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SYNTHESIS OF PERFLUOROCHEMICALS FOR USE AS BLOOD SUBSTITUTES, PART II: ELECTROCHEMICAL FLUORINATION OF PARTLY FLUORINATED COMPOUNDS

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SUMMARY

Electrochemical fluorination of 2-methoxy-1,1,1-trifluoro-2-(F-methyl) octane gave the corresponding perfluorinated ether in 27% yield, along with cyclic by-products in 9%. A mixture of partly fluorinated tertiary amines, consisting of 1-dipropylamino-F-1-propene and 1-dipropylamino-2-hydryl-F-propane, did not afford a superior yield of tri(F-propyl)amine compared to the unfluorinated tripropylamine. 1-Diethylamino-2-(F-methyl)-F-1-pentene was fluorinated to give the corresponding F-tertiary amine in fairly good yields, together with 1-di(F-ethyl)amino-2-hydryl-2-(F-methyl)-F-pentane and their fragmented products. The study indicates that blocking of the α-carbon atom of an ether with F-methyl groups seems to reduce fragmentation, resulting in good yields of an unrearranged product. However, partial fluorination of a tertiary amine prior to electrochemical fluorination rather allows high yields of undesired by-products, as far as our experiments were concerned.

INTRODUCTION

Electrochemical fluorination of organic ethers and amines often gives low yields of the desired products, accompanied by extensively rearranged and fragmented by-products. From such complicated mixtures the desired products are difficult to obtain in pure form. To overcome this problem, some workers have been trying to improve the technique itself [1, 2], others

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to take advantage of intramolecular cyclization to produce more complicated structures [3, 4] or to use partly fluorinated starting materials [5, 6, 7, 8], expecting improvement of the synthetic efficiency of the electrochemical fluorination.

The present work was undertaken to examine whether partial fluorination of an ether or tertiary amine substrate stabilizes the structure in electrochemical fluorination, and to compare partly fluorinated substrates with unfluorinated ones with regard to the synthetic efficiency of the fluorination

RESULTS AND DISCUSSION

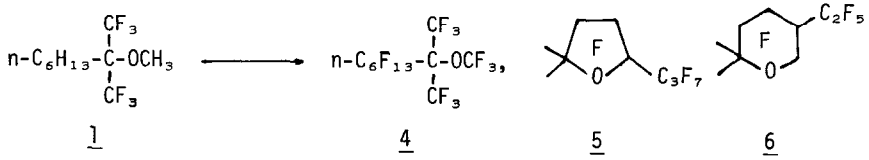
The use of partly fluorinated substrates as precursors for total fluorination has shown some promise as indicated in recent publications. For example, Sander obtained F-hexane and F-cyclohexane in high yields after introducing the CF_2 group into the molecules [5]. Subsequently, Plashkin and Sokolov have done an interesting comparative study between fluorinated and unfluorinated starting materials, and found better yields in the fluorination of partly fluorinated compounds [6]. Partial fluorinations of the substrate prior to exhaustive fluorination proved to be useful also in the cobalt trifluoride fluorination [9], despite the extra steps required. However, partial fluorination of the starting material for stabilization is not the whole story as evidenced by the fact that the electrochemical fluorination of 1-(F-methyl)naphthalene gave only a 4.4% yield of 1-(F-methyl)-F-decalin [8].

On the basis of the above precedent work, we chose 2-methoxy-1,1,1-trifluoro-2-(F-methyl)octane (1) as a model compound with the hope that two F-methyl groups on the α-carbon would stabilize intermediate radicals being produced during the fluorination. Since the α-carbon is already blocked there should be no formation of an unstable radical as exemplified in Scheme 1.

2 3

Scheme 1. Note that radical 3 tends to give R_FCOF to a greater extent compared to 2.

The electrochemical fluorination of 1 gave 2-(F-methoxy)-2-(F-methyl)-F-octane (4) and cyclic by-products (5 and 6) as shown in Scheme 2. To the best of our knowledge, there has been no report on the formation of cyclic ether products from the electrochemical fluorination of acyclic ethers. No F-isooctane which is considered one of the possible by-products, nor in fact any significant fluorocarbon fraction was found, indicating very little breakdown of the ether bond of $-(CF_3)_2C-O-$.



1 4 5 6

Scheme 2. The presence of F in a ring means that all unmarked positions are attached to fluorine.

These compounds were isolated by preparative-scale gas chromatography and identified by their spectroscopic data. In the ^{19}F-nmr spectrum of 4 strong signals at 54.1 ppm due to the OCF_3 group and typical t of t signal for the $-C(CF_3)_2-O-$ group were found together with signals of the CF_2 groups.

One of the by-products, 5, was unequivocally assigned as 2,2-di(F-methyl)-5-(F-propyl)-F-oxolane from spectroscopy. However, there is an additional viable structure, 2,2-di(F-methyl)-4-(F-ethyl)-F-oxane, for the by-product 6 from only spectroscopy, but 2,2-di(F-methyl)-5-(F-ethyl)-F-oxane is most likely from the proposed mechanism outlined in Scheme 3. The structural elucidation based on their spectroscopy is as follows.

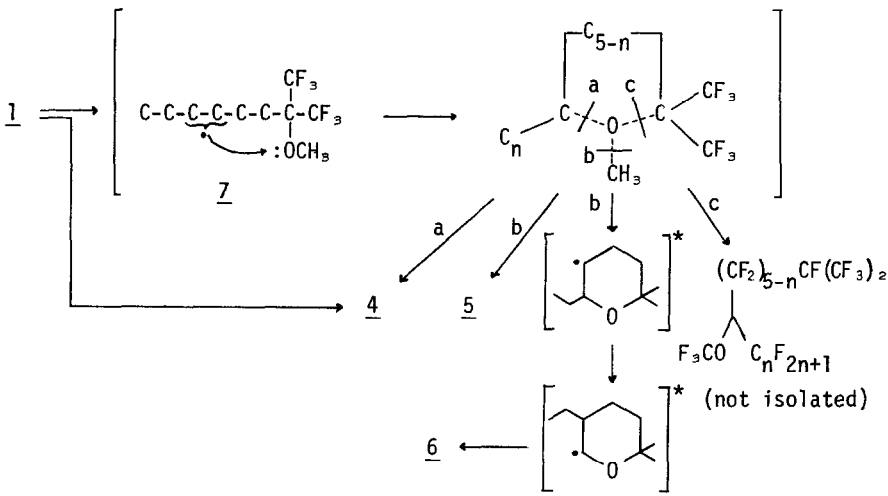
In the ^{19}F-nmr spectrum of 5, there were observed a $(CF_3)_2C<$ group at 73-74 ppm, a CF_2 group at 82 ppm, three CF_2 groups at 116-128 ppm with J_{AB}=240-265 Hz, a CF_2 group at 127 ppm (not an AB pattern) and a CF group adjacent to oxygen at 124 ppm. The three CF_2's with AB quartets appear to be attributed to the geminal fluorines of the ring and the side chain, but not to that adjacent to oxygen [4]. Similarily, the ^{19}F-nmr spectrum of 6 shows the presence of a $(CF_3)_2C<$ group at 70-73 ppm, a CF_3 group at 81 ppm, AB type quartets of three CF_2 groups at 73-127 ppm, one of which at 73-80 ppm is adjacent to oxygen, a CF_2 group at 119 ppm being not an AB quartet, and a CF group at 185 ppm. Their mass spectra showed no molecular ions, but characteristic ions $[M-F]^+$ and $[M-R_F]^+$ resulted from the loss of F-alkyl groups. Of these fragment ions, the largest ion (m/z 447 $[C_9F_{17}O]$) is

consistent with cyclic ether syructures. Further, m/z 297 [M-C_3F_7] was the second largest ion in 5 but was not observed in 6, and m/z 347 [M-C_2F_5] was found more abundantly in 6 than in 5.

Thus, on the basis of these observations, we assigned 5 and 6 as five- and six-membered ring compounds, respectively, as shown in Scheme 2. Details of spectral data for products 4, 5 and 6 are given in the experimental section.

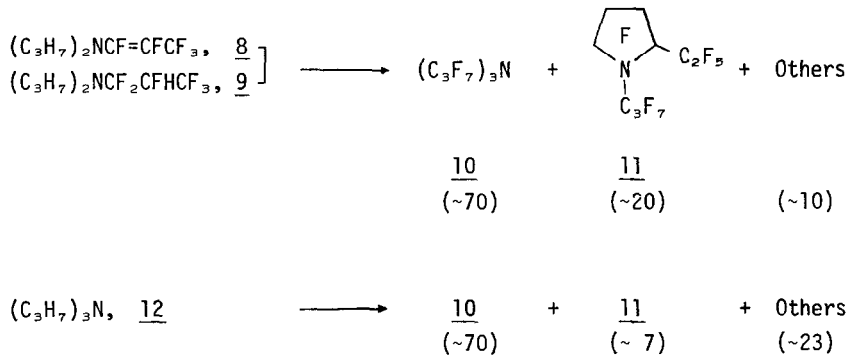
In general, the electrochemical fluorination of acyclic ethers tends to give poor yields with increasing molecular weight of starting material due to the usual problem of increase in C-C cleavage [10] and this trend is quite significant in the fluorination of ethers compared to that of amines. Formation of cyclic ethers, in our case, is probably explained by the following sequence of events in which radical 7 would attack the oxygen to give a fused ring at the begining of or during the reaction (Scheme 3).

These results suggested that the presence of two F-methyl groups on the α-carbon of an ether appears to be contributory to stabilizing the ether bond.



Scheme 3. * All unmarked bonds are to fluorine.

A mixture of 1-dipropylamino-F-1-propene (8) and 1-dipropylamino-2-hydryl-F-propene (9) (ca. 1:1.2 by nmr), which was obtained by the reaction of F-propene with dipropylamine, also underwent the electrochemical fluorination to give tri(F-propyl)amine (10) and N-(F-propyl)-2-(F-ethyl)-F-pyrrolidine (11), as main products, in a ratio of approximately 7:2 in 29-35% yields (Scheme 4).



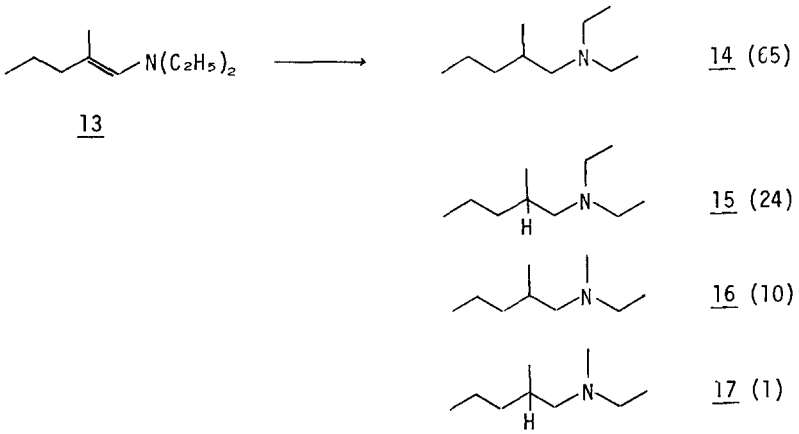
Scheme 4. Figures in parentheses indicate the product distribution in percentage. A fluorine symbol within a ring signifies that all unmarked bonds in that ring are bonds to fluorine.

In comparison, the electrochemical fluorination of tripropylamine (12) gave the corresponding structure 10 in much better yields, along with a small amount of cyclized product 11, than the foregoing reaction. This suggests that the partly fluorinated alkyl chain of the substrate was rather slowly perfluorinated thus allowing cyclization to some extent. Mechanism of the cyclization is not completely clarified yet, but one might be led to propose that the chain length of the substrate, propyl versus ethyl, is critical for the ring formation. This is also supported by the fluorination of 13 (see below), viz., the N-propyl-F-enamine such as 8 can form a five-membered ring intermediate more easily than the ethyl derivatives such as 13 to yield a cyclic product.

1-Diethylamino-2-(F-methyl)-F-1-pentene (13), which was obtained by the reaction of 2-(F-methyl)-2-F-pentene with diethylaminotrimethylsilane, was successfully fluorinated to yield the corresponding structure 14, together with fragmented and/or hydrogen-containing by-products (Scheme 5). Extension of the reaction time did not increase the yield of 14. Attempted isolation of compound 17 by preparative-scale gas chromatography proved fruitless.

An unequivocal allocation of the structure of 17 by ^{19}F-nmr is, therefore, not possible at the present time, but it seems quite likely that by-product 17 is N-(F-ethyl)-N-(F-methyl)-2-hydryl-2-(F-methyl)-F-pentylamine from its mass spectral data, in which m/z 484[$C_9F_{20}HN$; M-F] and similar fragmentation patterns as 15 were observed.

These results suggested that the addition of hydrogen fluoride to the double bond of 13 might occur at an early stage of or before the fluorination and the further fluorination proceeded, and that the hydrogen in a sterically crowded enviroment would be most likely to survive the fluorination.
The ^{19}F-nmr spectra of the products are summarized in Table 2 in the experimental section.



Scheme 5. Figures in parentheses indicate the product distribution in percentage. All unmarked positions are to fluorine unless otherwise described.

In conclusion, blocking of the α-carbon atom of an acyclic ether with F-methyl groups seems to be effective in reducing fragmentation in electrochemical fluorination, allowing high yields of an unrearranged product. Additionally, it is of interest to note that such kind of ether, 2-methoxy-1,1,1-trifluoro-2-(F-methyl)octane, gave the corresponding perfluorinated structure in fairly good yields, along with cyclic by-products which are unusual products in electrochemical fluorination of an acyclic ether.

On the other hand, partial fluorination of a tertiary amine prior to electrochemical fluorination rather allows high yields of undesired products such as cyclized or hydrogen-remaining products.

EXPERIMENTAL

Materials

F-Propene (PCR Res. Chem. Inc., USA) and F-acetone (Daikin Kogyo Co., Japan) were used as received. 2-(F-Methyl)-F-2-pentene was prepared from F-propene according to the known method [11]. All other reagents were used also as received unless otherwise stated.

Fluorination

Fluorinations were carried out in the usual way [10] using an electrolytic cell of 1.5 ℓ capacity fitted with reflux condenser (-20°) on the top of the cell: the electrodes consisted of six anodes and seven cathodes arranged alternatively. The effective anodic surface area was 10.2 dm^2. Conductivity additives were not used throughout the experiments.

Gas chromatography

Analytical gas chromatography work was done with a Shimadzu GC-RIA using 0.3 cm (i.d.) x 5 m glass column packed with either 10% OV 202 on Chromosorb W (HP) or 10% SE 30 on Chromosorb W (AW-DMCS). For preparative work, a Shimadzu 4BIT with either a 1 cm (i.d.) x 5 m copper column packed with 10% OV 202 on Chromosorb W (HP) or a 1 cm (i.d.) x 14 m copper column packed with 15% SE 30 on Diasolid L-1, 60/80 mesh, was used.

Spectroscopy

Infrared spectra were obtained on a Shimadzu IR420 spectrophotometer. Mass spectra (EI) were run on a Shimadzu 9020-DF with a Hitach Data Processing System M-003 and a Shimadzu LKB-9000 GC/MS system (70 eV). Only characteristic and predominant ions are described. ^{19}F-nmr spectra were recorded on a Hitachi R24F (56.4 MHz) and Varian EM-390 (84.6 MHz) spectrometer using $CFCl_3$ as an internal standard, and upfield shifts are quoted as positive.

Proton nmr spectra were obtained with a Hitachi R24B (60 MHz) spectrometer: chemical shifts are expressed in the δ scale using internal TMS.

2-Methoxy-1,1,1-trifluoro-2-(F-methyl)octane (1)

To a Grignard solution prepared from 44 g of magnesium turnings, 297 g of n-hexyl bromide and 1.5 ℓ tetrahydrofuran was added 230 g F-acetone through a gas inlet tube at room temperature over 2 hours. The reaction mixture was left overnight under nitrogen, and quenched by adding a saturated aqueous ammonium chloride solution (500 ml). The mixture was extracted with ether (500 ml x 3). The combined extract was washed with water (250 ml x 2) and brine (300 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The oily residue was distilled under reduced pressure to afford 1,1,1-trifluoro-2-(F-methyl)-2-octanol, 160 g (45.7%, based on F-acetone), bp 63-65° (18 mmHg). ν_{max} (film): 3600, 3540, 2980, 2940, 2860, 1460, 1215, 1150, 1120, 935, 720, 690, 660 cm^{-1}.

To a solution of the alcohol (159 g) in dioxane (1000 ml) was added sliced sodium metal (13.4 g) at 100° under nitrogen. The reaction mixture was refluxed until sodium metal was consumed (ca. 20 hours). To the ice-cooled reaction mixture was added dimethyl sulfate (61 ml) dropwise over 1.5 hours. After refluxing for 5 hours, the reaction mixture was poured into water (500 ml), and extracted with ether (500 ml x 2). The combined extract was washed with water (250 ml x 2), brine (250 ml) in that order and dried over anhydrous sodium sulfate. The extract was concentrated on a rotary evaporator to leave an oil. The resultant residue was purified by a fractional distillation to give 1, 96 g (62%)(nc). bp 161-164° $\delta(CDCl_3)$: 3.50 (s, 3H), 1.1-1.2 (br, 10 H), 0.9 (br t, 3H)

Fluorination of 1

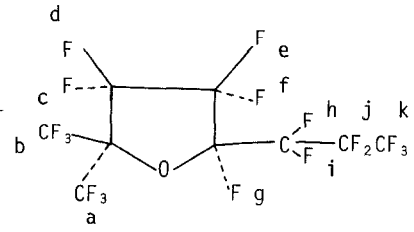
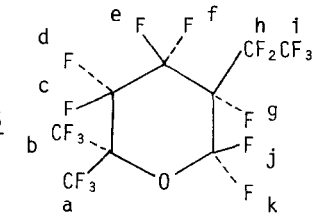
Ether 1 (32-49 g, 0.12-0.18 mol) was charged into the cell which contained 1.2 ℓ electrochemically purified anhydrous hydrogen fluoride, and the resulting solution was subjected to fluorination with an anodic current density of 1-3.5 A/dm^2, a cell voltage of 5.4-6.6 V, and a cell temperature of 5-12° over a period of 24-46 hours (145.8-207.0 Ahr). The mixture was agitated by bubbling with helium at an approximate rate of 50 ml/min. during the fluorination. After the electrolysis was over, most of hydrogen fluoride was distilled off from the cell. The volatile perfluorochemical layer was

collected from the cell (145.2 g) and from the recovered hydrogen fluoride phase (22.3 g). Total 167.5 g of the F-chemical was thus obtained from 165.3 g of the starting material in the four runs. The F-chemical layer was refluxed with a mixture of 100 ml of 70%(w/v) sodium hydroxide solution and 70 ml of diisobutylamine over 4 days, and poured into iced water after cooling. An F-chemical phase (136 g) which separated was collected, washed with acetone and water, and subjected to a fractional distillation using a spinning-band column (2000 rpm, R/P=10/2). All analytical samples were obtained by preparative-scale gas chromatography. A possible isomer such as 5-(F-methoxy)-2-(F-methyl)-F-octane could not be found under the present conditions. The following products were obtained: 2-(F-methoxy)-2-(F-methyl)-F-octane (4)(nc); Anal. Found: m/z, 534.9583. Calcd. for $C_{10}F_{22}O$-F: M-F, 534.9613. bp 145-145.5°, d_4^{19} 1.9871, 93.8g (27.3%, isolated yield). MS (given in the following order; mass number, formula, percent of intensity of base peak): 535[M-F](0.2), 497[$C_{10}F_{19}O$](7.7), 485[M-CF_3](0.3), 447[$C_9F_{17}O$](5.6), 397[$C_8F_{15}O$](3.2), 297[$C_6F_{11}O$](20.6), 269[C_5F_{11}](4.4), 231[C_5F_9](4.0), 181[C_4F_7](22.6), 169[C_3F_7](20.2), 131[C_3F_5](16.9), 119[C_2F_5](22.6), 100[C_2F_4](10.9), 97[C_2F_3O](10.1), 69[CF_3](base): 2,2-di(F-methyl)-5-(F-propyl)-F-oxolane (5)(nc); Anal. Found m/z, 396.9700. Calcd. for $C_9F_{18}O$-CF_3:M-CF_3, 396.9709. 22.3g (7.7%, isolated yield), bp 110-112°, MS; 447[M-F](25.8), 397[M-CF_3](3.0),359[$C_8F_{13}O$](5.9), 297[M-C_3F_7](48.7), 209[C_5F_7O](6.4), 197[C_4F_7O](3.2), 181[C_4F_7](40.3), 169(19.1), 147[C_3F_5O](7.0), 131(13.1), 119(36.4), 100(4.9), 97(16.1), 69(base): and 2.2-di(F-methyl)-5-(F-ethyl)-F-oxane (6)(nc); Anal. Found: m/z, 446.9671. Calcd. for $C_9F_{18}O$-F:M-F, 446.9677 (1%, estimated yield by g.c.), MS; 447[M-F](13.2), 397[M-CF_3](13.2), 359[$C_8F_{13}O$](6.6), 293[C F](5.9),231 231(11.8), 181(23.5), 169(16.2), 147(7.4), 131(15.4), 128[C_3F_4O](3.7), 119 (8.8), 100(3.7), 69(base). ^{19}F-nmr data for major products are summarized in Table 1. Other minor products were not identified completely, but spectral data of a by-product mixture indicate that one of them will be an isomer of 6, 2,2-di(F-methyl)-5-(F-ethyl)-F-oxane.

1-Dipropylamino-F-1-propene (8) and 1-dipropylamino-2-hydryl-F-propane (9)

A mixture of 8 and 9 was prepared according to the literature [12]. To a cooled solution of dipropylamine (73.2 g, 0.72 mol) in dry ether (100 ml) was introduced F-propene (ca. 115 g, ca. 0.77 mol) at a rate such that continuous reflux was observed. The entire mixture was allowed to stir at room temperature overnight. Dipropylamine hydrofluoride precipitates were filtered using a Buechner funnel. The filtrate was condensed on a rotary

TABLE 1.
^{19}F-nmr spectra of products 4, 5 and 6

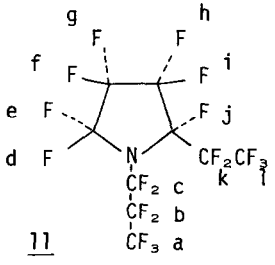
Compound	Chemical shift[1] [2]	J(Hz)
a b c d e f g h 4 $CF_3CF_2CF_2CF_2CF_2CF_2C(CF_3)_2OCF_3$	a 82.1 b 127.2 c 123.2 d 122.3 e 120.2 f 112.6 g 69.1 h 54.1	a-c= 11.3 b-d= 14.0
5 	a 74.0 b 73.0 c 115.5 d 127.5 J_{AB} e,f 119.3 123.4 J_{AB} g 123.7 h,i 127.3 128.0 J_{AB} J 126.5 k 82.2	a-b= 20.8 c-d=265 e-f=240 h-i=240 h(i)-k=10 J-k= 3
6 	a 69.9 b 72.7 c 125.8 d 112.1 J_{AB} e 118.8 f 127.0 J_{AB} g 185.0 h 118.5 i 82.3 J,k 72.6 79.7 J_{AB}	b-c= 11.3 c-d=292 e-f=292 j-k=158

[1] ϕ values in ppm relative to internal $CFCl_3$
[2] Only apparent chemical shifts and coupling constants are given.

evaporator at 40°. A crude product mixture (145.3 g) was distilled at an aspirator pressure to give colorless liquid, 8 and 9, bp 57-65°(16-17 mmHg), 131.9 g (ca. 75% yield), ^{19}F-nmr (neat, ppm) for 8; 65.1 (dd, 3F, J=14.1 Hz, 23.5 Hz): for 9; 74.4 (3F), 81.9, 90.0 (ABq, 2F, J=203.0 Hz), 206.1 (m, 1F). Based on the relative intensity of each CF_3 in the nmr, constituent ratio of 8 and 9 was determined to be 1:1.2.

Fluorination of a mixture of 8 and 9

A freshly distilled mixture of 8 and 9 (68.9 g) was fluorinated electrochemically under the conditions of 0.4-1.2 A/dm^2, 5.4-7.1 V, 3-6° and 52 hours. After scavenging hydrogen-containing products and nitrogen fluorides with a mixture of sodium hydroxide and diisobutylamine and with an aqueous potassium iodide-acetone solution (vide ante), a fluorochemical layer (22.9 g) was shown by gas chromatography to contain two major compounds of 10 and 11 in the ratio of 7:2. Preparative-scale gas chromatography gave 10, bp 129-130°, 12.8 g (ca. 8.6%, isolated yield) which was identified by its mass spectrum and by comparison of its ^{19}F-nmr spectrum with that of the authentic compound [13]. MS; 402[$C_7F_{16}N$], 314[$C_6F_{12}N$], 214[C_4F_8N], 169, 114 100, 69. ^{19}F-nmr (ϕ, neat, ppm); 81.5 (s, 3F), 84.0 (m, 2F), 121.2 (2F): and N-(F-propyl)-2-(F-ethyl)-F-pyrrolidine (11)(nc); 3.7 g (2.7%, isolated yield), MS; 464[M-F], 426[$C_9F_{16}N$], 364[M-C_2F_5], 326[$C_7F_{12}N$], 276[$C_6F_{10}N$], 169, 119, 69. ^{19}F-nmr spectrum of 11 is as follows.



11

	δ	J
a	81.3 ppm	f-g=245 Hz
b	124.7	h-i=254
c	95	j-l= 16.9
d	79	k-l= 10.3
e	82	
f	127.8] J_{AB}	
g	137.5]	
h	131.4] J_{AB}	
i	120.0]	
j	116.5	
k	127.5	
l	79.8	

Fluorination of tripropylamine (12)

Tripropylamine (116.0 g, 0.773 mol) was fluorinated under the similar conditions described before (5.0-6.5 V, 1.4 A/dm^2) giving 145 g of crude F-chemicals. Preparative-scale gas chromatography gave 10, 81.2 g (20.1%, isolated yield) and 11, 8.1 g (2.1 g, isolated yield).

1-Diethylamino-2-(F-methyl)-F-1-pentene (13)

2-(F-Methyl)-F-2-pentene (16.3 g, 54 mmol), dry ether (20 ml) and diethylaminotrimethylsilane (7.88 g, 54 mmol) were placed in that order in a flask equipped with a drying tube. The entire mixture was allowed to stand

at room temperature for 24 hours and condensed on a rotary evaporator under reduced pressure. Distillation of the residue gave a pale yellow liquid 13, 18.6 g (97.6%), bp 95-96°(30 mmHg), which was identified by comparison of its ^{19}F-nmr spectrum with that reported [14].

Fluorination of 13

In accordance with the fluorination of 1, enamine 13(70 g, 0.2 mol) was fluorinated under the following conditions: 0.6-2.2 A/dm^2, 5.6-6.5 V, 3-12°, 12 hours (154.1 Ahr). After the same treatment as before, 89 g of a product mixture was obtained, from which the following compounds were separated by preparative-scale gas chromatography and identified by ^{19}F-nmr and MS: N,N-Di(F-Ethyl)-2-(F-methyl)-F-pentylamine (14)(nc); Anal. Found: m/e, 501.9671. Calcd. for $C_{10}F_{23}N$-CF_3:M-CF_3,501.9711. bp 147-148°, 46.8 g (41.4%, isolated yield), MS; 502[M-CF_3], 414[$C_8F_{16}N$], 364[$C_7F_{14}N$], 319[C_6F_{13}], 302 [$C_5F_{12}N$], 231[C_5F_9], 181[C_4F_7], 169[C_3F_7], 164[C_3F_7N], 131[C_3F_5], 119[C_2F_5] 114[C_2F_4N], 100[C_2F_4], 69[CF_3]. N,N-Di(F-ethyl)-2-(F-methyl)-2-hydryl-F-pentylamine (15)(nc); Anal. Found: m/e, 483.9788. Calcd. for $C_{10}F_{22}HN$-CF_3: M-CF_3, 483.9806. bp 150-151°, 17.2 g (15.7%, isolated yield), IR (film, cm^{-1}) 3045 (CH), MS; 414[$C_8F_{16}N$], 396[$C_8F_{15}HN$], 302[$C_5F_{12}N$], 301[$C_6F_{12}H$], 296 [$C_7F_{10}HN$], 213[C_5F_8H], 201[C_4F_8H], 181[C_4F_7], 169[C_3F_7], 164[C_3F_6N], 163 [C_4F_6H], 131[C_3F_5], 119[C_2F_5], 114[C_2F_4N], 113[C_3F_4H], 100[C_2F_4], 93[C_3F_3] 69[CF_3].

N-(F-ethyl)-N-(F-methyl)-2-(F-methyl)-F-pentylamine (16)(nc); Anal. Found: m/e, 451.9705. Calcd. for $C_9F_{21}N$-CF_3: M-CF_3, 451.9743. bp 128-129°, 7.2 g (6.9%, isolated yield), MS; 452[M-CF_3], 414[$C_8F_{16}N$], 364[$C_7F_{14}N$], 319 [C_6F_{13}], 252[$C_4F_{10}N$], 231[C_5F_9], 181[C_4F_7], 169[C_3F_7], 164[C_3F_7N], 131 [C_3F_5], 119[C_2F_5], 114[C_2F_4N], 100[C_2F_4], 69[CF_3].
N-(F-ethyl)-N-(F-methyl)-2-(F-methyl)-2-hydryl-F-pentylamine (17)(nc); Anal. Found: 433.9823. Calcd. for $C_9F_{20}HN$-CF_3: M-CF_3, 433.9838.
MS; 484[M-F], 434[M-CF_3], 396[$C_8F_{15}HN$], 346[$C_7F_{13}HN$], 302[$C_5F_{12}N$], 296 [$C_7F_{10}HN$], 252[$C_4F_{10}N$], 213[C_5F_8H], 169[C_3F_7], 164[C_3F_6N], 119[C_2F_5], 114 [C_2F_4N], 113[C_3F_4H], 100[C_2F_4], 69[CF_3]. For product 17, only mass spectral data were obtained.

^{19}F-nmr data for 14, 15 and 16 are given in Table 2.

TABLE 2.

^{19}F-nmr spectra of compounds 14, 15 and 16

Compound	Chemical shift [1,2]	J (Hz)
a b c d e f,g h i $CF_3CF_2CF_2CF(CF_3)CF_2N(CF_2CF_3)_2$ 14	a 81.0 b 124.5 c 114.5 d 179.0 e 71.5 f 75 g 86 J_{AB} h 87.7 i 79.3	a-c=12
a b c d e f,g h i $CF_3CF_2CF_2CH(CF_3)CF_2N(CF_2CF_3)_2$ 15	a 80.9 b 124.5 c 110.5 d 4.1 (multiplet)[3] e 61.3 f 62 g 73 J_{AB} h 89.8 i 82.3	a-c=11
a b c d e f,g h i j $CF_3CF_2CF_2CF(CF_3)CF_2NCF_3(CF_2CF_3)$ 16	a 80.8 b 124.8 c 114.5 d 180.0 e 71.5 f 73 g 83 J_{AB} h 50.5 i 91.5 j 81.5	a-c=12 i-j= 9

1 ϕ Values in ppm relative to internal $CFCl_3$.
2 Only apparent chemical shifts and coupling constants are given.
3 Proton nmr, ppm (δ).

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