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# A Novel Synthesis of *N*-Fluoroperfluoroalkanimines. Reaction of Perfluorinated Secondary Amines with $SbF_5$

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Perfluorinated secondary amines prepared by the reaction of the corresponding internal azaalkenes with fluorine gas in the presence of a metal fluoride undergo a cleavage reaction with $SbF_5$ at elevated temperatures. The reaction results in the formation of a mixture of perfluoroalkane and *N*-fluoroalkanimine. Reaction of $(CF_3)_2CF{-}N(F){-}C_2F_5$ with $SbF_5$ is exothermic at 22 °C giving a mixture of $C_2F_6$ and perfluoro-2-azabutene-2. An intermediate step of the latter reaction is the isomerization of the *N*-fluoroalkanimine of hexafluoroacetone by $SbF_5$, resulting in the formation of perfluoro-2-azabutene-2.

## Introduction

Lewis acid induced cleavage of perfluorinated amines is a general reaction. It has been reported for difluoroamino compounds,[2] perfluorotrimethylamine,[3] and perfluorinated tertiary amines of different structures.[4-6] The last reaction was employed as an alternative route for synthesis of perfluoroazaalkanes.[4-6]

$$(R_f)_2N{-}CF_2R_f' \xrightarrow[SbF_5]{100\ ^\circ C} R_fN{=}CFR_f' + R_f{-}F$$

Perfluorinated secondary amines are readily available by the metal fluoride catalyzed addition of fluorine to perfluoroazaalkenes.

$$R_fN{=}CFR_f' + F_2 \xrightarrow{MF} (R_f)_2N{-}F$$

The reaction of these compounds with $SbF_5$ was undertaken as a possible route to *N*-fluoroalkanimines, which can only be obtained in general by dehalogenation of the corresponding primary amines of the type $R_fCFXNFX$ (X = Cl, F).[7]

## Experimental Section

*Caution! We did not experience any stability problems in this study, but N-fluoro compounds and elemental fluorine must be handled with caution and by well-trained personnel.* All volatile reactants were handled in either a stainless steel (Type 304 or 316) or a glass vacuum system equipped with stainless steel or Teflon–glass valves, respectively. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were measured by *PVT* measurements, assuming ideal gas behavior. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer with a Model 7500 data station using a 10-cm glass cell fitted with KCl windows. $^{19}F$ spectra were recorded on an IBM NR 200 AF instrument using $CFCl_3$ as internal reference and $CDCl_3$ as a lock solvent. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer at 70 eV for EI and CI ($CH_4$). Samples were introduced by direct gas injection.

Compound **15** and an isomeric mixture of imines **14a,b** were isolated by preparative GLC (Halocarbon K -352, 3 m, carrier gas He, 25 mL/min, oven temperatures 50 and 70 °C, respectively). Boiling points were determined by the Siwoloboff[8] method and are uncorrected.

Potassium fluoride and CsF were obtained from commercial sources and were activated by fusion in a platinum crucible and grinding in a ball mill under very anhydrous conditions. $SbF_5$ (PCR Inc.) was used as obtained. Fluorine was obtained from Air Products and Chemicals, Inc. and was passed through a NaF scrubber before use.

Compounds $C_3F_7N{=}CFC_2F_5$ (**3**), $C_4F_9N{=}CFC_3F_7$ (**4**),[4] and $(CF_3)_2CFN{=}CFCF_3$ (**6**)[9] were prepared according to literature methods. Compounds **1** and **5a,b** were prepared by an extension of literature method[4] and were characterized as follows:

**1.** Yield: 88.7%. Bp: 125–126 °C (130 mmHg). IR (liquid): 1769 cm$^{-1}$ (C=N). $^{19}F$ NMR for $CF_3{}^{A}CF_2{}^{G}CF_2{}^{I}CF_2{}^{F}CF_2{}^{F}$-$CF_2{}^{C}{-}N{=}CF^{D}{-}CF_2{}^{E}CF_2{}^{F}CF_2{}^{G}CF_3{}^{B}$: A, B = –81.2 (m), C = –93.2 (d–t), D = –19.9 (br s), E = –117.6 (q), F = –122.4, –122.9, –123.3, I = –125.1, G = –125.6 (m) ppm; $J_{C-D}$ = 19, $J_{C-F}$ = 9, $J_{E-D}$ = $J_{E-F}$ = 10 Hz. Mass spectrum, *m/z* [CI] (relative intensity): 634 (M + 1$^+$, 1), 614 ($C_{12}F_{24}N^+$, 2), 414 ($C_8F_{16}N^+$, 2), 364 ($C_7F_{14}N^+$, 6), 319 ($C_6F_{13}{}^+$, 6), 231 ($C_5F_9{}^+$, 6), 181 ($C_4F_7{}^+$, 10), 169 ($C_3F_7{}^+$, 23), 131 ($C_3F_5{}^+$, 100).

**5a,b.** Yield: 73% (mixture of two isomers, ratio **5a**:**5b** = 57:43). Bp: 125–127 °C; IR (mixture of isomers, liquid film): 1769 cm$^{-1}$ (C=N); $^{19}F$ NMR for $CF_3{}^{A}CF_2{}^{L}CF_2{}^{G}CF_2{}^{K}CF_2{}^{C}{-}N{=}CF^{D}CF_2{}^{E}CF_2{}^{I}CF_2{}^{F}CF_3{}^{B}$ (**5a**): A, B = –81.4 (t), C = –93.5 (d–t), D = –20.3 (m), *E* = –118.0 (d–t), I, K, L, F, G = –126.9, –125.4, –123.3 (m) ppm; $J_{E-D}$ = $J_{E-F}$ = 11, $J_{C-D}$ = 21, $J_{C-G}$ = 12 Hz. $^{19}F$ NMR for $CF_3{}^{A}CF_2{}^{M}CF_2{}^{L}CF_2{}^{K}$-$CF_2{}^{C}{-}N{=}CF^{D}CF^{I}(CF_3{}^{E})CF^{F}F^{G}CF_3{}^{B}$ (**5b**): A = –81.4 (t), B = –81.0 (d), C = –93.2 (d–t), D = –13.0 (br m), E = –73.0 (d), F = –119.8 (d–q), G = –122.9 (d–m), I = –181.8 (m), K = –123.3 (m), L = –123.6 (m), M = –126.4 (m) ppm; $J_{F-G}$ = 294, $J_{C-D}$ = 23, $J_{B-I}$ = 12, $J_{C-L}$ = $J_{F-I}$ = 11 Hz. Mass spectrum, *m/z* [EI] (relative intensity), mixture of isomers: 514 (M – F$^+$, 7), 314 ($C_6F_{12}N^+$, 20), 181 ($C_4F_7{}^+$, 11), 131 ($C_3F_5{}^+$, 27), 69 ($CF_3{}^+$, 100).

The known compounds $(C_3F_7)_2N{-}F$[10] (**7**), $C_3F_7CF{=}NF$[7a] (**12**), $C_2F_5CF{=}NF$[7b] (**14**), $CF_3N{=}CFCF_3$[11] (**20**), and $C_2F_6$[12] (**19**) were identified by a comparison of their IR and NMR spectra with literature data. Perfluoropropane (**13**), *n*-$C_4F_{10}$ (**11**), the isomeric perfluoropentanes **15a,b** and *n*-perfluorohexane (**17**) were identified by comparison with authentic samples.

**General Procedure for the Reaction of Imines with Fluorine Gas.** A 100-mL stainless steel reactor, which was briefly passivated with 1 atm of fluorine at 22 °C, was used in all reactions. The desired portion of fused alkali metal fluoride was placed into the reactor in a drybox. The vessel was evacuated and cooled by liquid nitrogen, and the corresponding imine was condensed in from the metal vacuum line. An excess of fluorine was then added by partial condensation, and the reactor was slowly warmed

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**Table I.** Addition of $F_2$ to Perfluoroazaalkenes

| imine (amount/mmol) | $F_2$, MF[a] | time/h[i] | product (%) |
|---|---|---|---|
| $C_6F_{13}N{=}CFC_5F_{11}$, **1** (5) | 10[b] | 44 | **1** (97) |
| $C_6F_{13}N{=}CFC_5F_{11}$, **1** (4.9) | 9, 3.9[c] | 30 | $(n\text{-}C_6F_{13})_2NF$, **2** (97) |
| $C_3F_7N{=}CFC_2F_5$, **3** (6.0) | 7.2, 0.7[d] | 28 | $(n\text{-}C_3F_7)_2NF$, **7** (97) |
| $C_4F_9N{=}CFC_3F_7$, **4** (2) | 9.4, 0.7[d] | 28 | $(n\text{-}C_4F_9)_2NF$, **8** (98) |
| $C_5F_{11}N{=}CFC_4F_9$,[e] **5** (4.7) | 8, 2[f] | 27 | $(C_5F_{11})_2NF$, **9**[g] (90) |
| $i\text{-}C_3F_7N{=}CFCF_3$, **6** (9.3) | 13, 39[c] | 28 | $\genfrac{}{}{0pt}{}{i\text{-}C_3F_7}{C_2F_5}{>}NF$, **10** (99) |

[a] In mmol. [b] Without catalyst. [c] CsF (dry). [d] CsF (fused). [e] Mixture of $n\text{-}C_5F_{11}N{=}CF{-}n\text{-}C_4F_9$ and $n\text{-}C_5F_{11}{-}N{=}CF{-}CF(CF_3)C_2F_5$ in a 57:43 ratio. [f] KF (fused). [g] Mixture of $(n\text{-}C_5F_{11})_2N{-}F$ (**9a**) and $n\text{-}C_5F_{11}{-}N(F){-}CF(CF_3)C_2F_5$ (**9b**) in a 58:42 ratio. [i] −196 °C to +22 °C (8–10 h), then at 22 °C.

to room temperature in a cold dewar (8–10 h). The total reaction time was 26–28 h. The reactor was then cooled to −196 °C, and unreacted fluorine was pumped out through a soda lime column. The product of fluorination was then removed from the reactor by vacuum transfer. The purity of the secondary amines according to GLC was >98%. The reaction conditions, yields and ratio of reactants are summarized in Table I.

**$(n\text{-}C_4F_9)_2N{-}F$ (8).** Bp: 114–115 °C. IR (10 Torr): 1354 (m), 1301 (m), 1249 (s), 1199 (m), 1141 (s), 1102 (m), 1055, 1026, 1001 (m), 955 (m), 933 (m), 909 (m), 888 (m), 734 (m), 708 (m), 686 (m), 605 (m), 582 (m), cm$^{-1}$. $^{19}$F NMR for $(CF_3{}^ACF_2{}^ECF_2{}^DCF_2{}^B)_2N{-}F^C$: A = −81.4 (6 F, t), B = −105.3 (4 F, pent), C = −90.5 (1 F, hept–m), D = −125.45 (4 F, m), E = −127.4 (4 F, br s) ppm; $J_{B-C}$ = 23, $J_{A-D}$ = $J_{D-E}$ = 10, $J_{B-E}$ = 6 Hz. Mass spectrum, *m/z* [CI] (relative intensity): 472 (M + 1$^+$, 5), 452 ($C_8F_{18}N^+$, 100), 414 ($C_8F_{16}N^+$, 29), 302 ($C_5F_{12}N^+$, 20), 131 ($C_3F_5{}^+$, 53), 100 ($C_2F_4{}^+$, 53).

**$(n\text{-}C_5F_{11})_2N\text{-}F$ (9a, 52%) and $n\text{-}C_5F_{11}N(F)CF_2CF(CF_3)C_2F_5$ (9b, 48%).** Bp: 156–158 °C. IR (gas): 1251 (s), 1222 (s), 1147 (m), 1047 (m), 1025, 895, 732, 577 (m) cm$^{-1}$. Mass spectrum, *m/z* [CI] (relative intensity): 572 (M + 1$^+$, 6), 552 ($C_{10}F_{22}N^+$, 27), 514 ($C_{10}F_{20}N^+$, 10), 352 ($C_6F_{13}N^+$, 95), 269 ($C_5F_{11}{}^+$, 58), 219 ($C_4F_9{}^+$, 9), 181 ($C_4F_7{}^+$, 21), 131 ($C_3F_5{}^+$, 100), 119 ($C_2F_5$, 84). $^{19}$F NMR for $(CF_3{}^ACF_2{}^FCF_2{}^ECF_2{}^D\text{-}CF_2{}^B)_2N{-}F^C$ (**9a**): A = −81.3 (6 F, t), B = −105.2 (4 F, d–pent), C = −90.5 (1 F, hept–m), D = −122.7 (4 F, m), E = −124.0 (4 F, br s), F = −126.5 (4 F, pent) ppm; $J_{A-E}$ = 10, $J_{B-E}$ = 24, $J_{D-E}$ = 11 Hz. $^{19}$F NMR for $CF_3{}^LCF_2{}^KCF^N(CF_3{}^M)CF^IF^G{-}N(F^C){-}CF_2{}^BCF_2{}^DCF_2{}^ECF_2{}^FCF_3{}^A$ (**9b**): A = −81 (3 F, t), B = −104 (2 F, d–oct), C = −87.3 (1 F, br m), D = −122.7 (2 F, m), E = −124.0 (2 F, m), F = −126.5 (2 F, pent), I = −98.7, G = −106.0 (2 F, A:B pattern), L = −80.9 (3 F, oct), M = −72.3 (3 F, m), N = −184.7 (1 F, m), K = −122.3 (2 F, m) ppm; $J_{I-G}$ = 248 Hz.

**$(n\text{-}C_6F_{13})_2N{-}F$ (2).** Bp: 50–51 (17 mmHg). IR (liquid): 1318 (s), 1237 (vs), 1203 (vs), 1144 (s), 1093 (m), 1062 (m), 1025 (m), 985 (m), 849 (m), 813 (m), 785 (s), 737 (m), 718 (m), 651 (m) cm$^{-1}$. $^{19}$F NMR for $(CF_3{}^ACF_2{}^GCF_2{}^FCF_2{}^ECF_2{}^DCF_2{}^B)_2N{-}F^C$: A = −81.7 (6 F, sext), B = −104.9 (4 F, d–m), C = −90.4 (1 F, hept–m), D = −122.5 (4 F, br m), E, F = −123.3 (8 F, br s), G = −126.5 (4 F, br s) ppm; $J_{B-C}$ = 24, $J_{A-F}$ = 7 Hz. Mass spectrum, *m/z* [CI] (relative intensity): 672 (M + 1$^+$, 2), 652 ($C_{12}F_{26}N^+$, 6), 464 ($C_9F_{18}N^+$, 4), 414 ($C_8F_{15}N^+$, 4), 364 ($C_7F_{14}N^+$, 4), 181 ($C_4F_7{}^+$, 10), 169 ($C_3F_7{}^+$, 31), 131 ($C_3F_5{}^+$, 69), 119 ($C_2F_5{}^+$, 69), 101 ($C_2F_4H^+$, 100).

**$(CF_3)_2CF\text{-}N(F)C_2F_5$ (10).** IR (gas, 10 Torr): 1256 (vs), 1188 (s), 1153 (s), 1136 (s), 1120 (m), 1079 (m), 1021 (m), 972 (m), 813 (m), 736 (m), 709 (s), 613 (w) cm$^{-1}$. $^{19}$F NMR for $(CF_3{}^A)_2CF^E{-}N(F^B)CF_2{}^CCF_3{}^D$: A = −74.6 (6 F, d–t–d), B = −90.0 (1 F, m), C = −108.5, (2 F, t–sept), D = −82.8 (3 F, d), E = −158.5 (1 F, t–m) ppm; $J_{A-B}$ = 17, $J_{A-C}$ = 9, $J_{A-E}$ = 4, $J_{B-D}$ = 17, $J_{C-E}$ = 21 Hz.

**General Procedure for the Reaction of Secondary Amines with $SbF_5$.** Into a 100-mL Pyrex round-bottom flask equipped with a glass–Teflon valve was added a portion of $SbF_5$, and then the secondary amine was condensed in by vacuum transfer. The reactor was then heated at 70–110 °C for 10–18 h. The mixture of alkane and the corresponding imine were isolated by trap-to-trap distillation in vacuum. Experimental data are summarized in Table II.

The isomeric mixture of *syn*-$n\text{-}C_4F_9CF{=}NF$ (**16a**) and *syn*-$C_2F_5\text{-}CF(CF_3)CF{=}NF$ (**16b**) was isolated by preparative GLC (ratio of isomers 59:41, respectively) and was characterized as follows. Bp: 51–53 °C. IR (10 Torr): 1677 (m) (C=N), 1354 (m), 1273 (m), 1246 (s), 1148 (m), 1103 (s), 1026 (s), 958 (m), 912 (m), 890 (m), 820, 797, 739, 646 (m) cm$^{-1}$. Mass spectrum, *m/z* [CI] (relative intensity): 284 (M + 1$^+$, 100), 264 ($C_5F_{10}N^+$, 5), 214 ($C_5F_8N_9{}^+$, 2), 181 ($C_4F_7{}^+$, 1), 131 ($C_3F_5{}^+$, 10), 119 ($C_2F_5{}^+$, 5). $^{19}$F NMR for $CF_3{}^ACF_2{}^FCF_2{}^ECF_2{}^BCF^C{=}NF^D$ (**16a**): A = −81.3 (3 F, t), B = −118.3 (2 F, d–t), C = −74.8 (1 F, d–m), D = −13.9 (1 F, br d), E = −123.7 (2 F, m), F = −126.9 (2 F, m) ppm; $J_{C-D}$ = 40, $J_{C-E}$ = $J_{A-E}$ = 11 Hz. $^{19}$F NMR for *syn*-$CF_3{}^ACF^FF^GCF^B(CF_3{}^E)\text{-}CF^C{=}NF^D$ (**16b**): A = −81.3 (3 F, m), B = −188.0 (1 F, m), C = −70.0 (1 F, d–m), D = −12.5 (1 F, br d), E = −72.83 (3 F, dtd), F = −120.1, G = −123.2 (2 F, typical A:B pattern); $J_{F-G}$ = 296, $J_{C-D}$ = 40, $J_{E-F}$ = $J_{B-F}$ = 10, $J_{B-C}$ = 12 Hz.

**Table II.** Reaction of Perfluorinated Secondary Amines with $SbF_5$

| reactant (amt/mmol) | $SbF_5$[a] | temp/°C, time/h | products (%)[b] |
|---|---|---|---|
| $(n\text{-}C_4F_9)_2NF$, **8** (5.4) | 6 | 80, 15 | $n\text{-}C_4F_{10}$, **11** (95)<br>$n\text{-}C_3F_7CF{=}NF$, **12** (78) |
| $(n\text{-}C_3F_7)_2NF$, **7** 2.0 | 0.5 | 120, 20 | $C_3F_8$, **13** (50); **7** (50)<br>$C_2F_5CF{=}NF$, **14** (18)[c] |
| $(C_5F_{11})_2NF$, **9a,b**[d] (1.4) | 3.5 | 110, 18 | $n\text{-}C_5F_{12}$, **15a**/$C_2F_5CF(CF_3)_2$, **15b** (52); $n\text{-}C_4F_9CF{=}NF$, **16a**/$C_2F_5CF(CF_3)CF{=}NF$, **16b** (50)[e,f] |
| $(n\text{-}C_6F_{13})_2NF$, **2** (1.1) | 1.9 | 80, 15 | $n\text{-}C_6F_{14}$, **17** (76)<br>$n\text{-}C_5F_{11}CF{=}NF$, **18** (76)[f] |

[a] In mmol. [b] Calculated yields (GLC and NMR). [c] Some unidentified polymeric material was formed. [d] Ratio of isomers 52:48 (normal and iso, respectively). [e] Ratio of isomers 59:41 (normal and iso, respectively). [f] Isolated by preparative GLC.

***syn*-$n\text{-}C_5F_{11}CF{=}NF$ (18) (Isolated by Preparative GLC).** Bp: 74–75 °C. IR (6 Torr): 1762 (w), 1676 (m, C=N), 1344 (m), 1232 (s), 1151 (s), 1109 (m), 1084, 1062 (m), 948 (s), 875 (m), 849 (m), 802 (m), 778 (m), 731 (m) cm$^{-1}$. $^{19}$F NMR for $CF_3{}^ACF_2{}^GCF_2{}^FCF_2{}^ECF_2{}^BCF^C{=}NF^D$: A = −81.2 (3 F, m), B = −118.1 (2 F, m), C = −74.7 (1 F, d–m), D = −14.0 (1 F, d–m), E, F = −123.0 (4 F, br s), G = −126.7 (2 F, br s) ppm; $J_{C-D}$ = 42, $J_{C-E}$ = 12 Hz. Mass spectrum, *m/z* [CI] (relative intensity): 334 (M + 1$^+$, 100), 314 ($C_6F_{12}N^+$, 3), 295 ($C_6F_{11}N^+$, 3), 284 ($C_5F_{11}\text{-}NH^+$, 3), 269 ($C_5F_{11}{}^+$, 3), 181 ($C_4F_7{}^+$, 5), 131 ($C_3F_5{}^+$, 7), 119 ($C_2F_5{}^+$, 6).

**Reaction of $(CF_3)_2CF{-}N(F){-}C_2F_5$ (10) with $SbF_5$.** Into a 100-mL glass flask fitted with a glass–Teflon valve and containing a Teflon-covered magnetic stir bar were placed 4.1 g (18.9 mmol) of $SbF_5$ and 3 mmol of **10** as above. The reaction mixture was warmed to room temperature over 10 min, and an exothermic reaction was observed after 5 min. The reaction mixture was stirred at 22 °C for 30 min, and the contents of the reactor were then separated by a trap-to-trap distillation through a series of traps which were kept at −70 and −196 °C. A 5.8-mmol (90%) yield of a mixture **19** and **20** was found in the −196 °C trap in a 1:1 ratio (NMR, IR).

**Reaction of the Imine $(CF_3)_2C{=}NF$ (21) with $SbF_5$.** As above a 1.1 mmol mixture of 85% of **21** and 15% of the amine $(CF_3)_2CFNF_2$ (**22**) with $SbF_5$ (2.2 g, 20 min, 22 °C) resulted in the isolation of 1 mmol of a mixture of **20** and **22** (87:13, respectively).

## Results and Discussion

The reaction of internal perfluoroazaalkenes with fluorine was chosen as a route for the synthesis of the perfluorinated secondary amines. It was previously known that at 22 °C, fluorine adds to some polyfluorinated compounds containing a C=N bond,[13] such as *N*-haloalkanimines and terminal azaalkenes, without a catalyst. Internal perfluoroazaalkenes are more resistant toward the addition of fluorine, and $C_6F_{13}N{=}CFC_5F_{11}$ (**1**) does not react with $F_2$ at 22 °C.

$$\mathbf{1} + F_2 \xrightarrow{44\text{ h, }22\text{ °C}} \text{no reaction}$$

However, in the presence of a catalytic amount of CsF, the secondary amine perfluoro-*n*-hexylamine (**2**) was isolated in 95% yield as a product of fluorination.

$$\mathbf{1} + F_2 \xrightarrow[\text{CsF}]{29\text{ h, }22\text{ °C}} \underset{\mathbf{2}}{(n\text{-}C_6F_{13})_2N\text{-}F}\ (95\%)$$

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Under similar reaction conditions the perfluoroazaalkenes **3–6** were also converted into the corresponding amines **7–10**.

$$R_fN{=}CF{-}R'_f \quad + F_2 \xrightarrow[\text{MF}]{\text{27–29 h, 22 °C}}$$

$R_f = n\text{-}C_3F_7$; $R_f' = C_2F_5$ (**3**)
$R_f = n\text{-}C_4F_9$; $R_f' = n\text{-}C_3F_7$ (**4**)
$R_f = n\text{-}C_5F_{11}$; $R_f' = n\text{-}/i\text{-}C_4F_9$ (**5a,b**)
$R_f = i\text{-}C_3F_7$; $R_f' = CF_3$ (**6**)

$$R_f{-}N(F){-}R''_f$$

$R_f = R_f'' = n\text{-}C_3F_7$ (**7**)
$R_f = R_f'' = n\text{-}C_4F_9$ (**8**)
$R_f = n\text{-}C_5F_{11}$; $R_f'' = n\text{-}/i\text{-}C_5F_{11}$ (**9a,b**)
$R_f = i\text{-}C_3F_7$; $R_f'' = C_2F_5$ (**10**)

Data for these reactions are summarized in Table I. Both CsF and KF may be used as catalysts, and no difference in catalytic activity was found when the dry powdered catalysts were employed.

Reaction of amines **2, 7–9** with $SbF_5$ on heating (70–100 °C) results in the formation of a mixture perfluoroalkane and the corresponding *N*-fluoroalkanimine (Table II).

$$\underset{\mathbf{2,\,7\text{–}9}}{(R_f)_2{-}NF} \xrightarrow[SbF_5]{\text{70–100 °C, 10–12 h}} R_f{-}F \quad + \quad R_f'{-}CF{=}N{-}F$$

| $R_f{-}F$ | $R_f'{-}CF{=}N{-}F$ |
|---|---|
| $R_f = n\text{-}C_4F_9$ (**11**) | $R_f' = n\text{-}C_3F_7$ (**12**) |
| $R_f = n\text{-}C_3F_7$ (**13**) | $R_f' = C_2F_5$ (**14**) |
| $R_f = i\text{-}C_5F_{11}$ (**15a**) | $R_f' = n\text{-}C_4F_9$ (**16a**) |
| $R_f = n\text{-}C_5F_{11}$ (**15b**) | $R_f' = i\text{-}C_4F_9$ (**16b**) |
| $R_f = n\text{-}C_6F_{13}$ (**17**) | $R_f' = n\text{-}C_5F_{11}$ (**18**) |

In the case of **7** the amount of $SbF_5$ was low and a temperature of 120 °C gave only a 50% conversion and a low yield of **14**. Some of the **14** was apparently polymerized under these conditions. The imine $CF_2{=}NF$ has previously been shown to polymerize with $SbF_5$.[14]

The cleavage of secondary amines by $SbF_5$ clearly proceeds under milder conditions than that of tertiary amines. For example, perfluorotributylamine[4] reacts with antimony pentafluoride only at 110–120 °C. Recently it has been demonstrated[15] that cyclic tertiary amines containing substituents in the α-position to nitrogen (i.e. perfluoro-1,2-dimethylpiperidine) are also more reactive toward $SbF_5$ than the 1,3- and 1,4-isomers. The result of the reaction of amine **10** with $SbF_5$ is in excellent agreement with the latter results. Compound **10** reacts with $SbF_5$ exothermally producing $C_2F_6$ and perfluoro-2-azabutene-2 (**20**) in high yield.

$$\underset{\mathbf{10}}{(CF_3)_2CF{-}N(F){-}C_2F_5} \xrightarrow[SbF_5]{22\,°C} \underset{\mathbf{19}}{C_2F_6} + \underset{\mathbf{20}}{CF_3{-}N{=}CF{-}CF_3} \qquad (1{:}1,\ 90\%)$$

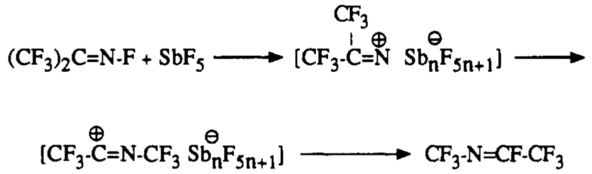
This reaction probably proceeds through the formation of the *N*-fluoroalkanimine of hexafluoroacetone (**21**), which then isomerizes into azaalkene **20**.

$$\underset{\mathbf{10}}{(CF_3)_2CF{-}N(F){-}C_2F_5} \xrightarrow{SbF_5} \mathbf{19} + [\underset{\mathbf{21}}{(CF_3)_2C{=}N{-}F}] \rightarrow \underset{\mathbf{20}}{CF_3{-}N{=}CF{-}CF_3}$$

This was proven in a separate experiment in which $SbF_5$ reacted exothermally with compound **21** to give azaalkene **20** in high yield.

$$\underset{\mathbf{21}}{(CF_3)_2C{=}NF}/\underset{\mathbf{22}}{(CF_3)_2CF{-}NF_2} \xrightarrow{SbF_5} \underset{\mathbf{20}}{CF_3{-}N{=}CF{-}CF_3} + \mathbf{22}$$

Under these conditions **22** did not react with $SbF_5$. A probable reaction pathway involves the ionization of the N–F bond by the strong Lewis acid, followed by a 1,2-migration of the $CF_3$ group from carbon to nitrogen.



$$(CF_3)_2C{=}N\text{-}F + SbF_5 \longrightarrow [CF_3\text{-}\overset{\overset{\textstyle CF_3}{|}}{C}{=}\overset{\oplus}{N}\ \overset{\ominus}{Sb_nF_{5n+1}}] \longrightarrow$$

$$[CF_3\text{-}\overset{\oplus}{C}{=}N\text{-}CF_3\ \overset{\ominus}{Sb_nF_{5n+1}}] \longrightarrow CF_3\text{-}N{=}CF\text{-}CF_3$$

This process leads to the formation of a more stable carbocation from the less stable aza cation. Addition of fluoride anion to the latter gives the observed product.

Formally, rearrangement of the imine of hexafluoroacetone with $SbF_5$ is a variant of the Beckmann rearrangement. This type of reaction is known for polyfluorinated compounds: decomposition of perfluoroacylazides giving isocyanates[16] and thermal reactions of azidoperfluoroazaalkenes forming perfluorinated carbodiimides.[17] These reactions include the formation of an energetic intermediate as a result of the thermal elimination of $N_2$ from the azido group. Our results on the reaction of imine **21** with $SbF_5$ demonstrate that related rearrangements of perfluoroorganic compounds are possible using strong Lewis acids as a catalyst.

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