2CClF_2$ (XIV) (9.6 g, 19.2%), and others (8.0 g).

(XIV) had b.p. 89.1°C and $n_D^{20}$ 1.3002. IR: 1394 (m, sh), 1352 (vs), 1313 (s), 1279 (s), 1244 (vs), 1226 (vs), 1190 (vs), 1179 (vs, sh), 1150 (m, sh), 1129 (s), 1114 (m, sh), 1077 (w), 1038 (m), 980 (vs), 971 (s, sh), 949 (m, sh), 907 (w), 876 (w), 801 (m), 776 (s), 730 (w), 672 (w), 621 (w), 560 (w) $cm^{-1}$. $^{19}F$ NMR (neat):



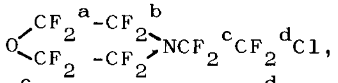
+56.7 ($CF_2^a$), +14.0 ($CF_2^b$), +16.7 ($CF_2^c$), -5.4 ppm ($CF_2^d$); $J_{cb}$ = 12.7, $J_{db}$ = 10.1, $J_{dc}$ = 2.3, $J_{ab} \leq 1$ Hz. The mass spectrum had peaks at 330

[M - F], 314 [M - Cl], 280 [$C_5ClF_9N$], and 264 [$C_5F_{10}N$]. Found: C, 20.17; F, 64.9%. $C_6ClF_{12}N$ requires C, 20.62; F, 65.2%.

## Fluorination of 4-(2-chloroethyl)morpholine

4-(2-Chloroethyl)morpholine.HCl (25.0 g, 0.134 mol) was fluorinated; 3.4 - 3.5 A $dm^{-2}$, 5.6 V, 7 - 9°C, 130 A h (300 min). The following compounds were obtained: $C_1$, $C_2$, and $NF_3$ (4.5 g), $CF_2CF_2OC_2F_4NC_2F_5$ (19.2 g, 41.0%), $CF_2CF_2OC_2F_4NCF_2$-$CClF_2$ (XV) (2.4 g, 4.9%), and others (5.6 g).

(XV) had b.p. 99.4°C and $n_D^{20}$ 1.3033. IR: 1343 (m), 1306 (vs), 1293 (s), 1234 (vs), 1226 (vs), 1196 (vs), 1183 (vs), 1152 (s), 1134 (m, sh), 1117 (m), 1102 (m), 970 (m), 959 (m), 932 (m), 799 (w), 778 (m), 672 (w), 646 (w), 627 (w), 488 (w) $cm^{-1}$. $^{19}F$ NMR (neat):



+10.7 ($CF_2{}^a$), +15.2 ($CF_2{}^b$), +15.5 ($CF_2{}^c$), -4.6 ppm ($CF_2{}^d$). The mass spectrum had peaks at 346 [M - F], 330 [M - Cl], 296 [$C_5ClF_9NO$], and 280 [$C_5F_{10}NO$]. Found: C, 19.42; F, 61.8%. $C_6ClF_{12}NO$ requires C, 19.71; F, 62.4%.

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