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THE ELECTROCHEMICAL FLUORINATION OF N-( $\omega$ -CHLOROALKYL)PIPECOLINES AND N-( $\omega$ -CHLOROALKYL)HEXAMETHYLENIMINES

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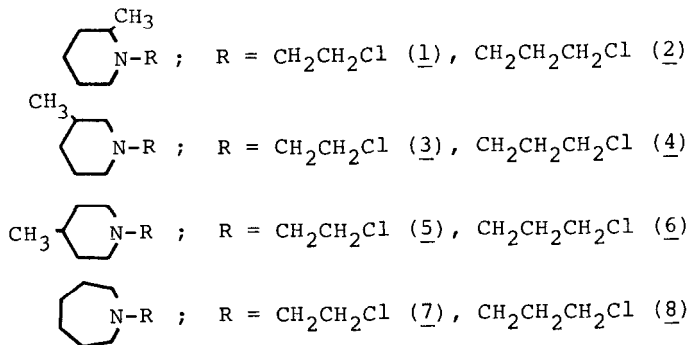
SUMMARY

Electrochemical fluorinations of six kinds of N-( $\omega$ -chloroalkyl)pipecolines [N-(2-chloroethyl)-2-, N-(3-chloropropyl)-2-, N-(2-chloroethyl)-3-, N-(3-chloropropyl)-3-, N-(2-chloroethyl)-4- and N-(3-chloropropyl)-4-pipecolines] and two kinds of N-( $\omega$ -chloroalkyl)-substituted hexamethyleneimines [N-(2-chloroethyl)- and N-(3-chloropropyl)hexamethyleneimines] were conducted. From these starting materials, corresponding chlorine-retained fully fluorinated amines together with ring isomerized products were formed in yields of 7.6~14.8% from the former and 5.4~5.5% from the latter, respectively. New chloropolyfluoroamines obtained in the present investigation have been isolated and characterized by spectroscopic (infrared,  $^{19}\text{F}$  nmr and mass) and elemental analysis.

INTRODUCTION

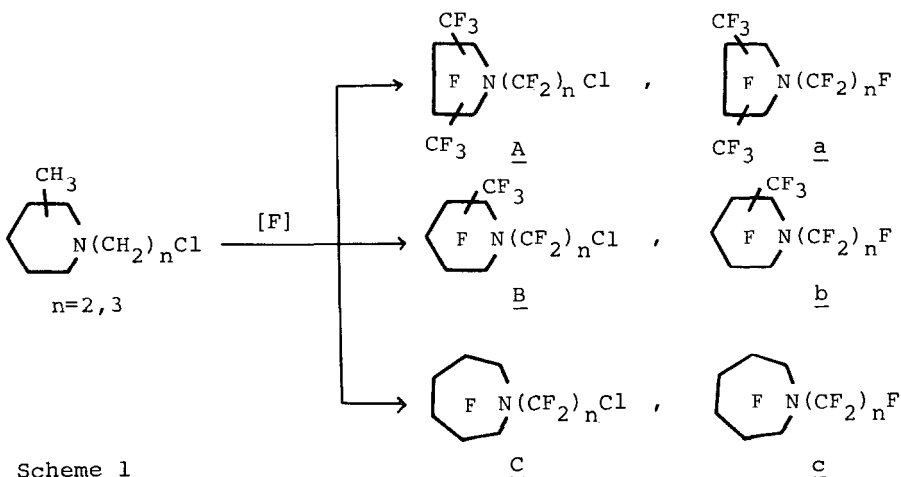
A number of papers have appeared on the fluorination of cyclic amines like N-alkyl piperidines [1,2] and N-alkyl hexamethyleneimines [3,4]. For example, several kind of methyl-substituted pyridines have been fluorinated electrochemically, from which corresponding perfluoro(N-fluoromethylpiperidine)s were obtained in the best yields when the methyl substituent was at the  $\alpha$ -position of the pyridine ring [5]. However no work has yet been reported on the fluorination of N-( $\omega$ -chloroalkyl)-substituted pipecolines and -hexamethyleneimines.

This paper describes the results of the electrochemical fluorination of the following six kinds of N-( $\omega$ -chloroalkyl)-pipercolines and two kind of N-( $\omega$ -chloroalkyl)-hexamethyleneimines, which were conducted as a part of study on the fluorination of chlorine-containing amines [6,7].



#### RESULTS AND DISCUSSION

The results of fluorinations of N-( $\omega$ -chloroalkyl)-substituted pipercolines and -hexamethyleneimines are summarized in Table 1. All the pipercolines (1~6) afforded the corresponding perfluorinated pipercolines (B and b) on fluorination in fair yields together with such isomeric products as perfluoropyrrolidines (A and a) and perfluorohexamethyleneimines (C and c), which were formed as a result of the ring-contraction and ring-expansion, respectively.



Scheme 1

TABLE 1

Summary of the fluorination of N-( $\omega$ -chloroalkyl)piperidines and N-( $\omega$ -chloroalkyl)hexamethyl-eneimines

Sample	Sample fed (mol)	Electricity passed (Ahr)	Products obtained (g)	Perfluoroamines (yield %)
<u>1</u>	0.129	159	30.2	<u>A*</u> (1.9), <u>1B</u> (10.7), <u>7C</u> (trace), <u>a*</u> (3.2), <u>1b</u> (18.0), <u>7c</u> (0.7)
<u>2</u>	0.129	160	40.8	<u>A*</u> (2.0), <u>2B</u> (7.6), <u>8C</u> (trace) <u>a*</u> (6.3), <u>2b</u> (22.6), <u>8c</u> (2.2)
<u>3</u>	0.123	167	54.2	<u>A*</u> (1.6), <u>3B</u> (10.0), <u>7C</u> (6.0), <u>a*</u> (2.8), <u>3b</u> (33.4), <u>7c</u> (12.3)
<u>4</u>	0.114	158	50.4	<u>A*</u> (1.1), <u>4B</u> (10.0), <u>8C</u> (7.5), <u>a*</u> (3.9), <u>4b</u> (22.8), <u>8c</u> (9.5)
<u>5</u>	0.131	166	45.4	<u>5A</u> (1.5), <u>5B</u> (11.7), <u>7C</u> (5.3), <u>5a</u> (3.0), <u>5b</u> (25.5), <u>7c</u> (13.3)
<u>6</u>	0.127	183	55.8	<u>6A</u> (1.2), <u>6B</u> (14.8), <u>8C</u> (6.4), <u>6a</u> (3.5), <u>6b</u> (25.6), <u>8c</u> (12.2)
<u>7</u>	0.123	152	44.7	<u>B†</u> (5.1), <u>7C</u> (5.5), <u>b†</u> (27.8), <u>7c</u> (21.6)
<u>8</u>	0.114	170	45.3	<u>B†</u> (5.0), <u>8C</u> (5.4), <u>b†</u> (24.2), <u>8c</u> (21.4)

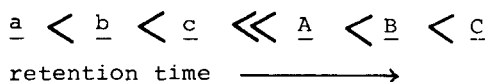
\* A mixture of perfluoropyrrolidines having a formula shown in Scheme 1.

† A mixture of perfluoropipercolines having a formula shown in Scheme 1.

However, the perfluoro(4-pipecoline)s (B and b) obtained from 4-pipecolines (5 and 6) were found to be contaminated with small quantities (less than 5%) of isomeric perfluoro(3-pipecoline)s (Yields=12~15% for B and ca.26% for b, respectively), though fluorinations of 2- and 3-pipecolines (1~4) afforded pure corresponding perfluorinated 2- and 3-pipecolines in yields of 7~10% for B and 18~33% for b, respectively.

With respect to the ring-isomerized by-products, an analogous product distribution and variation were observed in our former experiments dealing with the fluorination of 2-alkyloxanes from which isomeric perfluorooxolanes and an oxepane (only from 2-methyloxane) were formed as major products along with corresponding perfluoro(2-alkyloxane)s [8].

The structures of the products in Scheme 1 were assigned from different GLC retention times of A, B and C relative to a, b, and c isomers and then from spectral data and elemental analysis. It was found that the order of their GLC elution times was dependent firstly on whether the chlorine was retained or not in the perfluorinated molecule, and then on the ring size, a longer retention time being shown with an increase of the ring size characteristically, viz



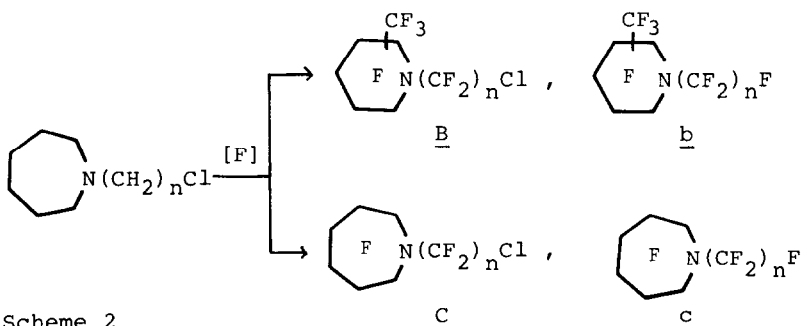
However, for the detailed positional determination of the alkyl substituents, for example, the CF<sub>3</sub> group on the piperidine ring, <sup>19</sup>F nmr spectroscopy was used.

Owing to the separation difficulties, only the ring-contraction products (A and a) from 5 and 6 were isolated in a pure form, which were found to be perfluoro(N-alkyl-3-ethylpyrrolidine)s (5A, 5a, 6A and 6a). Other perfluoropyrrolidines formed were a complex mixture of several kinds of isomers on the basis of <sup>19</sup>F nmr analysis.

A trend was observed that product yields of perfluoro-(2-pipecoline)s (B and b) and also of perfluorohexamethyleneimines (C and c) were low in the case of 2-pipecolines (1 and 2), compared with those from 3- and 4-pipecolines (3~6).

It has been reported that in the fluorination of pyridines, 2-fluoro- and/or 2-methyl-substituents on the pyridine ring reduce the cleavage of the C-N bond, resulting in the formation of an increased amount of the corresponding perfluoro(N-fluoropiperidine)s compared with pyridine itself [5]. Hence, it was considered that such substituents on the 2-position protected sterically the C-N bond. However, in the case of N-alkyl-substituted 2-pipecolines, contrary to the reason stated above for the 2-substituted pyridines, the scission of the C-N bond of the piperidine ring seems to occur more extensively due to steric interaction between the two alkyl groups (CH<sub>3</sub>- and N-alkyl groups).

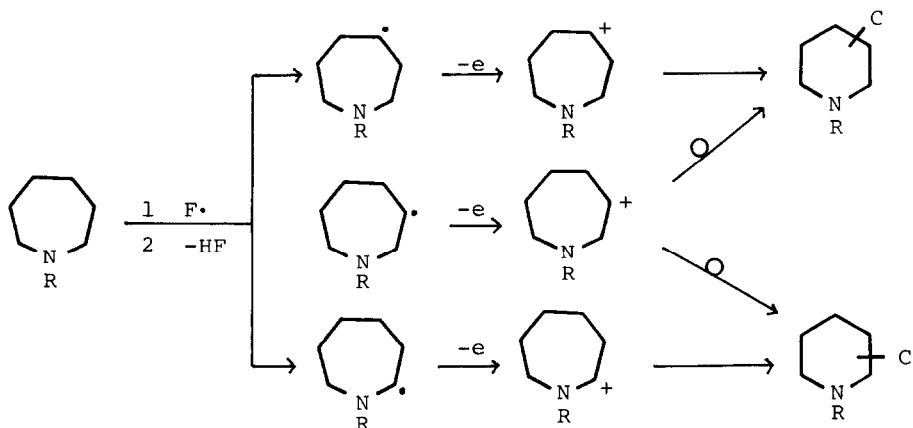
The fluorinations of 7 and 8 also afforded the desired chlorine-retaining perfluorohexamethyleneimines (7c and 8c) together with perfluorohexamethyleneimines (7c and 8c) and perfluoropiperidines (B and b) with just trace amounts of isomeric perfluoropyrrolidines being formed.



Perfluoropipecolines (B and b) produced from 7 and 8 were found to be a mixture consisting of three positional isomers by <sup>19</sup>F nmr spectroscopy. Their proportions were in a ratio of 2-CF<sub>3</sub>- : 3-CF<sub>3</sub>- : 4-CF<sub>3</sub>- = 0.14~0.18 : 0.53~0.58 : 0.26~0.33 as determined by integrating the three -CF absorption peaks which showed different chemical shifts from each other. Thus, in the <sup>19</sup>F nmr spectra of B and b, peaks assigned to -CF in the ring shifted characteristically to higher field from  $\phi$ -151~152 ppm at the 2-position to  $\phi$ -181~182 ppm at the 3-position and to  $\phi$ -189~190 ppm at the 4-position as the number of bonds separating the nitrogen and carbon increased. These data can be compared favor-

ably with the reported values for perfluoro (N-butyl-3-pipecoline) and perfluoro(N-butyl-4-pipecoline) [4]. The comparability of the proportions of the three isomers in both B and b irrespective of the starting materials used should be noted.

The lack of perfluoropyrrolidines in the products from 7 and 8 suggests that the ring contraction ceased at the stage of six-membered from seven-membered ring, at which stage the basicity of the molecule had been decreased considerably by the fluorine substitution. Such ring-isomerization during electrolysis can be explained via a carbonium ion intermediate which may be formed by an anodic oxidation of radicals formed on the ring, viz



Scheme 3

The mass spectra of perfluorohexamethyleneimine derivatives (C) contained parent ion peaks at relative intensities of 2~5%, while those of perfluoropipecolines (B) did not show the parent one but  $[M-CF_3]^+$  ions together with such ions as  $[M-F]^+$  and  $[M-Cl]^+$  ions characteristically.

The properties of chlorine-retaining perfluoropipecolines (B) and -perfluorohexamethyleneimines (C) are summarized in Table 2.

TABLE 2

Properties of chlorine-containing perfluoropipercolines (B) and perfluorohexamethyleneimines (C)

Compd	Source	BP (°C)*	$n_D^{20}$	Elemental C (%)	Analysis N (%)
<u>1B</u>	<u>1</u>	123.0 ~ 124.0	1.3122	21.13 (21.37) <sup>†</sup>	3.35 (3.12)
<u>2B</u>	<u>2</u>	145.0 ~ 146.0	1.3155	21.50 (21.64)	2.69 (2.80)
<u>3B</u>	<u>3</u>	123.5 ~ 125.0	1.3099	21.27 (21.37)	3.31 (3.12)
<u>4B</u>	<u>4</u>	145.5 ~ 146.5	1.3122	21.55 (21.64)	2.81 (2.80)
<u>5B</u>	<u>5</u>	123.5 ~ 124.5	1.3093	21.30 (21.37)	3.34 (3.12)
<u>6B</u>	<u>6</u>	143.5 ~ 145.0	1.3117	21.56 (21.64)	3.10 (2.80)
<u>7C</u>	<u>3,5,7</u>	124.0 ~ 125.5	1.3156	21.17 (21.37)	3.05 (3.12)
<u>8C</u>	<u>4,6,8</u>	150.5 ~ 151.5	1.3178	21.62 (21.64)	2.80 (2.80)

\* Boiling points are not corrected.

† Calculated values in parentheses.

## EXPERIMENTAL

### Reagents

All amines were fluorinated in the form of the hydrochloride salts recrystallized from ethyl acetate. Except for N-(2-chloroethyl)hexamethyleneimine (7), other amines were prepared by the chlorination of corresponding hydroxyamines with thionyl chloride (Wako Junyaku Co.). Hydroxyamines were prepared by the reaction of ethylenechlorohydrin (Wako Junyaku Co.) or trimethylenechlorohydrin (Tokyo Kasei Co.) and the corresponding amines (Wako Junyaku Co.). N-(2-chloroethyl)hexamethyleneimine·HCl salt (7) was purchased from Aldrich Chemical Co. Anhydrous hydrogen fluoride (Daikin Industries Co.) was more than 99.9% pure.

### Apparatus

Fluorination was carried out in a similar way to that reported previously [7]. The electrolytic cell having a capacity of 500 ml was used. Its effective anodic surface area was 7.5 dm<sup>2</sup>.

A gas chromatographic analysis (compositions were calculated on the basis of chromatographic peak areas, assuming equal weight sensitivities for all components) was carried out with a Shimadzu GC-2C gas chromatograph using a stainless steel column (3 mm dia) packed with 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (60/80 mesh) (6.4 m).

For semi-preparative work, fluorination products were roughly separated into a few portions with a Shimadzu GC-6C using a copper column (10 mm dia) packed with a 30% Silicone DC QF-1 on Chromosorb PAW (4.0 m), and then further purified with a Shimadzu GC-1C using a stainless steel column (10 mm dia) packed with 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (4.0 m) (for products obtained from 1, 3, 5 and 7) or a Varian model 920 using an aluminum column (10 mm dia) packed with 30% Silicone KF-96 on Chromosorb PAW (5.0 m) (for products obtained from 2, 4, 6 and 8).

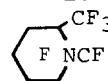
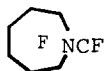
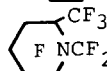
Infrared spectra were measured on a Hitachi EPI-G3 spectrometer, using a 6-cm gas cell with KBr windows. <sup>19</sup>F nmr spectra were measured on a Hitachi R-20 high resolution spectrometer operating at 56.46 MHz using CCl<sub>3</sub>F as an internal standard. Mass spectra were measured on a Shimadzu GC-MS 7000 instrument at 20 eV.

### Fluorination of N-(2-chloroethyl)-2-pipecoline (1)

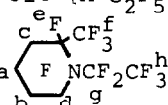
N-(2-chloroethyl)-2-pipecoline (1) hydrochloride salt (25.0 g) was dissolved in electrically purified hydrogen fluoride (500 ml), and the resulting solution was electrolyzed over a period of 309 min (159 Ahr) with an anodic current density of 4.0 A/dm<sup>2</sup>, a cell voltage of 6.2~8.1 V and a cell temperature of 8~12 °C. Helium (50 ml/min) was introduced through the bubbler from 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 20% aqueous solution of potassium sulfite containing a small amount of potassium iodide, and then led into a series of cold traps immersed in ice and dry ice-acetone baths, respectively. The products sunk at the bottom of the cell were also obtained as cell drainings after the completion of electrolysis. These products were subjected to gas chromatographic analysis. Thus, the following compounds were found:  $n\text{-C}_4\text{F}_{10}$  (2.7 g),  $n\text{-C}_5\text{F}_{10}$

(2.8 g),  $n\text{-C}_6\text{F}_{14}$  (3.4 g), a (1.8 g),  (1b) (10.0 g),  (7c) (0.4 g), A (1.1 g),  (1B) (6.2 g) and unidentified compounds (1.8 g).

1b (nc); bp 103.5~104.5 °C,  $n_D^{20}$  1.2880. IR (gas): 1363 (m,sh), 1350 (m,sh), 1340 (m), 1325 (m), 1297 (vs), 1270 (vs), 1247 (vs), 1225 (s), 1204 (s), 1170 (m), 1157 (s), 1128 (m), 1117 (m,sh), 1097 (s), 1064 (s), 1040 (m), 995 (s), 914 (s), 873 (w), 849 (w), 824 (m), 748 (m), 738 (s), 719 (w), 697 (w), 667 (w), 654 (w), 623 (w), 538 (w). Mass: 414  $[\text{M-CF}_3]^+$  (27.1), 314  $[\text{M-C}_2\text{F}_5]^+$  (5.6), 119  $\text{C}_2\text{F}_5^+$  (82.2), 69  $\text{CF}_3^+$  (100).  $^{19}\text{F}$  nmr (neat):

	-72.7 ( $\text{CF}_3^f$ ), -85.1 ( $\text{CF}_3^h$ ), -82.0~-90.5 ( $\text{CF}_2^d$ and $\text{CF}_2^g$ ), -116.0~-141.5 ( $\text{CF}_2^a$ , $\text{CF}_2^b$ and $\text{CF}_2^c$ ), -151.4 ( $\text{CF}^e$ ).
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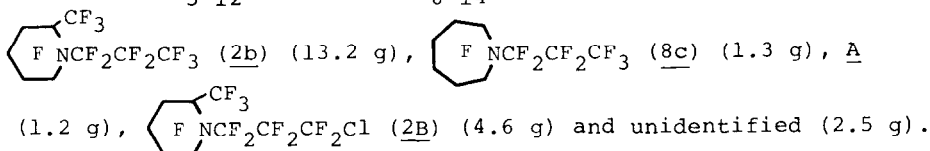
Found: C, 21.93%, N, 3.46%. Calculated for  $\text{C}_8\text{F}_{17}\text{N}$ : C, 22.19%, N, 3.24%.

1B (nc): IR (gas): 1359 (m), 1342 (m), 1322 (m), 1295 (vs), 1270 (vs), 1248 (vs), 1200 (s), 1185 (m,sh), 1170 (s), 1156 (s), 1124 (m), 1094 (m), 1077 (w), 1042 (m), 999 (s), 972 (m), 948 (m), 915 (s), 880 (w), 849 (w), 797 (m), 771 (m), 748 (m), 721 (w), 698 (w), 678 (w), 649 (w), 637 (w), 628 (w), 550 (w). Mass: 430  $[\text{M-F}]^+$  (6.6), 414  $[\text{M-Cl}]^+$  (2.9), 380  $[\text{M-CF}_3]^+$  (11.7), 364  $[\text{M-CF}_2\text{Cl}]^+$  (8.7), 314  $[\text{M-C}_2\text{F}_4\text{Cl}]^+$  (11.5), 119  $\text{C}_2\text{F}_5^+$  (65.7), 69  $\text{CF}_3^+$  (100).  $^{19}\text{F}$  nmr (neat): -70.3 ( $\text{CF}_2^h$ ), -72.2 ( $\text{CF}_3^f$ ), -81.0 (-87.5 ( $\text{CF}_2^d$  and  $\text{CF}_2^g$ ), -115.0~-142.0 ( $\text{CF}_2^a$ ,  $\text{CF}_2^b$  and  $\text{CF}_2^c$ ), -151.6 ( $\text{CF}^e$ ).

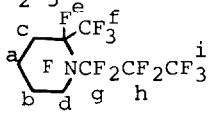
The properties of 1B and the results of elemental analysis are shown in Table 2.

Fluorination of N-(2-chloropropyl)-2-pipecoline (2)

The sample (2)·HCl (25.5 g) was fluorinated similarly under the following conditions: 4.0 A/dm<sup>2</sup>, 6.1~7.5 V, 8~13 °C, 168 Ahr (330 min), and the following compounds were obtained: n-C<sub>4</sub>F<sub>10</sub> (2.5 g), n-C<sub>5</sub>F<sub>12</sub> (3.5 g), n-C<sub>6</sub>F<sub>14</sub> (4.8 g), a (3.7 g), 1b (3.5 g),

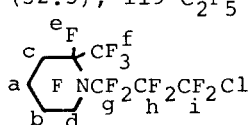


2b (nc): bp 123.0~124.0 °C, n<sub>D</sub><sup>20</sup> 1.3122. IR (gas): 1348 (s), 1336 (s), 1320 (m), 1292 (vs), 1267 (vs), 1246 (s), 1227 (s), 1198 (s), 1181 (m,sh), 1166 (m), 1149 (m), 1141 (m), 1091 (m), 1041 (s), 996 (s), 980 (m,sh), 962 (m), 911 (s), 886 (w,sh), 867 (w), 846 (w), 791 (m), 744 (m), 732 (s), 714 (w), 694 (w), 664 (w), 649 (w), 627 (w), 622 (w), 539 (w). Mass: 469 [M-F]<sup>+</sup> (8.1), 414 [M-CF<sub>3</sub>]<sup>+</sup> (19.3), 364 [M-C<sub>3</sub>F<sub>7</sub>]<sup>+</sup> (27.1), 169 C<sub>3</sub>F<sub>7</sub><sup>+</sup> (56.8), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (65.5), 69 CF<sub>3</sub><sup>+</sup> (100).


<sup>19</sup>F nmr (neat): -71.9 (CF<sub>3</sub><sup>f</sup>), -80.9 (CF<sub>3</sub><sup>i</sup>), -81.5~ -89.5 (CF<sub>2</sub><sup>d</sup> and CF<sub>2</sub><sup>g</sup>), -114.0~-141.5 (CF<sub>2</sub><sup>a</sup>, CF<sub>2</sub><sup>b</sup>, CF<sub>2</sub><sup>c</sup> and CF<sub>2</sub><sup>h</sup>), -150.9 (CF<sup>e</sup>).

Found: C, 22.20%, N, 3.42%. Calculated for C<sub>9</sub>F<sub>19</sub>N: C, 22.38%, N, 3.10%.




2B (nc): IR (gas): 1358 (m), 1343 (m), 1322 (m), 1292 (s), 1269 (s), 1251 (vs), 1199 (s), 1164 (m,sh), 1156 (m), 1144 (m,sh), 1127 (m), 1109 (m), 1092 (m), 1041 (m), 1023 (w), 997 (m), 969 (m), 937 (w), 912 (m), 883 (w), 868 (w), 846 (w), 782 (w), 769 (w,sh), 746 (m), 734 (w,sh), 719 (m), 689 (w), 666 (w), 644 (w), 542 (w). Mass: 480 [M-F]<sup>+</sup> (9.3), 414 [M-Cl]<sup>+</sup> (2.7), 430 [M-CF<sub>3</sub>]<sup>+</sup> (9.3), 414 [M-CF<sub>2</sub>Cl]<sup>+</sup> (5.7), 364 [M-C<sub>3</sub>F<sub>6</sub>Cl]<sup>+</sup> (15.6), 185 C<sub>3</sub>F<sub>6</sub>Cl<sup>+</sup> (32.5), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (57.5), 69 CF<sub>3</sub><sup>+</sup> (100).


<sup>19</sup>F nmr (neat): -68.1 (CF<sub>2</sub><sup>i</sup>), -72.0 (CF<sub>3</sub><sup>f</sup>), -82.5~-86.5 (CF<sub>2</sub><sup>d</sup> and CF<sub>2</sub><sup>g</sup>), -119.0~-143.5 (CF<sub>2</sub><sup>a</sup>, CF<sub>2</sub><sup>b</sup>, CF<sub>2</sub><sup>c</sup> and CF<sub>2</sub><sup>h</sup>), -151.3 (CF<sup>e</sup>).

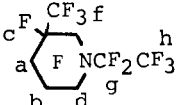
The properties of 2B and the results of elemental analysis are shown in Table 2.

Fluorination of N-(2-chloroethyl)-3-pipecoline (3)

The sample (3)·HCl (25.5 g) was fluorinated; 4.0 A/dm<sup>2</sup>, 6.2~7.5 V, 7~12 °C, 160 Ahr (311 min). The following compounds were obtained: n-C<sub>4</sub>F<sub>10</sub> (1.7 g), n-C<sub>5</sub>F<sub>12</sub> (3.1 g), iso-C<sub>6</sub>F<sub>12</sub>

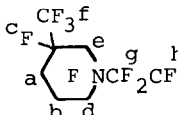
(4.0 g), a (1.6 g),  (18.6 g), 7c (6.8 g), A (1.0 g)  (12.4 g),  (3.5 g) and unidentified (1.5 g).

3b (nc): bp 103.5~104.5 °C, n<sub>D</sub><sup>20</sup> 1.2860. IR (gas): 1365 (m), 1344 (s), 1324 (vs), 1268 (vs), 1247 (vs), 1232 (s), 1220 (s), 1195 (s), 1175 (s), 1167 (m,sh), 1150 (s), 1128 (m), 1119 (m,sh), 1077 (s), 1023 (m), 1018 (m), 962 (w), 900 (s), 877 (w), 845 (w), 822 (w), 806 (w), 749 (m), 737 (w,sh), 710 (w), 698 (s), 675 (w), 642 (w), 604 (w), 569 (w), 584 (w), 495 (w). Mass: 414 [M-F]<sup>+</sup> (11.5), 364 [M-CF<sub>3</sub>]<sup>+</sup> (25.5), 314 [M-C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (9.4), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (66.7), 69 CF<sub>3</sub><sup>+</sup> (100).

 <sup>19</sup>F nmr (neat): -79.9 (CF<sub>3</sub><sup>f</sup>), -86.3 (CF<sub>3</sub><sup>h</sup>), -82.0 (-89.5 (CF<sub>2</sub><sup>d</sup>, CF<sub>2</sub><sup>e</sup> and CF<sub>2</sub><sup>g</sup>), -124.0~-143.0 (CF<sub>2</sub><sup>a</sup> and CF<sub>2</sub><sup>b</sup>), -181.8 (CF<sup>c</sup>).

Found: C, 22.25%, N, 3.17%. Calculated for C<sub>8</sub>F<sub>17</sub>N: C, 22.19%, N, 3.24%.




3B (nc): IR (gas): 1366 (m,sh), 1343 (s), 1326 (vs), 1293 (m), 1277 (s), 1246 (s), 1234 (s), 1224 (s), 1211 (s), 1192 (s), 1179 (s), 1147 (s), 1128 (m), 1118 (m), 1107 (m), 1073 (w), 1062 (w,sh), 1026 (s), 963 (m), 954 (m), 887 (m), 862 (w), 845 (w), 802 (w), 781 (w), 769 (m), 747 (w), 716 (w), 697 (m), 674 (m), 652 (w), 636 (w), 599 (w), 560 (w), 534 (w), 491 (w). Mass: 430 [M-F]<sup>+</sup> (6.9), 414 [M-Cl]<sup>+</sup> (3.1), 380 [M-CF<sub>3</sub>]<sup>+</sup> (13.5), 364 [M-CF<sub>2</sub>Cl]<sup>+</sup> (5.6), 314 [M-C<sub>2</sub>F<sub>4</sub>Cl]<sup>+</sup> (8.7), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (55.5), 69 CF<sub>3</sub><sup>+</sup> (100).

 <sup>19</sup>F nmr: -70.4 (CF<sub>2</sub><sup>h</sup>), -79.2 (CF<sub>3</sub><sup>f</sup>), -82.0~-88.5 (CF<sub>2</sub><sup>d</sup>, CF<sub>2</sub><sup>e</sup> and CF<sub>2</sub><sup>g</sup>), -123.0~-143.0 (CF<sub>2</sub><sup>a</sup> and CF<sub>2</sub><sup>b</sup>), -182.0 (CF<sup>c</sup>).

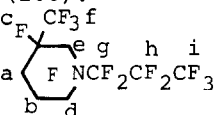
The properties of 3B and the results of elemental analysis are shown in Table 2.

Fluorination of N-(3-chloropropyl)-3-pipecoline (4)

The sample (4)·HCl (24.1 g) was fluorinated; 4.0A/dm<sup>2</sup>, 5.8 ~7.5 V, 8~13 °C, 157 Ahr (303 min). The following compounds were obtained: n-C<sub>4</sub>F<sub>10</sub> (1.5 g), n-C<sub>5</sub>F<sub>12</sub> (3.4 g), iso-C<sub>6</sub>F<sub>14</sub> (7.1 g),

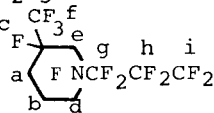
3b (4.1 g), 7c (1.2 g),  (4b) (12.5 g), 8c (5.2 g), A (2.2 g),  (4B) (6.2 g),  (8C) (4.3 g) and unidentified.

4b (nc): bp 121.0~122.5 °C, n<sub>D</sub><sup>20</sup> 1.2922. IR (gas): 1361 (m,sh), 1344 (s), 1325 (vs), 1300 (s), 1267 (vs), 1240 (vs), 1214 (s), 1192 (s), 1175 (s), 1147 (s), 1126 (m), 1093 (w,sh), 1029 (s), 996 (w), 981 (w), 967 (m), 912 (w), 890 (s), 846 (w), 783 (w), 770 (w), 746 (m), 715 (w), 697 (s), 684 (w), 643 (m), 600 (w), 559 (w), 492 (w). Mass: 469 [M-F]<sup>+</sup>(11.3), 414 [M-CF<sub>3</sub>]<sup>+</sup>(20.5), 364 [M-C<sub>3</sub>F<sub>7</sub>]<sup>+</sup>(25.1), 169 C<sub>3</sub>F<sub>7</sub><sup>+</sup>(49.2), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup>(53.8), 69 CF<sub>3</sub><sup>+</sup>(100).

 <sup>19</sup>F nmr (neat): -79.8 (CF<sub>3</sub><sup>f</sup>), -81.7 (CF<sub>3</sub><sup>i</sup>), -82.7~-88.0 (CF<sub>2</sub><sup>d</sup>, CF<sub>2</sub><sup>e</sup> and CF<sub>2</sub><sup>g</sup>), -124.0~-143.5 (CF<sub>2</sub><sup>a</sup>, CF<sub>2</sub><sup>b</sup> and CF<sub>2</sub><sup>h</sup>), -181.6 (CF<sup>c</sup>).

Found: C, 22.26%, N, 2.94%. Calculated for C<sub>9</sub>F<sub>19</sub>N: C, 22.38%, N, 2.90%.

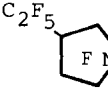
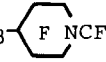
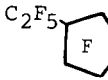
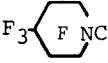
4B (nc): IR (gas): 1354 (s), 1342 (s,sh), 1321 (vs), 1296 (s,sh), 1264 (s), 1253 (s), 1234 (vs), 1212 (s), 1186 (m), 1172 (s), 1160 (s), 1141 (s), 1114 (m), 1043 (w), 1015 (m), 1013 (m,sh), 970 (m), 958 (m,sh), 942 (m), 881 (m), 875 (m,sh), 854 (w), 774 (w), 742 (w), 734 (w,sh), 688 (s), 674 (w), 641 (w), 546 (w). Mass: 480 [M-F]<sup>+</sup>(8.7), 464 [M-Cl]<sup>+</sup>(2.2), 430 [M-CF<sub>3</sub>]<sup>+</sup>(12.1), 414 [M-CF<sub>2</sub>Cl]<sup>+</sup>(4.0), 364 [M-C<sub>3</sub>F<sub>6</sub>Cl]<sup>+</sup>(21.7), 185 C<sub>3</sub>F<sub>6</sub>Cl<sup>+</sup>(27.8), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup>(68.5), 69 CF<sub>3</sub><sup>+</sup>(100).

 <sup>19</sup>F nmr (neat): -69.8 (CF<sub>2</sub><sup>i</sup>), -79.6 (CF<sub>3</sub><sup>f</sup>), -81.0~-89.0 (CF<sub>2</sub><sup>d</sup>, CF<sub>2</sub><sup>e</sup> and CF<sub>2</sub><sup>g</sup>), -123.0~-144.5 (CF<sub>2</sub><sup>a</sup>, CF<sub>2</sub><sup>b</sup> and CF<sub>2</sub><sup>h</sup>), -182.0 (CF<sup>c</sup>).

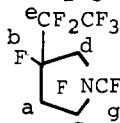
The properties of 4B and the results of elemental analysis are shown in Table 2.

Fluorination of N-(2-chloroethyl)-4-pipecoline (5)

The sample (5)·HCl (26.0 g) was fluorinated; 4.0 A/dm<sup>2</sup>, 6.1~7.8 V, 6~13 °C, 167 Ahr (312 min). The following compounds were obtained; n-C<sub>4</sub>F<sub>10</sub> (1.2 g), iso-C<sub>5</sub>F<sub>12</sub> (2.7 g), sec-C<sub>6</sub>F<sub>14</sub>

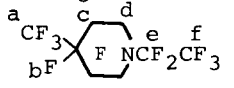
(4.5 g),  (5a) (1.7 g),  (5b) (14.6 g), (7c) (7.6 g),  (5A) (0.9 g),  (5B) (6.9 g), 7c (3.1 g) and unidentified (2.2 g).

5a (nc): bp 107.5~108.0 °C, n<sub>D</sub><sup>20</sup> 1.2860. IR (gas): 1384 (m), 1348 (s), 1287~1304 (vs), 1236~1249 (vs), 1194 (s), 1184 (s,sh), 1174 (s,sh), 1107 (m), 1082 (s), 1046 (m), 989 (w,sh), 966 (m), 886 (m), 797 (m), 745 (m), 717 (s), 614 (w,sh), 604 (w), 532 (w). Mass: 414 [M-F]<sup>+</sup> (14.7), 364 [M-CF<sub>3</sub>]<sup>+</sup> (2.7), 314 [M-C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (39.8), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (100), 69 CF<sub>3</sub><sup>+</sup> (67.5).

 <sup>19</sup>F nmr (neat): -81.7 (CF<sub>3</sub><sup>f</sup>), -85.2 (CF<sub>3</sub><sup>h</sup>), -72.8 ~ -111.4 (CF<sub>2</sub><sup>c</sup>, CF<sub>2</sub><sup>d</sup> and CF<sub>2</sub><sup>g</sup>), -120.7 (CF<sub>2</sub><sup>e</sup>), -123.4 ~ -130.2 (CF<sub>2</sub><sup>a</sup>), -181.4 (CF<sup>b</sup>).

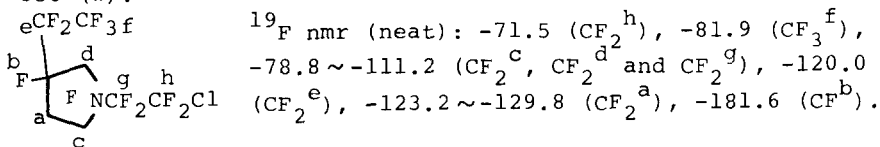
Found: C, 22.10%, N, 3.46%. Calculated for C<sub>8</sub>F<sub>17</sub>N: C, 22.19%, N, 3.29%.

5b (nc): bp 103.5~104.5 °C, n<sub>D</sub><sup>20</sup> 1.2899. IR (gas): 1377 (m,sh), 1365 (m), 1343 (s,sh), 1325 (vs), 1306 (s), 1285 (s), 1258 (s), 1246 (vs), 1232 (s,sh), 1209 (s), 1195 (s), 1183 (s,sh), 1150 (s), 1118 (m), 1070 (s), 1021 (w), 1008 (w), 965 (s), 901 (s), 881 (s), 845 (w), 822 (s), 806 (w), 740 (s), 718 (w,sh), 708 (w), 697 (m), 672 (w,sh), 646 (m), 632 (w), 602 (w), 568 (w), 548 (w,sh), 531 (w), 478 (w). Mass: 414 [M-F]<sup>+</sup> (13.5), 364 [M-CF<sub>3</sub>]<sup>+</sup> (21.6), 314 [M-C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (8.7), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup> (75.2), 69 CF<sub>3</sub><sup>+</sup> (100).

 <sup>19</sup>F nmr (neat): -80.2 (CF<sub>3</sub><sup>a</sup>), -86.8 (CF<sub>3</sub><sup>f</sup>), -81.0 ~ -89.0 (CF<sub>2</sub><sup>d</sup>), -95.2 (CF<sub>2</sub><sup>e</sup>), -121.0 ~ -134.0 (CF<sub>2</sub><sup>c</sup>), -189.9 (CF<sup>b</sup>).

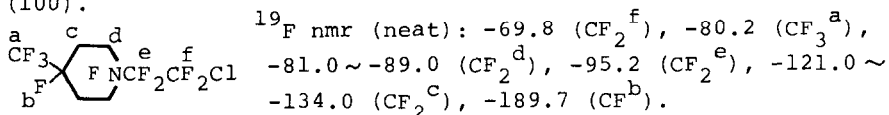
Found: C, 22.32%, N, 3.47%. Calculated for C<sub>8</sub>F<sub>17</sub>N: C, 22.19%, N, 3.24%.

5A (nc): bp 125.0 ~ 125.5 °C,  $n_D^{20}$  1.3110. IR (gas): 1384 (m), 1331 (s), 1304 (s), 1280 (s,sh), 1247 (vs), 1196 (s), 1109 (m), 1081 (s,sh), 1056 (w), 1009 (w), 972 (m), 881 (w), 861 (w), 838 (m), 771 (w), 731 (s), 686 (w), 656 (w,sh), 617 (w), 598 (w), 536 (w).



Found: C, 21.20%, N, 3.05%. Calculated for  $\text{C}_8\text{F}_{16}\text{ClN}$ : C, 21.37%, N, 3.12%.

5B (nc): IR (gas): 1375 (w,sh), 1361 (m), 1340 (m,sh), 1325 (vs), 1306 (s), 1284 (s), 1256 (s), 1247 (s), 1225 (s), 1195 (vs), 1160 (m,sh), 1145 (m,sh), 1115 (m), 1094 (m), 1068 (m), 1025 (w), 973 (s), 931 (w), 912 (w,sh), 889 (w,sh), 878 (m), 858 (w,sh), 845 (w,sh), 818 (w), 794 (w), 771 (s), 737 (m), 720 (w,sh), 709 (w), 673 (w), 652 (w), 633 (w), 601 (w), 555 (w).  
Mass: 430  $[\text{M-F}]^+$  (7.5), 414  $[\text{M-Cl}]^+$  (3.2), 380  $[\text{M-CF}_3]^+$  (10.9), 364  $[\text{M-CF}_2\text{Cl}]^+$  (9.5), 314  $[\text{M-C}_2\text{F}_4\text{Cl}]^+$  (15.2), 119  $\text{C}_2\text{F}_5^+$  (72.8), 69  $\text{CF}_3^+$  (100).



The properties of 5B and the results of elemental analysis are shown in Table 2.

#### Fluorination of N-(3-chloropropyl)-4-pipecoline (6)

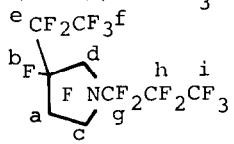
The sample 6·HCl (27.0 g) was fluorinated; 4.0 A/dm<sup>2</sup>, 5.6 ~ 8.3 V, 6 ~ 13 °C, 184 Ahr (357 min). The following compounds were obtained: n-C<sub>4</sub>F<sub>10</sub> (1.4 g), iso-C<sub>5</sub>F<sub>12</sub> (2.8 g), sec-C<sub>6</sub>F<sub>14</sub>

(4.2 g), 5b (4.7 g), 7b (1.5 g), (2.1 g),

(12.6 g), 8c (7.5 g), (4.1 g) and

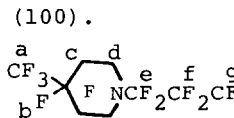
6A (0.8 g), (9.4 g), 8C (4.1 g) and unidentified.

6a (nc): bp 126.5~127.0 °C,  $n_D^{20}$  1.2915. IR (gas): 1385 (w), 1348 (m), 1325 (s), 1305 (s), 1286 (s,sh), 1242 (vs), 1194 (s), 1181 (s,sh), 1134 (m), 1107 (w), 1080 (w,sh), 1043 (w), 987 (m), 966 (w), 878 (w), 841 (w), 802 (w), 783 (w), 742 (w), 721 (s), 615 (w), 567 (w), 535 (w). Mass: 469 [M-F]<sup>+</sup>(11.7), 414 [M-CF<sub>3</sub>]<sup>+</sup>(4.5), 364 [M-C<sub>2</sub>F<sub>5</sub>]<sup>+</sup>(91.5), 169 C<sub>3</sub>F<sub>7</sub><sup>+</sup>(100), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup>(22.6), 69 CF<sub>3</sub><sup>+</sup>(78.5).

 <sup>19</sup>F nmr (neat): -81.6 (CF<sub>3</sub><sup>f</sup>), -82.1 (CF<sub>3</sub><sup>i</sup>), -79.8~-111.0 (CF<sub>2</sub><sup>c</sup>, CF<sub>2</sub><sup>d</sup> and CF<sub>2</sub><sup>g</sup>), -120.9 (CF<sub>2</sub><sup>e</sup>), -123.0~-129.0 (CF<sub>2</sub><sup>a</sup>), -127.0 (CF<sub>2</sub><sup>h</sup>), -181.6 (CF<sup>b</sup>).

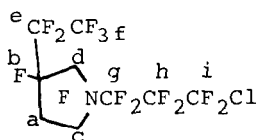
Found: C, 22.29%, N, 2.95%. Calculated for C<sub>9</sub>F<sub>19</sub>N: C, 22.38%, N, 2.90%.

6b (nc): bp 121.5~122.5 °C,  $n_D^{20}$  1.2938. IR (gas): 1378 (w,sh), 1352 (m,sh), 1342 (m,sh), 1324 (vs), 1307 (vs), 1283 (s), 1248 (s), 1240 (vs), 1218 (s), 1194 (s), 1176 (s), 1157 (m), 1138 (m), 1108 (w,sh), 1094 (w,sh), 1068 (w), 1043 (w,sh), 1029 (w), 990 (w), 980 (m), 963 (s), 911 (w), 890 (w), 878 (m), 847 (w,sh), 800 (w,sh), 792 (w), 745 (w,sh), 738 (m), 713 (w), 697 (w), 631 (w), 553 (w). Mass: 469 [M-F]<sup>+</sup>(7.9), 414 [M-CF<sub>3</sub>]<sup>+</sup>(17.6), 364 [M-C<sub>3</sub>F<sub>7</sub>]<sup>+</sup>(33.7), 169 C<sub>3</sub>F<sub>7</sub><sup>+</sup>(65.6), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup>(76.2), 69 CF<sub>3</sub><sup>+</sup>(100).

 <sup>19</sup>F nmr (neat): -80.1 (CF<sub>3</sub><sup>a</sup>), -82.1 (CF<sub>3</sub><sup>g</sup>), -80.0~-101.0 (CF<sub>2</sub><sup>d</sup> and CF<sub>2</sub><sup>e</sup>), -121.0~-133.5 (CF<sub>2</sub><sup>c</sup> and CF<sub>2</sub><sup>f</sup>), -189.3 (CF<sup>b</sup>).

Found: C, 22.19%, N, 2.70%. Calculated for C<sub>9</sub>F<sub>19</sub>N: C, 22.38%, N, 2.90%.

6A (nc): bp 146.5~147.0 °C,  $n_D^{20}$  1.3158. IR (gas): 1383 (w), 1348 (m,sh), 1328 (s), 1298 (s), 1248 (vs), 1212 (m,sh), 1193 (m), 1178 (m), 1129 (m), 1107 (m), 1038 (w), 1009 (w), 974 (m), 951 (m), 877 (w), 839 (w), 776 (w), 736 (w), 717 (m), 604 (w), 576 (w), 536 (w). Mass: 480 [M-F]<sup>+</sup>(6.5), 464 [M-Cl]<sup>+</sup>(2.5), 430 [M-CF<sub>3</sub>]<sup>+</sup>(2.1), 380 [M-C<sub>2</sub>F<sub>5</sub>]<sup>+</sup>(19.7), 364 [M-C<sub>2</sub>F<sub>4</sub>Cl]<sup>+</sup>(100), 119 C<sub>2</sub>F<sub>5</sub><sup>+</sup>(33.3), 69 CF<sub>3</sub><sup>+</sup>(67.0).



$^{19}\text{F}$  nmr (neat):  $-71.7$  ( $\text{CF}_2^{\text{i}}$ ),  $-81.7$  ( $\text{CF}_3^{\text{f}}$ ),  $-79.0 \sim -111.4$  ( $\text{CF}_2^{\text{c}}$ ,  $\text{CF}_2^{\text{d}}$  and  $\text{CF}_2^{\text{g}}$ ),  $-120.9$  ( $\text{CF}_2^{\text{e}}$ ),  $-124.2 \sim -128.8$  ( $\text{CF}_2^{\text{a}}$ ),  $-125.8$  ( $\text{CF}_2^{\text{h}}$ ),  $-181.7$  ( $\text{CF}^{\text{b}}$ ).



Found: C, 21.58%, N, 2.70%. Calculated for  $\text{C}_9\text{F}_{18}\text{ClN}$ : C, 21.64%, N, 2.80%.

6B (nc): IR (gas): 1367 (m,sh), 1354 (m,sh), 1341 (m,sh), 1322 (vs), 1306 (vs), 1285 (s), 1257 (vs), 1236 (s), 1215 (s), 1195 (s), 1168 (m,sh), 1148 (m,sh), 1131 (m), 1104 (m), 1067 (w), 1026 (w), 988 (w,sh), 976 (m), 964 (m), 956 (m,sh), 931 (w), 911 (w), 885 (w,sh), 878 (m), 845 (w,sh), 788 (w,sh), 781 (w), 770 (w), 749 (m), 746 (m), 708 (w), 681 (w,sh), 646 (w). Mass: 480  $[\text{M-F}]^+$  (7.6), 464  $[\text{M-Cl}]^+$  (2.9), 430  $[\text{M-CF}_3]^+$  (8.1), 414  $[\text{M-CF}_2\text{Cl}]^+$  (7.2), 364  $[\text{M-C}_3\text{F}_6\text{Cl}]^+$  (39.2), 185  $\text{C}_3\text{F}_6\text{Cl}^+$  (28.2), 119  $\text{C}_2\text{F}_5^+$  (62.3), 69  $\text{CF}_3^+$  (100).

$^{19}\text{F}$  nmr (neat):  $-68.3$  ( $\text{CF}_2^{\text{g}}$ ),  $-80.1$  ( $\text{CF}_3^{\text{a}}$ ),  $-81.0 \sim -102.0$  ( $\text{CF}_2^{\text{d}}$  and  $\text{CF}_2^{\text{f}}$ ),  $-189.3$  ( $\text{CF}^{\text{b}}$ ).

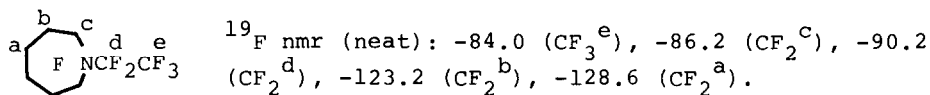
The properties of 6B and the results of elemental analysis are shown in Table 2.

### Fluorination of N-(2-chloroethyl)hexamethyleneimine (7)

The sample (7)·HCl (24.5 g) was fluorinated; 4.0 A/dm<sup>2</sup>, 6.3~8.5 V, 6~13 °C, 152 Ahr (305 min). The following compounds were obtained; n-C<sub>4</sub>F<sub>10</sub> (1.4 g), n-C<sub>5</sub>F<sub>12</sub> (2.7 g), n-C<sub>6</sub>F<sub>14</sub> (4.4 g), b (14.8 g),  NCF<sub>2</sub>CF<sub>3</sub> (7c) (11.5 g), B (2.8 g),  NCF<sub>2</sub>CF<sub>2</sub>Cl (7C) (3.0 g) and unidentified (4.1 g).

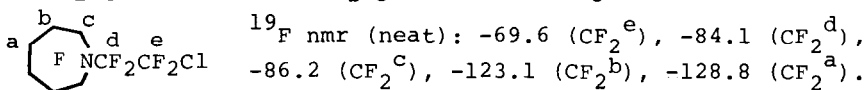
7c (nc): bp 103.5~104.5 °C,  $n_D^{20}$  1.2861. IR (gas): 1362 (m), 1325 (s,sh), 1308 (s,sh), 1292 (s), 1242 (vs), 1223 (s), 1204 (m), 1188 (m), 1161 (s), 1150 (m,sh), 1133 (m), 1114 (s), 1058 (s), 1047 (m), 987 (s), 948 (m), 933 (s), 872 (s), 839 (w), 827 (w), 817 (w), 748 (m), 733 (w), 680 (w), 663 (w), 639 (w), 619 (w). Mass: 433  $\text{M}^+$  (2.0), 414  $[\text{M-F}]^+$  (6.9), 364  $[\text{M-CF}_3]^+$  (8.7), 314  $[\text{M-C}_2\text{F}_5]^+$  (12.2), 119  $\text{C}_2\text{F}_5^+$  (69.6), 69  $\text{CF}_3^+$  (100).







Found: C, 21.98%, N, 3.23%. Calculated for  $\text{C}_8\text{F}_{17}\text{N}$ : C, 22.19%, N, 3.24%.

7C (nc): IR (gas): 1330 (m,sh), 1314 (s), 1305 (s), 1295 (m,sh), 1273 (m), 1237 (vs), 1223 (s), 1202 (m), 1188 (m), 1159 (s), 1132 (m), 1117 (m), 1081 (w), 1043 (w), 1000 (s), 958 (w), 931 (m), 908 (w), 863 (w), 829 (m), 799 (s), 761 (w), 744 (w), 660 (w), 641 (w). Mass: 449  $\text{M}^+$ (2.3), 430  $[\text{M}-\text{F}]^+$ (4.0), 414  $[\text{M}-\text{Cl}]^+$ (3.9), 380  $[\text{M}-\text{CF}_3]^+$ (0.9), 364  $[\text{M}-\text{CF}_2\text{Cl}]^+$ (10.0), 314  $[\text{M}-\text{C}_2\text{F}_4\text{Cl}]^+$ (7.4), 119  $\text{C}_2\text{F}_5^+$ (56.2), 69  $\text{CF}_3^+$ (100).

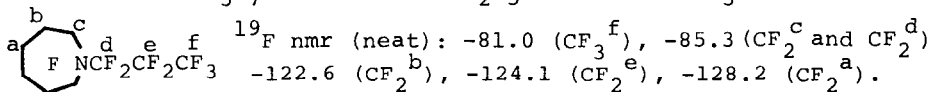


The properties of 7C and the results of elemental analysis are shown in Table 2.

#### Fluorination of N-(3-chloropropyl)hexamethyleneimine (8)

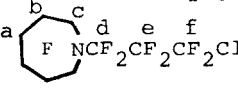
The sample (8)·HCl (24.2 g) was fluorinated; 4.0 A/dm<sup>2</sup>, 5.7~7.5 V, 6~13 °C, 170 Ahr (323 min). The following compounds were obtained: n-C<sub>4</sub>F<sub>10</sub> (1.1 g), n-C<sub>5</sub>F<sub>12</sub> (1.5 g), n-C<sub>6</sub>F<sub>14</sub> (7.8 g), b (13.3 g),  (8c) (11.7 g), B (2.9 g),  (8C) (3.1 g) and unidentified (4.3 g).

8c (nc): bp 122.5~123.5 °C,  $n_D^{20}$  1.2970. IR (gas): 1401 (w,sh), 1352 (m,sh), 1327 (s,sh), 1312 (vs), 1300 (s,sh), 1292 (s,sh), 1235 (vs), 1210 (m,sh), 1184 (m), 1155 (s), 1142 (m), 1127 (m,sh), 1091 (m), 1042 (m), 1005 (s), 970 (m), 931 (s), 884 (w), 835 (m), 817 (m), 787 (w), 740 (m), 691 (w), 659 (w), 640 (w), 618 (w). Mass: 487  $\text{M}^+$ (2.3), 464  $[\text{M}-\text{F}]^+$ (5.1), 414  $[\text{M}-\text{CF}_3]^+$ (6.1), 314  $[\text{M}-\text{C}_3\text{F}_7]^+$ (13.4), 119  $\text{C}_2\text{F}_5^+$ (62.1), 69  $\text{CF}_3^+$ (100).



Found: C, 22.21%, N, 2.96%. Calculated for  $\text{C}_9\text{F}_{19}\text{N}$ : C, 22.38%, N, 2.90%.

$\delta_C$  (nc): IR (gas): 1316 (s), 1284 (s), 1237 (vs), 1223 (s,sh), 1209 (m,sh), 1184 (m), 1152 (m), 1135 (m), 1120 (m,sh), 1078 (w,sh), 1045 (w), 1001 (s), 988 (m), 933 (m), 845 (w), 809 (m), 802 (m,sh), 758 (w), 742 (w), 723 (m), 660 (w), 637 (w).  
 Mass: 499  $M^+$  (4.2), 480  $[M-F]^+$  (9.2), 464  $[M-Cl]^+$  (2.5), 430  $[M-CF_3]^+$  (1.9), 414  $[M-CF_2Cl]^+$  (6.2), 364  $[M-C_3F_6Cl]^+$  (29.7), 185  $C_3F_6Cl^+$  (31.5), 119  $C_2F_5^+$  (66.7), 69  $CF_3^+$  (100).


 $^{19}F$  nmr (neat): -64.8 ( $CF_2^f$ ), -85.7 ( $CF_2^c$  and  $CF_2^d$ ), -122.5 ( $CF_2^b$ ), -123.0 ( $CF_2^e$ ), -126.8 ( $CF_2^a$ ).

The properties of  $\delta_C$  and the results of elemental analysis are shown in Table 2.

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