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Electrochemical fluorination of aliphatic secondary amines

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Abstract

Electrochemical fluorination (ECF) has been examined for six aliphatic secondary amines: *N*,*N*-di-ethylamine, *N*-ethyl,*N*-*n*-propylamine, *N*,*N*-di-*n*-propylamine, *N*-ethyl,*N*-*iso*-propylamine, *N*,*N*-di-*iso*-propylamine, and *N*-methyl,*N*-*n*-butylamine. It was found from these amines that not only the corresponding *F*-(*N*-fluoro-*N*,*N*-dialkylamines) but also *F*-imines having the same number of the carbon atoms were formed in low yields. The suppression of the C–N bond cleavage (blocking effect) which is expected to occur during fluorination due to the presence of bulky *N*-alkyl group was not observed as a result of the ECF of these aliphatic secondary amines. It was also found that the change of the initial solute concentration of *N*,*N*-di-*n*-propylamine did not affect on the product yields, which is usually observed for cyclic secondary amines. Several *F*-(*N*-fluoro-*N*,*N*-dialkylamines) were treated with triphenylphosphine for conversion into the corresponding *F*-imines. An imine bond was generated during this defluorination exclusively at the site of the alkyl group with a longer chain length when there were two different alkyl groups present in *F*-(*N*-fluoro-dialkylamines).

Keywords: Electrochemical fluorination; Aliphatic secondary amines; *F*-(*N*-fluoro-dialkylamines); *F*-imines; Triphenylphosphine; Defluorination

1. Introduction

Many papers have dealt with the electrochemical fluorination (ECF) of tertiary amines [1,2], because *F*-*tert*-amines which are obtained as the main fluorination product are used in applications, such as artificial blood, thermal shock test liquids for semi-conductors and VPS liquids [3]. Perfluorocarbons including *F*-*tert*-amines and *F*-ethers have recently been a focus of attention as a new application for FBS [4]. In contrast to the good ECF yield of *F*-*tert*-amines by the fluorination of tertiary amines, poor yields of corresponding *F*-(*N*-fluoro-*N*,*N*-dialkylamines) have generally been obtained in the case of secondary amines. Thus little data is available on the ECF of aliphatic secondary amines [5–7]. However, the ECF of cyclic secondary amines has been well investigated, because this is the optimal method for the preparation of *F*-(*N*-fluoro-cyclic-alkylamines) [8–10]. As a part of a series of investigations on the preparation of *F*-amines [10], we have conducted the fluorination of aliphatic secondary amines, and present the results herein of the fluorination of *N*,*N*-di-ethylamine (**1**), *N*-ethyl,*N*-*n*-propylamine (**2**), *N*-ethyl,*N*-*iso*-propylamine (**3**), *N*,*N*-di-*n*-propylamine (**4**), *N*,*N*-di-*iso*-propylamine (**5**) and *N*-methyl,*N*-*n*-butylamine (**6**): $(C_2H_5)_2NH$ (**1**), $C_2H_5(n\text{-}C_3H_7)NH$ (**2**), $C_2H_5(iso\text{-}C_3H_7)NH$ (**3**), $(n\text{-}C_3H_7)_2NH$ (**4**), $(iso\text{-}C_3H_7)_2NH$ (**5**), $CH_3(n\text{-}C_4H_9)NH$ (**6**).

2. Results and discussion

2.1. Fluorination of aliphatic secondary amines (1–6)

The results of the fluorination are summarized in Table 1. It was found that not only *F*-(*N*-fluoro-*N*,*N*-dialkylamines) (**A**) but also *F*-imines (**B**) having the same number of the carbon atoms as the former were formed in low yields together with large quantities of cleaved products by ECF of aliphatic secondary amines. Among the perfluorocarbons which are major products as a result of the cleave of the C–N bond, a small amount of *F*-(*N*,*N*-difluoroalkylamine) with a formula of R_FNF_2 was also formed (Scheme 1).

The combined yields of **A** and **B** were in the range of 3–16%. The yields (**A** and **B**) and the ratio of **A**:**B** depended greatly on the type of alkyl groups in the aliphatic secondary amines. It is known that aliphatic *F*-imines (**B**) can be prepared by various reactions involving, for example, pyrolysis of *F*-*tert*-amines [11], the reaction of nitrosylfluoride and *F*-olefins [12], pyrolysis of alkali metal salts of *F*-nitrogen-containing propionic acids [13], and the photolytic

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Table 1
Results of the fluorination of secondary amines

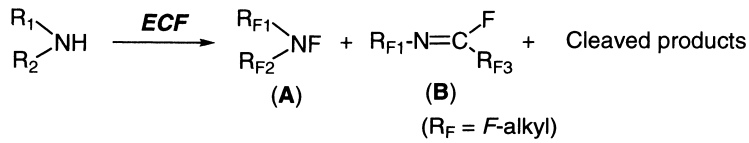
Run	Sample g (mol)	Current passed (Ah)	Fluorinated product (g)	Fluoroamines and fluoroimines[a] (yield %)
1	$C_2H_5(C_2H_5)NH$ (**1**) 24.3 (0.443)	222	8.3[b]	$C_2F_5N{=}CF(CF_3)$ (**30**) (3.1), $(C_2F_5)_2NF$ (**31**) (6.2)
2	*n*-$C_3H_7(C_2H_5)NH$ (**2**) 18.2 (0.386)	164	5.0	*n*-$C_3F_7NF_2$ (**15**) (2.6), $C_2F_5N{=}CF(C_2F_5)$ (**22**) (2.4), *n*-$C_3F_7(C_2F_5)NF$ (**23**) (2.7)
3	*iso*-$C_3H_7(C_2H_5)NH$ (**3**)18.0 (0.386)	161	6.0	*iso*-$C_3F_7NF_2$ (**16**) (2.3), *iso*-$C_3F_7N{=}CF(CF_3)$ (**20**) (3.3), *iso*-$C_3F_7(C_2F_5)NF$ (**24**) (2.4)
4	*n*-C_3H_7(*n*-C_3H_7)NH (**4**) 25.4 (0.252)	207	18.9 (0.9)[c]	**15** (1.3), *n*-$C_3F_7N{=}CF(C_2F_5)$ (**13**) (1.8), (*n*-$C_3F_7)_2NF$ (**12**) (7.8)
5	*iso*-C_3H_7(iso-C_3H_7)NH (**5**) 27.0 (0.386)	221	21.0	**16** (4.9), *iso*-$C_3F_7N{=}CF(CF_3)$ (**17**) (1.4), *iso*-$C_3F_7N{=}CF\ C_2F_5$) (**20**)+*iso*-$C_3F_7N{=}C(CF_3)_2$ (**21**) (3.4), **17** (0.9), *iso*-C_3F_7(*n*-C_3F_7)NF (**19**) (6.0), (*iso*-$C_3F_7)_2NF$ (**18**) (1.5)
6	*n*-$C_4H_9(CH_3)NH$ (**6**) 21.8 (0.386)	196	29.6	*n*-$C_4F_9NF_2$ (**32**) (2.7), $CF_3N{=}CF$(*n*-C_3F_7) (**26**) (1.4), *n*-$C_4F_9(CF_3)NF$ (**25**) (1.2)

[a] Arranged in order of the elution time on GC.
[b] Products obtained in a cold trap.
[c] Products obtained as cell drainings.

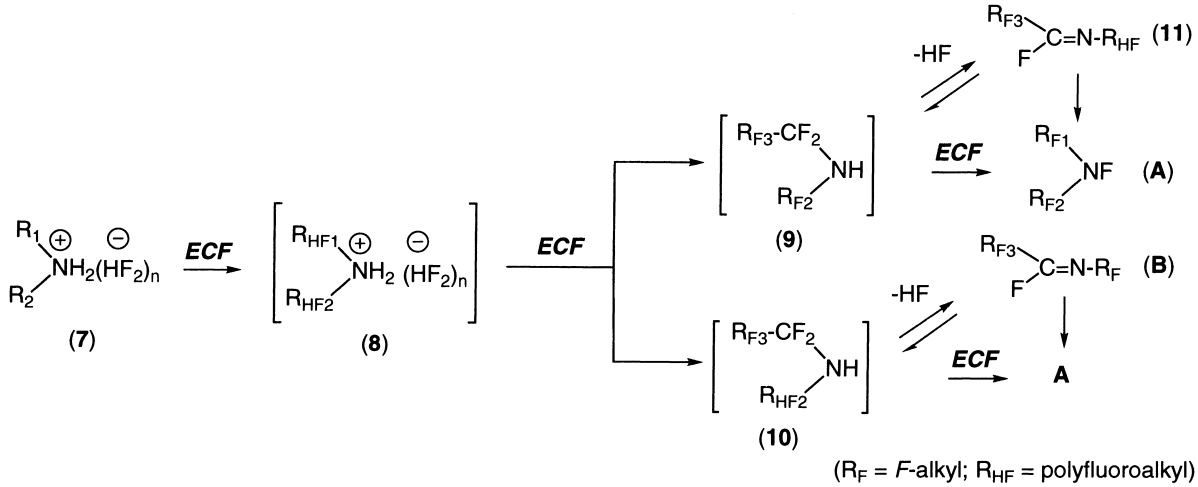
reaction of $R_FNCl(CF_2CFCl)Cl$ [14]. Recently, a convenient preparative method which consists of the reaction of *F-tert*-amines with SbF_5 has been described by Petrov and Des-Marteau [15].

Looking at the behavior of the carbon–nitrogen multiple bond during ECF, it is known that the nitrile group of acetonitrile can survive during ECF under a controlled potential [16]. Thus, CF_3CN is known to be formed at low yields together with such cleaved products as $C_2F_5NF_2$, C_2F_6, C_2F_5H, NF_3 by ECF of acetonitrile. However, the formation of *F*-imines (**B**) by ECF has never been reported.

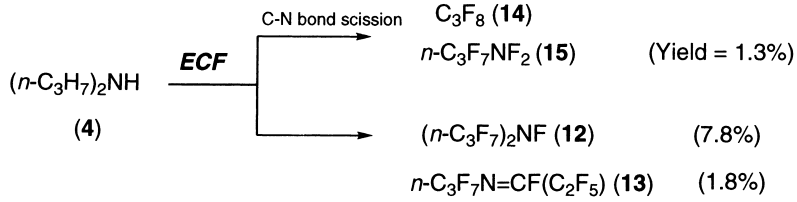
The reaction path for the formation of *F*-imines can be explained by the –HF reaction at the final stage of the fluorination as is shown in a simplified form in Scheme 2. It is generally accepted that ECF starts from the C–H bond of the carbon where the electron density is higher [17]. Thus, the alkyl group of ammonium salts (**7**) of secondary amines



Scheme 1.



Scheme 2.



Scheme 3.

will be fluorinated from the carbon which is farthest from the nitrogen atom. As the reaction proceeds, partially fluorinated ammonium salts (**8**) of secondary amines which survived without exhibiting C–N bond cleavage will form a weak ammonium salt due to the decreasing basicity caused by the inductive effect of fluorine. Partially fluorinated secondary amines (**9** and **10**) which exist as a very weak cationic species in AHF progresses to **A**. However, in some parts of **9** and **10**, the fluorine α of the nitrogen is eliminated as HF resulting in fluorinated imines (**11** and **B**). *F*-(*N*-fluoro-*N*,*N*-dilakylamines) (**A**) are also formed from these imines as fluorination products. It is known that *F*-(2-azapropene) easily takes on HF resulting in *F*-(*N*,*N*-dimethylamine) with a formula of $(CF_3)_2NH$ [18].

Therefore, the addition of HF to fluorinated imines (**11** and **B**) to form partially fluorinated secondary amines (**9** and **10**) in AHF is considered to occur as a reversible interconversion between them although the formation of *F*-(*N*,*N*-dialkylamines) (**9**) was not confirmed among the ECF products in our investigation.

The results of the fluorination of *N*,*N*-di-*n*-propylamine (**4**) are shown in Scheme 3 as a typical example of the ECF of aliphatic secondary amines. *F*-(*N*-fluoro,*N*,*N*-di-*n*-propylamine) (**12**) and a *F*-imine, $n\text{-}C_3F_7N{=}CF(C_2F_5)$ (**13**), which retained the original framework of **4** but with a newly formed –N=CF– bond, were obtained as the corresponding fluorination products in low yields together with cleaved products such as C_3F_8 (**14**) (major product) and $n\text{-}C_3F_7NF_2$ (**15**).

The effect of the solute concentration of **4** on the yields of fluorination products was examined, because it is known that ECF at a higher solute concentration is one of the most effective ways for raising yields in the fluorination of tertiary amines [19–21] and secondary cyclic amines [9]. The results are shown in Table 2. However, it was found that changing the solute concentration of **4** within the range of 2.5–8.9% under comparable conditions did not improve the yield of **12**.

In the case of the ECF of *N*,*N*-di-*iso*-propylamine (**5**), the isomerization of the *iso*-propyl group to *n*-propyl group occurred at high levels which resulted in the formation of a complex mixture of products (Scheme 4). In addition, a *F*-*tert*-amine, *F*-(*N*-ethyl,*N*-methyl,*N*-*iso*-propylamine) was also obtained in small yields ($Y{=}1.5\%$).

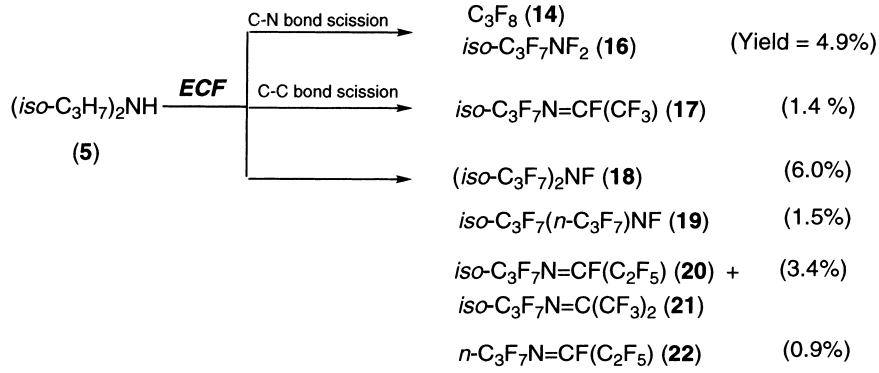
A small quantity of an isomerized product, *F*-(*N*-fluoro,*N*-*iso*-propyl,*N*-*n*-propylamine) (**19**) was also obtained ($Y{=}1.5\%$) together with the desired *F*-(*N*-fluoro-di-*iso*-propylamine) (**18**) (6.0%). As a result of the isomerization of an *iso*-propyl group, a *F*-imines mixture was formed, and *iso*-$C_3F_7N{=}C(CF_3)_2$ (**21**) could not be isolated from the mixture by means of GC. It was obtained only as an inseparable mixture with its isomeric *F*-imine, *iso*-$C_3F_7N{=}CF(C_2F_5)$ (**20**). Therefore, the composition and determination of the former *F*-imine (**21**) was conducted by comparing the sample with an authenticated sample which was prepared by reacting compound **18** with triphenylphosphine according to a method described in [22] (also see the experimental section (Scheme 3)). The formation of compound **21** is not unprecedented. It has been prepared by the photolytic reaction of perfluoropropene with nitrosylfluoride by Andreads [12].

It is known that 2-fluoro and/or a 2-methyl substituent in a pyridine ring inhibit the cleavage of the C–N bonds during ECF, which results in the enhancement of the ECF yield of pyridines with a substituent at the 2-position compared with that of pyridine [22,23]. The reason for this reduction of the

Table 2
Effect of the solute concentration of amine **4** on the composition and the yield of products

Run	Sample concentration (wt.%)	Current passed (Ah)	Fluorinated product (g)	Products[a] (yield %)
1	2.5[b]	104	7.8	C_3F_8 (**14**) (16.8), $n\text{-}c_3F_7NF_2$ (**15**) (0.3), $n\text{-}C_3F_7N{=}CF(C_2F_5)$ (**13**) (1.3), $(n\text{-}C_3F_7)_2NF$ (**12**) (5.8)
2	5.2[c]	207	18.9 (0.9)[d]	**14** (20.1), **15** (1.3), **13** (1.8), **12** (7.8)
3	8.9[e]	319	28.6 (1.3)	**14** (18.2), **15** (1.3), **13** (2.0), **12** (6.7)

[a] Arranged in order of the elution time on GC.
[b] **4** (12.8 g) was used.
[c] **4** (25.4 g) was used. The datum is duplicated with that given in Table 1.
[d] Products obtained as cell drainings.
[e] **4** (41.2 g) was fed. After 202 A h had been passed, 120 ml of AHF was added.



Scheme 4.

cleavage in the case of 2-methyl substituent is explained by the blocking effect on the C–N bond scission due to the presence of methyl group(s) which sterically protects the C–N bond. Therefore, it was expected that the degree of the scission of the C–N bond of secondary amines would be reduced when two bulky groups like di-*iso*-propylamine (**5**) are present. However, the results of ECF of **5** showed that such an effect was not observed when the *F*-(*N*-fluoro,*N*,*N*-di-*iso*-propylamine) (**18**) (*Y*=6.0%) was compared with that of *F*-(*N*-fluoro-*N*,*N*-di-*n*-propylamine) (**12**) (*Y*=6.2%) obtained from **4**.

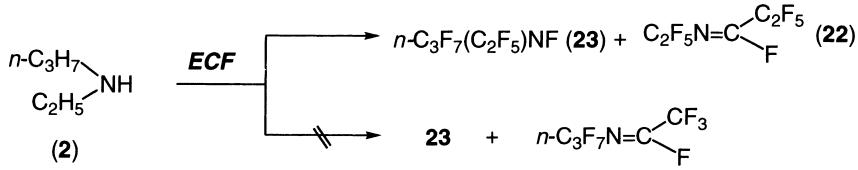
From the fluorination of such compounds as **2**, **3** and **6** which have different alkyl groups (R_1 is not equal to R_2 in Scheme 1), not only corresponding *F*-(*N*-fluoro-*N*,*N*-dialkylamines) (**A**) but also *F*-imines (**B**) were obtained in similar low yields. Although the formation of two isomeric *F*-imines (**B**) having the C=N bond at a different position was expected to be formed from these initial materials, only one **B** was formed. For example, from **2**, an imine, $C_2F_5N{=}CF(C_2F_5)$ (**22**), was formed dominantly rather than an imine with the molecular formula of n-$C_3F_7N{=}CF(CF_3)$ (Scheme 5).

Similarly, only one kind of imine, *iso*-$C_3F_7N{=}CF(CF_3)$ (**17**), was formed as the sole *F*-imine at low yield from aliphatic secondary amines such as **3** which have a branched *N*-*iso*-propyl group and a *N*-ethyl group (Scheme 6).

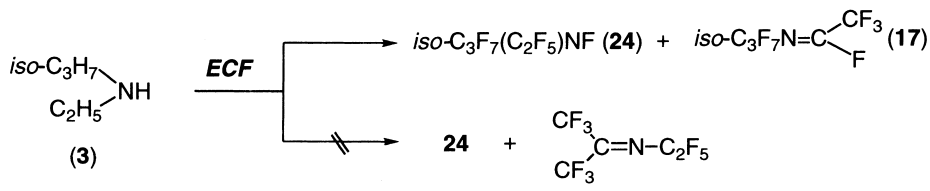
This result shows that an imine bond is apt to be formed at the site of the secondary rather than the tertiary carbon during ECF. The mechanism of the formation of *F*-imines by the ECF of secondary amines seems to be very complex as shown in Scheme 2. However, the reversible interconversion in AHF between fluorinated imines (**11** and **B**) and partially fluorinated secondary amines (**9** and **10**) seems to be an important stage for the determination of the structure of thermodynamically more stable *F*-imines as the final products. It was thus surmised that the position of the –N=C– bond of the *F*-imine formed is governed by the alkyl group of the starting aliphatic secondary amines; an imine bond forms at the site of the longer alkyl chain length and at the site of a secondary rather than a tertiary carbon, regiospecifically.

2.2. The reaction of F-(N-fluoro-N,N-di-alkylamines) (A) with triphenylphosphine

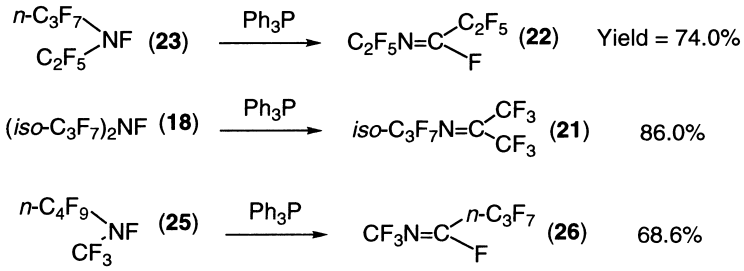
Several reactions have been known for compounds having a N–F bond [24]. For example, the fluorine of N–F of *F*-(*N*-fluoro-*N*,*N*-dialkylamines) (**A**) oxidizes iodide ion [25],



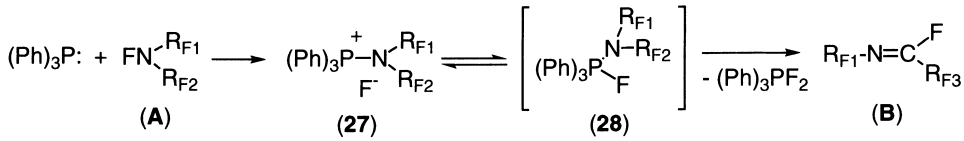
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

cyclopentadienyl iron [26,27] and dicumene chromium [26]. Furthermore, the fluorine of N–F of **A** reacts with triphenylphosphine yielding *F*-imines (**B**) as a result of the defluorination reaction [22].

We have investigated similar reactions using *F*-amines (**23**, **18** and **25**), which were separated from the ECF products of **2**, **5** and **6**, respectively, with triphenylphosphine in order to examine the product. The reaction proceeded smoothly resulting in *F*-imines at good yield as shown in Scheme 7.

It was found that only one isomic *F*-imine (**22** and **26**) was formed from **23** and **25** which have two different *N*-alkyl groups, regiospecifically. These results show that the defluorination of **A** proceeds in the same way as expected from the observation that a –C=N– bond of *F*-imine is formed at the site of the longer alkyl group.

It is considered that this reaction proceeds in a similar way to that reported for the reaction of $(Et_2N)_3P$ and CF_3Br, for example, [32]. Mechanistically, this reaction is considered to proceed via the formation of the phosphonium salt **27**, which is in equilibrium with pentavalent intermediate **28**, through a 'fluorophilic' attack of the phosphorous center of $(Ph)_3P$ by N–F of **A** (Scheme 8). Therefore, the defluorination step from this intermediate (**27** and **28**) is considered to be the key for the determination of the structure of **B** in this reaction.

3. Experimental details

Boiling points were uncorrected. All samples which were subjected to ECF were used as received. The purity of anhydrous hydrogen fluoride (AHF) (Daikin Industries Co.) was more than 99.9%. The electrolytic fluorination apparatus and operating procedures were similar to those described previously [10]. Glass vacuum line equipped with a Heise Burdon tube gauge was used for handling the volatile compounds in the reaction of *F*-(*N*-fluoro-di-alkylamines) with triphenylphosphine and the determination of the vapor pressure curve of $(C_2F_5)_2NF$. Analytical GLC work was carried out with a Shimadzu GC-2C gas chromatograph using stainless steel columns (3 mm diameter) packed with 30% 1,6-bis(1H, 1H, 12H-*F*-decyloxy)hexane on Chromosorb PAW/60–80 mesh (6.0 m) and a Shimadzu GC-14B gas chromatograph using stainless steel columns (3 mm diameter) packed with 25% Fomblin YR on Chromosorb PAW (6.4 m). A Shimadzu GC-1C gas chromatograph using stainless steel columns (10 mm diameter) packed with 30% 1,6-bis(1H, 1H, 12H-*F*-dodecyloxy)hexane on Chromosorb PAW/60–80 mesh (6.0 m) was used for semi-preparative work. The carrier gas was helium in all cases. Infrared spectra were measured on a Hitachi EPI-G3 spectrometer using a 6 cm gas cell with KBr windows. ^{19}F NMR spectra were measured on a Hitachi 20B spectrometer (56.4 MHz for ^{19}F). Chemical shifts for ^{19}F were reported respective to $CFCl_3$. Positive shifts are downfield from the reference. Mass spectra were measured on a Shimadzu GC/MS-7000 instrument at 70 eV and a Shimadzu GC/MS-QP5000 instrument fitted with a capillary column (Neutra Bond-1, 30 m long, 0.25 mm i.d., 1.5 μm thick).

3.1. Fluorination of N,N-diethylamine (1)

Sample **1** (24.3 g, 0.333 mol) was charged into a cell containing 420 ml electrically purified AHF, and the solution was subjected to fluorination with an anodic current density of 3.7 A/dm^2, a cell voltage of 5.2–5.5 V, and a cell temperature of 7–8°C over a period of 490 min (222 Ah). At the final stage of the fluorination, the voltage reached 6.2 V.

The effluent gases from the cell were passed over NaF pellets and then condensed in a trap cooled to −78°C. The

gaseous products which did not condense in the −78°C trap were then bubbled through a fluoropolymer bottle containing water and a gas washing bottle containing an aqueous solution of a mixture of K_2CO_3, KOH and KI. All products except new ones were identified by comparison of their infrared spectra and GLC retention times with those of authenticated samples. When unknown compounds existed among the fluorination products whose IR data were not available in our laboratory, they were separated from other products by use of semi-preparative GLC, and their structures were determined on the basis of ^{19}F NMR and mass spectra.

The products (8.3 g) condensed in the −78°C trap consisted of C_2F_6 (**29**) (0.3 g), $C_2F_5N{=}CF(CF_3)$ (**30**) [26] (2.2 g), $(C_2F_5)_2NF$ (**31**) [26] (5.6 g) and unidentified products (0.2 g). The GC yields of **30** and **31** were 3.1 and 6.2%, respectively. Spectral data (IR and ^{19}F NMR) of **30** and **31** are shown below.

$C_2F_5N{=}CF(CF_3)$ (**30**): IR (gas): 1785 *v*(C=N), 1344 (s), 1255 (s), 1240 (vs), 1215 (vs), 1193 (s), 1111 (m), 1095 (m), 1072 (m), 850 (w), 745 (w), 700 (w), ^{19}F NMR ($CDCl_3$): δ −29.0 (s, 1F, =CF), δ −74.1 (m, 3F, $=CCF_3$), δ −86.3 (s, 3F, CF_3), δ −97.8 (m, 2F, CF_2).

$(C_2F_5)_2NF$ (**31**): IR (gas): 1358 (w), 1227–1265 (vs), 1190 (vs), 1129 (ms), 1104 (s), 1086 (ms), 1027 (w), 857 (w), 820 (w), 740 (m), 701 (s), 651 (w), 533 (w). ^{19}F NMR ($CDCl_3$): δ −82.9 (d, 6F, J_{F-F}=16.1 Hz, CF_3), δ −108.9 (d, 4F, J_{F-F}=23.1 Hz, CF_2), δ −92.2 (m, 1F, NF). The equation $\log P$ (mm)=7.84−1474/T describes the vapor pressure curve from which ΔHv (6.8 kcal/mol), ΔSv (22.7 eu), and the bp of 24.1°C ([22]: bp 30.5°C) are obtained.

3.2. Fluorination of N-ethyl,N-n-propylamine (2)

Sample **2** (18.2 g, 0.209 mol) was fluorinated similarly under the following conditions: 2.9 A/dm^2, 5.8–6.1 V, 7–8°C, 164 Ah (393 min). The work-up gave the following products in the −78°C trap (5.0 g): C_3F_8 (**14**) (0.8 g), $C_2F_5N{=}CF(C_2F_5)$ (**22**) (1.3 g), *n*-$C_3F_7(C_2F_5)NF$ (**23**) (1.7 g), and unidentified products (1.2 g). The yield of **22** and **23** were 2.4 and 2.8%, respectively. Spectral data of **22** and **23** are shown below.

$C_2F_5N{=}CF(C_2F_5)$ (**22**): IR (gas): 1780 (s) *v*(C=N), 1344 (m), 1316 (ms), 1238 (vs), 1211 (vs), 1186 (s), 1133 (m), 1091 (ms), 1011 (m), 930 (w), 755 (w), 714 (w), ^{19}F NMR ($CDCl_3$): δ −22.5 (m, 1F, =**C**F(C_2F_5)), δ −83.4 (d, t, 3F, J_{F-F}=5.1, 1.5 Hz, **C**F_3CF_2N=), δ −86.4 (d, 3F, J_{F-F}=4.8 Hz, =C(F)CF_2**C**F_3), δ −98.0 (d, 2F, J_{F-F}=19.7 Hz, CF_3**C**F_2N=), δ −121.1 (d, q, 3F, J_{F-F}=12.8, 1.5 Hz, =C(F)**C**F_2CF_3).

n-$C_3F_7(C_2F_5)NF$ (**23**): IR (gas): 1352 (w), 1314 (m), 1256 (vs), 1206 (ms), 1180 (ms), 1136 (m), 1106 (m), 1029 (w), 986 (w), 744 (w), 714 (w), 693 (w). ^{19}F NMR ($CDCl_3$): δ −82.4 (t, d, 3F, J_{F-F}=9.0, 4.0 Hz, CF_2CF_2**C**F_3), δ −83.3 (d, 3F, J_{F-F}=16.9 Hz, CF_2**C**F_3), δ −106.9 (m, 2F, **C**$F_2CF_2CF_3$), δ −108.7 (m, 2F, **C**F_2CF_3), δ −127.2 (d, 2F, J_{F-F}=9.7 Hz, CF_2**C**F_2CF_3).

3.3. Fluorination of N-ethyl,N-iso-propylamine (3)

Sample **3** (18.0 g, 0.207 mol) was fluorinated similarly under the following conditions: 2.9 A/dm^2, 5.7–6.0 V, 7–8°C, 161 Ah (388 min). The work-up gave the following products in the −78°C trap (6.6 g): C_2F_6 (**29**)+C_3F_8 (**14**) (0.6 g), *iso*-$C_3F_7NF_2$ (**16**) (1.1 g), *iso*-$C_3F_7N{=}CF(CF_3)$ (**17**) [28] (2.0 g), *iso*-$C_3F_7(C_2F_5)NF$ (**24**) [29] (1.6 g), and unidentified products (1.3 g). The GC yields of **20** and **24** were 3.3 and 2.4%, respectively. Spectral data of **16**, **17** and **24** are shown below.

iso-$C_3F_7NF_2$ (**16**): IR (gas): 1320 (ms), 1300 (s), 1263 (vs), 1220 (ms), 1178 (s), 1131 (m), 1017 (s), 958 (m), 927 (ms), 740 (m).

iso-$C_3F_7N{=}CF(CF_3)$ (**17**): IR (gas): 1794 (ms) *v*(C=N), 1373 (w), 1219 (s), 1297 (ms), 1262 (vs), 1187 (s), 1113 (ms), 1097 (w), 1003 (s), 838 (w), 747 (w), 722 (w), 671 (m), 555 (w). ^{19}F NMR ($CDCl_3$): δ −33.4 (m, 1F, =**C**F(CF_3)), δ −74.4 (d, 3F, J_{F-F}=2.0 Hz, –CF(**C**F_3)), δ −79.2 (m, 6F, –CF(**C**F_3)$_2$), δ −153.0 (d, 1F, J_{F-F}=26.6 Hz, –**C**F(CF_3)$_2$).

iso-$C_3F_7(C_2F_5)NF$ (**24**): bp 38–39°C. IR (gas): 1311 (m, sh), 1286 (s, sh), 1261 (vs), 1188 (ms), 1154 (m), 1138 (m), 1113 (m), 1079 (w), 1023 (w), 979 (w), 741 (w), 712 (w). MS: 264 $[M-F]^+$ (36.2), 214 $C_4F_8N^+$ (100), 169 $C_3F_7^+$ (18.1), 164 $C_3F_6N^+$ (66.5), 119 $C_2F_5^+$ (48.8), 114 $C_2F_4N^+$ (25.2), 100 $C_2F_4^+$ (7.9), 69 CF_3^+ (74.4). ^{19}F NMR ($CDCl_3$): δ −74.9 (t, d, 6F, J_{F-F}=8.7, 3.7 Hz, –CF(**C**F_3)$_2$), δ −83.5 (d, 3F, J_{F-F}=17.8 Hz, –CF_2**C**F_3), δ −89.9 (m, 1F, –NF), δ −108.2 (m, 2F, –**C**F_2CF_3), δ −158.6 (m, 1F, –**C**F(CF_3)).

3.4. Fluorination of N,N-di-n-propylamine (4)

Sample **4** (25.4 g, 0.252 mol) was fluorinated similarly under the following conditions: 2.9 A/dm^2, 5.6–5.9 V, 7–8°C, 207 Ah (655 min). The products (18.9 g) condensed in the −78°C trap and the cell drained products (0.9 g) were combined and were analyzed by GC similarly. The work-up gave the following products: C_3F_8 (**14**) (9.5 g), *n*-$C_3F_7NF_2$ (**15**) (0.7 g), *n*-$C_3F_7N{=}CF(C_2F_5)$ (**13**) [29] (1.5 g), (*n*-C_3F_7)NF (**12**) [30] (7.3 g) and unidentified products (0.8 g). The yields of **13** and **12** were 1.9 and 6.2%, respectively. Spectral data of **15**, **13** and **12** are shown below.

n-$C_3F_7NF_2$ (**15**): IR (gas): 1352 (m), 1312 (m), 1265 (vs), 1213 (ms), 1175 (m), 1145 (m), 1123 (w), 1020 (m), 939 (m), 885 (m), 800 (w), 746 (m).

n-$C_3F_7N{=}CF(C_2F_5)$ (**13**): IR (gas): 1780 (s) *v*(C=N), 1345 (m), 1318 (m), 1293 (m), 1238 (vs), 1195 (s), 1175 (ms), 1138 (s), 1023 (m), 988 (ms), 968 (w), 829 (w), 751 (w), 730 (w). ^{19}F NMR ($CDCl_3$): δ −23.0 (m, 1F, =**C**F(CF_2F_3)), δ −81.4 (t, 3F, J_{F-F}=8.7 Hz, **C**$F_3F_2CF_2N$), δ −83.6 (m, 3F, =CF(CF_2**C**F_3)), δ −94.6 (m, 2F, CF_3CF_2**C**F_2N), δ −121.3 (d, 2F, J_{F-F}=13.5 Hz, =CF(**C**F_2CF_3)), δ −129.7 (m, 2F, CF_3**C**F_2CF_2N)).

(*n*-C_3F_7)$_2$NF (**12**): IR (gas): 1624–1356 (ms), 1302 (s), 1226–1256 (vs), 1204 (s), 1181 (s), 1161 (s), 1031 (s), 1012

(s), 991 (ms), 971 (m), 826 (w), 788 (w), 746 (m), 729 (m), 706 (ms), 651–681 (w). ^{19}F NMR ($CDCl_3$): δ −90.4 (m, 1F, NF), δ −82.1 (m, 6F, CF_3), δ −106.1 (m, 4F, $CF_3CF_2\mathbf{CF}_2$), δ −126.9 (m, 4F, $CF_3\mathbf{CF}_2CF_2$).

3.5. Fluorination of **4** at a lower solute concentration

Sample **4** (12.8 g, 0.126 mol) was fluorinated under similar conditions as above except for the amount of the sample fed: 3.0 A/dm^2, 6.2–6.7 V, 7–8°C, 104 A h (283 min). The products (7.8 g) condensed at −78°C were similarly analyzed by GC. The work-up gave the following products: **14** (4.0 g), **15** (0.1 g), **13** (0.5 g), **12** (2.7 g) and unidentified products (0.5 g). The yields of **14**, **15**, **13** and **12** were 16.8, 0.3, 1.2 and 5.8%, respectively.

3.6. Fluorination of **4** at a higher solute concentration

Sample **4** (41.2 g and 0.408 mol) was fluorinated under the similar conditions as above except for the amount of the sample fed and the addition of 120 ml of AHF after 202 Ah had passed: 3.0 A/dm^2, 5.9–7.1 V, 7–8°C, 320 Ah (877 min). The products (28.5 g) condensed in the −78°C trap and the cell drained products (1.3 g) were combined and were similarly analyzed by GC. The work-up gave the following products: **14** (14.0 g), **15** (1.2 g), **13** (2.8 g), **12** (8.9 g) and unidentified products (1.8 g). The yields of **14**, **15**, **13** and **12** were 18.2, 1.3, 2.0 and 6.7, respectively.

3.7. Fluorination of N,N-di-iso-propylamine (**5**)

Sample **5** (27.0 g, 0.267 mol) was fluorinated similarly under the following conditions: 3.5 A/dm^2, 5.7–6.2 V, 7–8°C, 221 Ah (580 min). The work-up gave the following products in the −78°C trap (21.0 g): C_2F_6 (**29**)+C_3F_8 (**14**) (1.6 g), *iso*-$C_3F_7NF_2$ (**16**) (2.9 g), *iso*-$C_3F_7N{=}CF(CF_3)$ (**17**) (1.1 g), *iso*-$C_3F_7N{=}CF(C_2F_5)$ (**20**)+*iso*-$C_3F_7N{=}C(CF_3)_2$ (**21**) (1.0 g), *n*-$C_3F_7N{=}CF(C_2F_5)$ (**13**) (0.8 g), *iso*-$C_3F_7NCF_3(C_2F_5)$ [28] (1.5 g), *iso*-C_3F_7(*n*-C_3F_7)NF (**19**) (2.0 g), (*iso*-$C_3F_7)_2$NF (**18**) (6.0 g), and unidentified products (4.1 g). The GC yield of **18** was 5.3%. The physicochemical properties and spectral data of **19** and **18** are shown below.

iso-C_3F_7(*n*-C_3F_7)NF (**19**): bp 74.2–74.8°C, n_D^{20}<1.28, d_4^{20} 1.7260. IR (gas): 1357 (m), 1235–1290 (vs), 1205 (s), 1179 (s), 1157 (s), 1129 (ms), 1106 (m), 1030 (ms), 997 (s), 800 (w), 742 (ms), 654 (w), 539 (w). MS: 352 $[M–F]^+$ (36.5), 314 $C_6F_{12}N^+$ (34.9), 302 $C_5F_{12}N^+$ (21.4), 264 $C_5F_{10}N^+$ (47.1), 252 $C_4F_{10}N^+$ (10.0), 214 $C_4F_8N^+$ (16.2), 169 $C_3F_7^+$ (38.7), 164 $C_3F_6N^+$ (13.6), 119 $C_2F_5^+$ (22.2), 114 $C_2F_4N^+$ (7.2), 100 $C_2F_4^+$ (6.8), 76 $C_2F_2N^+$ (6.1), 69 CF_3^+ (100), 50 CF_2^+ (3.9). ^{19}F NMR ($CDCl_3$): δ −89.2 (m, 1F, NF), δ −75.4 (s, 6F, $(\mathbf{CF}_3)_2$CF–), δ −82.6 (t, d, 3F, $J_{F–F}$=9.0, 4.2 Hz, $\mathbf{CF}_3CF_2CF_2$–), δ −105.5 (m, 2F, $CF_3CF_2\mathbf{CF}_2$–), δ −126.5 (d, 2F, $CF_3\mathbf{CF}_2CF_2$–), δ −157.8 (m, 1F, $(CF_3)_2\mathbf{CF}$–).

(*iso*-$C_3F_7)_2$NF (**18**): bp 72.8–73.5°C, n_D^{20}<1.28, d_4^{20} 1.7610. IR (gas): 250–1278 (vs), 1223 (m), 1196 (s), 1166 (s), 1122 (s), 1080 (m), 1013 (m), 987 (s), 963 (ms), 800 (w), 750 (s), 708 (s), 532 (w). MS: 371 M^+ (1.1), 352 $[M–F]^+$ (1.1), 314 $C_6F_{12}N^+$ (7.0), 302 $C_5F_{12}N^+$ (34.6), 264 $C_3F_{12}^+$ (15.9), 214 $C_4F_8N^+$ (11.0), 169 $C_3F_7^+$ (36.8), 164 $C_3F_6N^+$ (11.1), 119 $C_2F_5^+$ (12.5), 114 $C_2F_4N^+$ (6.0), 100 $C_2F_4^+$ (6.1), 76 $C_2F_2N^+$ (3.1), 69 CF_3^+ (100). ^{19}F NMR ($CDCl_3$): δ −85.1 (m, 1F, NF), δ −75.5 (s, 12F, $(\mathbf{CF}_3)_2$CF–), δ −155.3 (s, 2F, $(CF_3)_2\mathbf{CF}$–).

3.8. Fluorination of N-methyl,N-n-butylamine (**6**)

Sample **6** (21.8 g, 0.251 mol) was fluorinated similarly under the following conditions: 2.9 A/dm^2, 6.1–7.1 V, 7–8°C, 196 Ah (434 min). The work-up gave the following products in the −78°C trap (29.6 g): C_4F_{10} (25.1 g), *n*-$C_4F_9NF_2$ (**32**) [26] (2.2 g), $CF_3N{=}CF$(*n*-C_3F_7) (**26**) [31] (1.1 g), *n*-$C_4F_9(CF_3)$NF (**25**) (0.8 g), and unidentified products (0.4 g). The GC yields of **26** and **25** were 1.4 and 1.2%, respectively. Spectral data of **25**, **26** and **32** are shown below.

n-$C_4F_9NF_2$ (**32**): IR (gas): 1366 (ms), 1310 (m, sh), 1293 (ms, sh), 1265 (s, sh), 1255 (vs), 1237 (s, sh), 1203 (m), 1168 (m), 1148 (ms), 1116 (m), 1095 (w), 1065 (w), 990 (w), 947 (m), 892 (ms), 830 (w), 795 (w), 742 (ms).

$CF_3N{=}CF$(*n*-C_3F_7) (**26**): IR (gas): 1777 (m) *v*(C=N), 1350 (ms), 1287 (ms), 1256 (s, sh), 1230 (vs), 1176 (m), 1158 (w), 1140 (w), 1103 (w), 1026 (m), 978 (w), 823 (w), 742 (w), 651 (w). ^{19}F NMR ($CDCl_3$): δ −23.3 (m, 1F, $=\mathbf{CF}$(*n*-C_3F_7)), δ −57.9 (d, 3F, $J_{F–F}$=15.0 Hz, $\mathbf{CF}_3N{=}$), δ −81.2 (t, d, 3F, $J_{F–F}$=6.5, 6.8 Hz, $=C(F)CF_2CF_2\mathbf{CF}_3$), δ −118.8 (q, d, 2F, $J_{F–F}$=9.6 Hz, $=C(F)\mathbf{CF}_2CF_2CF_3$), δ −127.0 (d, 2F, $J_{F–F}$=9.6 Hz, $=C(F)CF_2\mathbf{CF}_2CF_3$).

n-$C_4F_9(CF_3)$NF (**25**): IR (gas): 1309 (s, sh), 1281 (vs), 1248 (vs), 1236 (s, sh), 1188–1218 (s, sh), 1146 (ms), 1101 (w), 1063 (w), 1032 (m), 915 (w), 861 (m), 814 (w), 743 (ms), 710 (w). ^{19}F NMR ($CDCl_3$): δ −88.0 (m, 1F, NF), δ −68.3 (d, t, 3F, $J_{F–F}$=13.5 Hz, CF_3N), δ −82.0 (t, t, 3F, $J_{F–F}$ =0.4, 1.7 Hz, $CF_2CF_2CF_2\mathbf{CF}_3$), δ −108.7 (m, 2F, $\mathbf{CF}_2CF_2CF_2CF_3$), δ −124.1 (m, 2F, $CF_2\mathbf{CF}_2CF_2CF_3$), δ −127.6 (m, 2F, $CF_2CF_2\mathbf{CF}_2CF_3$).

3.9. Reaction of F-(N-fluoro-N-ethyl,N-n-propylamine) with triphenylphosphine

In a 50 ml round bottom flask which contained 1.99 g of $P(Ph)_3$, *F*-(*N*-fluoro,*N*-ethyl,*N*-*n*-propylamine) (0.78 g, 2.43 mmol), which had been purified by GC among the fluorination products obtained from **6**, was condensed using a vacuum line, and the contents were allowed to stand overnight. The volatile products (0.59 g), which was separated from the solid residue, were obtained as clear volatile compounds. By studying the spectroscopic analysis, it was determined to be $C_2F_5N{=}CF(C_2F_5)$ (**22**). The yield for **22** was 86.0%.

3.10. Reaction of F-(N-fluoro-N,N-di-iso-propylamine) with triphenylphosphine

The reaction of *F*-(*N*-fluoro-*N*,*N*-di-*iso*-propylamine) (0.87 g, 2.35 mmol) and $P(Ph)_3$ (1.99 g, 7.59 mmol) was conducted similarly. The work-up of the product yielded 0.58 g of *iso*-$C_3F_7N{=}C(CF_3)_2$ (**21**) (Y=74.0%). The physicochemical properties and spectral data of **21** are shown below.

iso-$C_3F_7N{=}C(CF_3)_2$ (**21**): bp 50.7–51.0°C, n_D^{20}<1.28, d_4^{20} 1.6117. IR (gas): 1746 ν(C=N), 1337 (ms), 1310 (s), 1250–1280 (vs), 1220 (vs), 1187 (m), 1171 (w), 1143 (ms), 1099 (ms), 998 (s), 987 (ms, sh), 743 (m), 733 (m), 687 (m), 655 (w). ^{19}F NMR of this compound shows a very peculiar spectra at room temperature due to the slow conversion between two tutomers, which has been published by Andreads [12]. ^{19}F NMR ($CDCl_3$): δ −78.4 (m, 6F, $(\mathbf{CF}_3)_2$CF–), δ −149.2 (m, 1F, $(CF_3)_2\mathbf{CF}$–), δ −68.0 (broad, 6F, $=C(\mathbf{CF}_3)_2$.

3.11. Reaction of F-(N-fluoro-N-methyl,N-n-butylamine) with triphenylphosphine

The reaction of *F*-(*N*-fluoro,*N*-methyl,*N*-*n*-butylamine) (**25**) (1.01 g, 3.15 mmol) and $P(Ph)_3$ (1.95 g, 7.43 mmol) was conducted similarly. The work-up of the product yielded 0.61 g (2.16 mmol) of $CF_3N{=}CF(n\text{-}C_3F_7)$ (**26**) as the defluorination product (Y=68.6%).

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