

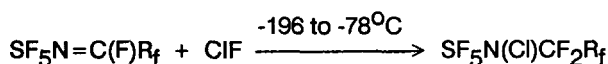
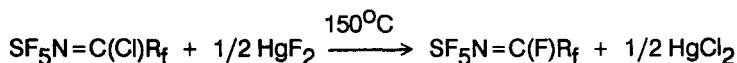
SYNTHESIS OF NEW PERFLUOROTERTIARY AMINES CONTAINING GEMINAL PENTAFLUOROSULFANYL, SF₅, GROUPS

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SUMMARY

The perfluorinated tertiary amines (SF₅)₂NCF₃ [1], (SF₅)₂NC₂F₅, and (SF₅)₂NC₃F₇ have been prepared by the following scheme. Their overall yields were found to decrease markedly with respect to increases in the length of the perfluoro-



alkyl chain. In fact, attempts to prepare (SF₅)₂NC₄F₉ have been unsuccessful thus far. The *N*-chloroamines were also reacted with simple olefins to give a variety of addition products such as SF₅N(CF₃)CH₂CH₂Cl, SF₅N(CF₃)CF₂CF₂Cl, SF₅N(C₂F₅)CH₂CH₂Cl, and SF₅N(C₄F₉)CH₂CH₂Cl.

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INTRODUCTION

Amines of the type $(R_f)_3N$, where R_f = perfluoroalkyl, are increasingly becoming the most commercially important of all fluorinated organonitrogen compounds [2]. The two primary areas of application include the electronics industry, where perfluorinated tertiary amines (PTAs) are being used as evaporation coolants for electrical equipment [3], and the medical field, where PTAs are being studied as potential blood substitutes [4]. The diverse utility of the PTAs is due largely to their great thermal stability (up to ca. 250°C in stainless steel) and resistance to chemical attack (not attacked by most oxidizing or reducing agents and strong acids or bases) [5]. Other useful properties are the direct result of the low intermolecular forces and low polarizabilities of the PTAs. These two factors help account for the high solubility of gases such as oxygen and carbon dioxide in the PTAs, thus making them far more attractive as blood substitutes than traditional plasma materials [4,5]. Currently the only commercial method of preparing the PTAs is by electrochemical fluorination. This method is limited because of the large number of side products obtained along with each desired product.

An ongoing project in our laboratory concentrates on the synthesis of new PTAs which would fit the formula type $(R_f)_{3-x}N(EF_5)_x$, where E = S, Se, or Te. Our interest herein is not only to synthesize more members of this interesting class of compounds, but also to prepare examples which might help answer fundamental questions about chemistry. The choice of the pentafluorochalcogen group is based on the well-known inertness of sulfur hexafluoride [6]. In fact, sulfur hexafluoride is used in the electronics industry as a gaseous insulator [6], and two SF_6 derivatives, namely $C_4F_9SF_5$ and $(C_4F_9)_2SF_4$, have been tested as perfluorinated blood substitutes [4]. It is not expected that the proposed selenium and tellurium analogues would have the same chemical inertness based on the increased reactivity of their parent hexafluorides, and thus their potential for toxicity would be greatly increased. The interest in preparing these derivatives would be in completing a systematic study moving down Group 16, especially when considering the fact that not a single $SeF_5N<$ derivative has been prepared to date [7].

At the outset only a few compounds such as $(CF_3)_2NSF_5$ [8] and $CF_3(C_2F_5)NSF_5$ [9] were known which would fit the proposed formula type $(R_f)_{3-x}N(EF_5)_x$. We have recently been able to prepare several new members including $CF_3N(SF_5)_2$ [1], $CF_3N(SF_5)TeF_5$, and $CF_3N(TeF_5)_2$ [10]. These tertiary amines were prepared in two steps from the respective mercurial $Hg[N(CF_3)EF_5]_2$, where E = S or Te. A number of other tertiary amines of the type $CF_3N(X)EF_5$, where X = H, F, Cl, Br, I, CH_3 , CH_2CH_2Br , $CF_2CF(Br)CF_3$, and $CF(CF_3)CF_2Br$,

were also prepared [1,10]. An X-ray crystal structure analysis of $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$, included as part of our study, provided yet another example of the ability of highly electron-withdrawing, bulky substituents to flatten the geometry about an otherwise pyramidal amine [1].

Herein we describe the synthetic methodology employed to prepare the new perfluorinated tertiary amines $(\text{SF}_5)_2\text{NCF}_2\text{CF}_3$ and $(\text{SF}_5)_2\text{NCF}_2\text{CF}_2\text{CF}_3$. Additional tertiary amines were prepared from the reactions between the *N*-chloroamines $\text{SF}_5\text{N}(\text{Cl})\text{R}_f$ with olefins.

EXPERIMENTAL

Infrared spectra were recorded on either a Perkin-Elmer 283B or a Bio-Rad FTS-40 infrared spectrophotometer on gases at pressures between 1 and 10 torr. Mass spectra were obtained on a Hewlett-Packard 5985A GC/MS system by using a controlled gas inlet probe. Only the most important ions are reported. The mass numbers are given for ^{35}Cl where applicable; the intensities include all isotopes. Electron impact-exact mass spectra were taken on a JEOL SX-302 high resolution mass spectrometer, while chemical ionization-exact mass spectra were recorded on a Finnigan MAT 90. The ^{19}F , ^{13}C , and ^1H NMR spectra were recorded on either a Varian EM360L, a Nicolet NIC 200FT, a Bruker AM360, or a Bruker AM500 nuclear magnetic resonance spectrometer; CCl_3F and $\text{Si}(\text{CH}_3)_4$ were used as standards, respectively. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

The compounds ClF [11], SF_5Cl [12], HgF_2 [13], $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_3$, and $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_3$ [14] were prepared by literature methods. All other reagents were taken from laboratory stock and purified, where necessary, before use.

Preparation of $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$

Sulfur chloride pentafluoride (100 mmol) was condensed into a 5-L photolysis vessel fitted with a quartz immersion well, followed by 100 mmol of $\text{CF}_3\text{CF}_2\text{CN}$. The mixture was allowed to warm to room temperature. At this time the mixture was irradiated with a low-pressure mercury vapor lamp for 4 h, after which the contents were removed to a liquid nitrogen cooled trap and then distilled through -60 and -196°C traps. The -60°C trap contained the desired product $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$ and small amounts of $[\text{CF}_3\text{CF}_2(\text{Cl})\text{C}=\text{N}]_2$ which were removed by further distillation. The contents of the -196°C trap were returned to the reaction

flask for further irradiation. After two such cycles, the pure product $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$ amounted to 8.88 g (28.9 mmol) corresponding to a 29% conversion.

$\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$ (nc): IR (gas): 1677 (s), 1335 (m), 1236 (s), 1082 (m), 905 (vsb), 731 (w), 693 (w), 609 (s) cm^{-1} ; mass spectrum (70 eV): major m/z = 307 (M^+ , <1%), 288 ($\text{M}-\text{F}^+$, 13%), 272 ($\text{M}-\text{Cl}^+$, 12%), 188 ($\text{M}-\text{C}_2\text{F}_5^+$, 31%), 127 (SF_5^+ , 100%), 119 (C_2F_5^+ , 11%), 89 (SF_3^+ , 7%), 69 (CF_3^+ , 5%); chemical ionization mass spectrum (methane): major m/z = 308 ($\text{M}+\text{H}^+$, 44%), 288 ($\text{M}-\text{F}^+$, 97%), 127 (SF_5 , 100%), 89 (SF_3^+ , 64%), 69 (CF_3 , 46%); ^{19}F NMR [$^{\text{A}}\text{SF}_4^{\text{B}}\text{N}=\text{C}(\text{Cl})\text{CF}_2^{\text{M}}\text{CF}_3^{\text{X}}$]: $\delta_{\text{A}} = 67.1$, $\delta_{\text{B}} = 62.5$, $\delta_{\text{M}} = -113.3$, $\delta_{\text{X}} = -81.9$ ($J_{\text{AB}} = 156.2$ Hz); ^{13}C NMR $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$: $\delta_{\text{NC}} = 143.2$ ($^2\text{J}_{\text{C-F}} = 34.0$ Hz, $^3\text{J}_{\text{SF}_4\text{-C}} = 8.0$ Hz), $\delta_{\text{CF}_2} = 108.2$ ($^1\text{J}_{\text{C-F}} = -265.1$ Hz, $^2\text{J}_{\text{C-F}} = 39.4$ Hz), $\delta_{\text{CF}_3} = 117.8$ ($^1\text{J}_{\text{C-F}} = -286.2$ Hz, $^2\text{J}_{\text{C-F}} = 34.6$ Hz). Anal. Calcd for $\text{C}_3\text{NClF}_{10}\text{S}$: C, 11.72; N, 4.55. Found: C, 11.40; N, 4.42.

Preparation of $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_3$ [14]

Mercuric fluoride (10.43 g, 43.8 mmol) was placed in a 30-mL stainless steel cylinder in a dry box under nitrogen atmosphere. The cylinder was removed from the dry box, evacuated, and $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_3$ (4.67 g, 18.2 mmol) was condensed in at -196°C . The reaction mixture was then heated at 150°C for 15 days. After that time the volatile materials were removed to a liquid nitrogen trap and distilled through a series of traps cooled to -90 and -196°C . The -90°C trap contained the desired product which was further distilled through traps at -70 and -196°C . The -196°C trap contained the pure product $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_3$ (2.30 g, 9.51 mmol), corresponding to a 53% yield.

$\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_3$: IR (gas): 1769 (s), 1345 (vs), 1253 (vs), 1200 (vs), 1130 (vs), 900 (vs), 835 (vs), 740 (m), 648 (m), 601 (s) cm^{-1} ; mass spectrum (70 eV): major m/z = 241 (M^+ , <1%), 222 ($\text{M}-\text{F}^+$, 8%), 127 (SF_5^+ , 100%), 119 (C_2F_5^+ , 29%), 89 (SF_3^+ , 23%), 69 (16%); chemical ionization mass spectrum (methane): major m/z = 242 ($\text{M}+\text{H}^+$, 100%), 222 ($\text{M}-\text{F}^+$, 64%), 127 (SF_5^+ , 25%), 89 (SF_3^+ , 37%); ^{19}F NMR [$^{\text{A}}\text{SF}_4^{\text{B}}\text{N}=\text{C}(\text{F}^{\text{M}})\text{CF}_3^{\text{X}}$]: $\delta_{\text{A}} = 67.0$, $\delta_{\text{B}} = 70.0$, $\delta_{\text{M}} = -29.5$, $\delta_{\text{X}} = -72.8$ ($J_{\text{AB}} = 159.7$ Hz, $J_{\text{BM}} = 18.8$ Hz).

Preparation of $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_2\text{CF}_3$

A mixture of HgF_2 (10.2 g, 42.8 mmol) and $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_3$ (5.76 g, 18.7 mmol) was heated at 150°C in a 30-mL stainless steel cylinder for four days. At this

time the volatile materials were distilled through a series of traps cooled to -90 and -196°C. The contents of the -90°C trap were further distilled through traps at -70 and -196°C. The -196°C trap contained $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_2\text{CF}_3$ (4.77 g, 16.4 mmol) corresponding to a 88% yield.

$\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_2\text{CF}_3$ (nc): IR (gas): 1762 (s), 1341 (m), 1310 (m), 1235 (vs), 1150 (s), 1030 (s), 915 (s), 880 (s), 820 (s), 750 (m), 605 (m) cm^{-1} ; mass spectrum (70eV): major m/z = 272 ($\text{M}-\text{F}^+$, 8%), 169 ($\text{CF}_3\text{CF}_2\text{CF}_2^+$, 22%), 127 (SF_5^+ , 100%), 119 (CF_3CF_2^+ , 9%), 89 (SF_3^+ , 13%), 69 (CF_3^+ , 30%); chemical ionization mass spectrum (methane): major m/z = 292 ($\text{M}+\text{H}^+$, 3%), 272 ($\text{M}-\text{F}^+$, 100%), 127 (SF_5^+ , 33%), 119 (CF_3CF_2^+ , 7%), 100 (CF_2CF_2^+ , 12%), 89 (SF_3^+ , 49%), 70 (SF_2^+ , 16%), 69 (CF_3^+ , 51%); ^{19}F NMR [$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{N}=\text{C}(\text{F}^{\text{H}})\text{CF}_2^{\text{M}}\text{CF}_3^{\text{X}}$]: δ_{A} = 66.7, δ_{B} = 68.3, δ_{H} = -23.2, δ_{M} = -120.1, δ_{X} = -82.9 (J_{AB} = 145.0 Hz, J_{HM} = 9.3 Hz).

Preparation of $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_2\text{CF}_2\text{CF}_3$ [14]

Mercuric fluoride (20.5 g, 86.1 mmol) and $\text{SF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_3$ (10.42 g, 29.2 mmol) were placed in a 30-mL stainless steel cylinder. The cylinder was then held at 150°C for ten days, after which time the volatile materials were distilled through a series of traps cooled to -50 and -196°C. The -196°C trap contained the desired product $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_2\text{CF}_2\text{CF}_3$ (9.26 g, 27.2 mmol) corresponding to a 93% yield. The IR and ^{19}F NMR spectra matched those reported in the literature [14].

Preparation of $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$

Both $\text{SF}_5\text{N}=\text{C}(\text{F})\text{CF}_3$ (1.45 g, 6.02 mmol) and ClF (7.0 mmol) were condensed at -196°C into a well-passivated stainless cylinder. The cylinder was then placed in a Dry Ice slush bath for 1.5 h before being allowed to warm slowly to room temperature. Several hours later the volatile materials were removed and distilled through traps at -90 and -196°C. The -90°C trap contained $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ (1.55 g, 5.25 mmol) corresponding to a 87% yield.

$\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ (nc): IR (gas): 1339 (w), 1283 (m), 1239 (s), 1209 (s), 1159 (s), 1089 (s), 919 (s), 873 (s), 805 (m), 739 (w), 697 (m), 605 (m) cm^{-1} ; chemical ionization mass spectrum (methane): major m/z = 296 ($\text{M}+\text{H}^+$, 8%), 295 (M^+ , 5%), 276 ($\text{M}-\text{F}^+$, 70%), 242 ($[\text{M}+\text{H}]-\text{ClF}^+$, 100%), 222 ($\text{SF}_5\text{NC}_2\text{F}_3^+$, 66%), 127 (SF_5^+ , 17%), 89 (SF_3^+ , 7%); ^{19}F NMR [$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{N}(\text{Cl})\text{CF}_2^{\text{M}}\text{CF}_3^{\text{X}}$]: δ_{A} = 64.9, δ_{B} = 68.0, δ_{M} = -95.3, δ_{X} = -79.2 (J_{AB} = 150.3 Hz, J_{MB} = 16.7 Hz).

Preparation of SF₅N(Cl)CF₂CF₂CF₃

The imine SF₅N=C(F)CF₂CF₃ (3.83 g, 13.1 mmol) and ClF (16.1 mmol) were reacted in the same fashion as described in the preceding reaction. Distillation of the volatile products through -60 and -196°C traps gave SF₅N(Cl)CF₂CF₂CF₃ (4.01 g, 11.6 mmol) stopping in the -60°C trap in 89% yield.

SF₅N(Cl)CF₂CF₂CF₃ (nc): IR (gas): 1347 (w), 1285 (w), 1250 (s), 1205 (m), 1150 (m), 1085 (m), 995 (s), 915 (s), 860 (s), 790 (w), 690 (w), 600 (m) cm⁻¹; chemical ionization mass spectrum (methane): major m/z = 292 ([M+H]-ClF⁺, 43%), 272 (SF₅NC₃F₅⁺, 100%), 169 (CF₃CF₂CF₂⁺, 14%), 127 (SF₅⁺, 42%), 119 (CF₃CF₂⁺, 8%), 100 (CF₂CF₂⁺, 8%), 70 (SF₂⁺, 8%), 69 (CF₃⁺, 33%); ¹⁹F NMR [F^ASF₄^BN(Cl)CF₂^MCF₂^RCF₃^X]: $\delta_A = 65.0$, $\delta_B = 68.6$, $\delta_M = -90.4$, $\delta_R = -119.3$, $\delta_X = -81.6$ (J_{AB} = 146.4 Hz, J_{BM} = 14.1 Hz, J_{MX} = 9.4 Hz).

Preparation of SF₅N(Cl)CF₂CF₂CF₂CF₃

Chlorine monofluoride (11.5 mmol) and SF₅N=C(F)CF₂CF₂CF₃ (2.42 g, 7.01 mmol) were reacted as in the preceding reaction. Trap-to-trap distillation of the volatile materials gave SF₅N(Cl)CF₂CF₂CF₂CF₃ (1.76 g, 4.46 mmol) stopping in a -60°C trap in 64% yield.

SF₅N(Cl)CF₂CF₂CF₂CF₃ (nc): IR (gas): 1360 (m), 1250 (vsb), 1150 (s), 1090 (m), 1029 (m), 995 (m), 912 (s), 860 (s), 782 (w), 730 (s), 700 (m), 600 (m) cm⁻¹; chemical ionization mass spectrum (methane): major m/z = 396 (M+H⁺, 15%), 395 (M⁺, 9%), 376 (M-F⁺, 83%), 342 ([M+H]-ClF⁺, 100%), 326 (M-CF₃⁺, 39%), 322 (SF₅NC₄F₄⁺, 16%), 292 (SF₅NHC₃F₅⁺, 24%), 276 (M-CF₂CF₃⁺, 27%), 250 ([M+H]-SF₆⁺, 47%), 127 (SF₅⁺, 27%), 89 (SF₃⁺, 3%); ¹⁹F NMR [F^ASF₄^BN(Cl)CF₂^HCF₂^MCF₂^PCF₃^X]: $\delta_A = 64.8$, $\delta_B = 68.5$, $\delta_H = -90.7$, $\delta_M = -116.9$, $\delta_P = -126.5$, $\delta_X = -80.9$ (J_{AB} = 152.1 Hz, J_{BH} = 15.0 Hz, J_{HP} = 14.0 Hz, J_{MX} = 11.7 Hz). Anal. Calcd for C₄NCIF₁₄S: C, 12.15; N, 3.54. Found: C, 11.54; 3.53.

Preparation of (SF₅)₂NCF₂CF₃

The chloroamine SF₅N(Cl)CF₂CF₃ (1.55 g, 5.25 mmol) was condensed at -196°C into a 1-L photolysis vessel fitted with a quartz immersion well. The reactants were allowed to vaporize before being irradiated with a low-pressure mercury lamp for 1.25 h. The volatile contents were then removed to the vacuum line and distilled through -80 and -196°C traps. Following successive distillations, the -80°C trap

contained 0.60 g of a clear liquid later identified as $(\text{SF}_5)_2\text{NCF}_2\text{CF}_3$. Vapor pressure data treated by least-squares methods gave $\ln(P/P_0) = 17.82 - 4591.69 T^{-1} + 141715.78 T^{-2}$ (-19 to +23°C), bp 103.9°C, $\Delta H_{\text{vap}} = 7.63 \text{ kcal mol}^{-1}$, $\Delta S_{\text{vap}} = 20.2 \text{ eu}$.

$(\text{SF}_5)_2\text{NCF}_2\text{CF}_3$ (nc): 58% yield; IR (gas): 1301 (w), 1234 (vs), 1147 (s), 1089 (w), 1060 (s), 972 (m), 948 (s), 917 (m), 864 (w), 825 (m), 796 (s), 717 (m), 568 (m) cm^{-1} ; chemical ionization mass spectrum (methane): major $m/z = 242$ ($[\text{M}+\text{H}]^+$ - SF_6^+ , 29%), 222 ($\text{SF}_5\text{NCFCF}_2^+$, 100%), 127 (SF_5^+ , 42%), 89 (SF_3^+ , 19%); ^{19}F NMR [$(\text{F}^{\text{A}}\text{SF}_4^{\text{B}}(\text{F}^{\text{A}'}\text{SF}_4^{\text{B}'}))\text{NCF}_2^{\text{M}}\text{CF}_3^{\text{X}}$]: $\delta_{\text{A}} = \delta_{\text{A}'} = 68.4$, $\delta_{\text{B}} = \delta_{\text{B}'} = 84.3$, $\delta_{\text{M}} = -77.9$, $\delta_{\text{X}} = -74.7$ ($J_{\text{AB}} = J_{\text{A'B'}} = 155 \text{ Hz}$, $J_{\text{BM}} = J_{\text{B'M}} = 25.9 \text{ Hz}$, $J_{\text{BX}} = J_{\text{B'X}} = 6.1 \text{ Hz}$); ^{13}C NMR: $\delta_{\text{CF}_2} = 115.2$ ($^1J_{\text{C-F}} = -284.7 \text{ Hz}$, $^2J_{\text{C-F}} = 43.5 \text{ Hz}$), $\delta_{\text{CF}_3} = 117.9$ ($^1J_{\text{C-F}} = -291.7 \text{ Hz}$, $^2J_{\text{C-F}} = 44.1 \text{ Hz}$).

Preparation of $(\text{SF}_5)_2\text{NCF}_2\text{CF}_2\text{CF}_3$

As in the preceding reaction, the chloroamine $(\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_3$ (4.00 g, 11.6 mmol) was irradiated with a low-pressure mercury lamp for 3 h. The volatile materials were then vacuum distilled through a series of traps cooled to -45 and -196°C. The -196°C trap contained 3.29 g of a mixture of Cl_2 , $\text{SF}_5\text{N}=\text{CF}_2$ [14], $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$ [15], and $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_3$. The -45°C trap retained 0.20 g of a material which was subsequently identified as $(\text{SF}_5)_2\text{NCF}_2\text{CF}_2\text{CF}_3$. The 0.20 g (0.5 mmol) corresponds to a yield of 8%.

$(\text{SF}_5)_2\text{NCF}_2\text{CF}_2\text{CF}_3$ (nc): IR (gas): 1280 (m), 1251 (s), 1205 (m), 1140 (m), 1111 (w), 1080 (w), 1005 (s), 946 (s), 917 (m), 845 (m), 797 (s), 731 (m), 718 (w), 568 (m) cm^{-1} ; chemical ionization mass spectrum (methane): major $m/z = 292$ ($[\text{M}+\text{H}]^+$ - SF_6^+ , 30%), 272 ($\text{SF}_5\text{NCFCF}_2\text{CF}_2^+$, 29%), 127 (SF_5^+ , 97%), 119 (CF_3CF_2^+ , 9%), 103 (NSF_3^+ , 7%), 100 (CF_2CF_2^+ , 9%), 89 (SF_3^+ , 100%), 70 (SF_2^+ , 32%), 69 (CF_3^+ , 63%), 51 (SF^+ , 12%); ^{19}F NMR [$(\text{F}^{\text{A}}\text{SF}_4^{\text{B}}(\text{F}^{\text{A}'}\text{SF}_4^{\text{B}'}))\text{NCF}_2^{\text{H}}\text{CF}_2^{\text{M}}\text{CF}_3^{\text{X}}$]: $\delta_{\text{A}} = \delta_{\text{A}'} = 68.3$, $\delta_{\text{B}} = \delta_{\text{B}'} = 84.9$, $\delta_{\text{H}} = -74.9$, $\delta_{\text{M}} = -116.3$, $\delta_{\text{X}} = -82.1$ ($J_{\text{AB}} = J_{\text{A'B'}} = 150 \text{ Hz}$, $J_{\text{BH}} = J_{\text{B'H}} = 26 \text{ Hz}$, $J_{\text{BM}} = J_{\text{B'M}} = 12 \text{ Hz}$, $J_{\text{HX}} = 12 \text{ Hz}$); ^{13}C NMR: $\delta_{\text{NCF}_2} = 116.9$ ($^1J_{\text{C-F}} = -283.9 \text{ Hz}$, $^2J_{\text{C-F}} = 33.2 \text{ Hz}$), $\delta_{\text{CF}_2\text{CF}_3} = 109.3$ ($^1J_{\text{C-F}} = -275. \text{ Hz}$, $^2J_{\text{C-F}}(\text{CF}_2) = 45.4 \text{ Hz}$, $^2J_{\text{C-F}}(\text{CF}_3) = 38.9 \text{ Hz}$), $\delta_{\text{CF}_3} = 116.8$ ($^1J_{\text{C-F}} = -287.1 \text{ Hz}$, $^2J_{\text{C-F}} = 35.0 \text{ Hz}$).

Attempted Preparation of $(\text{SF}_5)_2\text{NCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$

The chloroamine $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ (1.51 g, 3.82 mmol) was condensed into a 1-L photolysis vessel, allowed to vaporize, and irradiated for 1.5 h.

The volatile contents were then removed to the vacuum line and distilled through -40 and -196°C traps. The -40°C trap contained 0.57 g of unreacted starting material, while the -196°C trap contained a mixture (0.89 g) of Cl₂, SF₅N=CF₂, and CF₃CF₂CF₂CF₂CF₂CF₃. The latter two compounds were identified by IR and NMR spectroscopy [14,15].

Preparation of SF₅N(CF₃)CH₂CH₂Cl

Both SF₅N(Cl)CF₃ (2.0 g, 8.1 mmol) and C₂H₄ (0.54 g, 19.3 mmol) were condensed at -196°C into a 250- mL round-bottomed Pyrex flask fitted with a Teflon stopcock. The reaction mixture was then allowed to warm to room temperature and react for 24 h. After that time, the volatile materials were moved to the vacuum line and distilled through a series of traps cooled to -70 and -196°C. The -70°C trap retained 1.93 g (7.1 mmol) of a colorless liquid later identified as the desired product SF₅N(CF₃)CH₂CH₂Cl. Vapor pressure data treated by least-squares methods gave $\ln(P/P_0) = 16.58 - 3557.51 T^{-1} - 94047.30 T^{-2}$ (-15 to +22°C), bp 109.3°C, $\Delta H_{\text{vap}} = 8.05 \text{ kcal mol}^{-1}$, $\Delta S_{\text{vap}} = 21.0 \text{ eu}$.

SF₅N(CF₃)CH₂CH₂Cl (nc): 88% yield; IR (gas): 2950 (w), 1284 (s), 1259 (sh), 1218 (m), 1185 (s), 1166 (s), 940 (m), 916 (s), 837 (s), 606 (m) cm⁻¹; mass spectrum (70 eV): major m/z = 224 (SF₅N(CF₃)CH₂⁺, 41%), 127 (SF₅⁺, 100%), 89 (SF₃⁺, 33%), 69 (CF₃⁺, 69%); chemical ionization mass spectrum (methane): major m/z = 274 (M+H⁺, 26%), 254 (M-F⁺, 95%), 238 (M-Cl⁺, 37%), 224 (SF₅N(CF₃)CH₂, 21%), 192 (SF₅NCF₂ + H⁺, 100%), 127 (SF₅⁺, 15%), 63 (ClCH₂CH₂⁺, 14%); ¹⁹F NMR [¹⁸FSF₄^BN(CF₃^X)CH₂CH₂Cl]: $\delta_A = 76.3$, $\delta_B = 67.6$, $\delta_X = -57.7$ (J_{AB} = 154.3 Hz, J_{BX} = 11.4 Hz); ¹H NMR: δ 3.01 (bt, NCH₂), 2.80 (t, CH₂Cl) (J_{H-H} = 8.0 Hz). Chemical ionization-exact mass for C₃H₅NCIF₈S: calcd, 273.9703; found, 273.9730 ± 0.0004.

Preparation of SF₅N(CF₃)CF₂CF₂Cl

A mixture of SF₅N(Cl)CF₃ (1.74 g, 7.1 mmol) and C₂F₄ (1.03 g, 10.3 mmol) were condensed into a 100-mL glass reaction vessel at -196°C and allowed to warm to room temperature. The reaction vessel was then heated for 30 h at 60°C. At that time the volatile materials were moved to the vacuum line for distillation. Repeated distillations gave SF₅N(CF₃)CF₂CF₂Cl (1.27 g, 3.7 mmol; 52% yield) stopping in a trap at -70°C.

SF₅N(CF₃)CF₂CF₂Cl (nc): IR (gas): 1308 (s), 1255 (s), 1217 (s), 1189 (s), 1138 (m), 1111 (m), 1000 (m), 974 (m), 928 (s), 854 (s), 798 (s), 745 (m), 717 (m),

692 (w), 603 (s) cm^{-1} ; chemical ionization mass spectrum (methane): major m/z = 326 (M-F^+ , 100%), 200 ($[\text{M+H}]\text{-SF}_6^+$, 12%), 192 ($\text{SF}_5\text{NCF}_2 + \text{H}^+$, 48%), 180 ($\text{ClCF}_2\text{CF}_2\text{NCF}^+$, 43%), 172 (SF_5NCF^+ , 14%), 127 (SF_5^+ , 39%). ^{19}F NMR [$^{\text{A}}\text{SF}_4^{\text{B}}\text{N}(\text{CF}_3^{\text{M}})\text{CF}_2^{\text{R}}\text{CF}_2^{\text{X}}\text{Cl}$]: $\delta_{\text{A}} = 67.0$, $\delta_{\text{B}} = 80.3$, $\delta_{\text{M}} = -50.6$, $\delta_{\text{R}} = -86.5$, $\delta_{\text{X}} = -66.5$ ($J_{\text{AB}} = 154.9$ Hz, $J_{\text{BM}} = 15.9$ Hz, $J_{\text{BR}} = 15.9$ Hz, $J_{\text{BX}} = 7.9$ Hz, $J_{\text{MR}} = 15.9$ Hz). GC-electron impact-exact mass for $[\text{M-F}]^+$, $\text{C}_3\text{NClF}_{11}\text{S}$: calcd, 325.9265; found, 325.9240.

Preparation of $\text{SF}_5\text{N}(\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$

The chloroamine $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ (2.30 g, 7.8 mmol) was condensed into a 100-mL glass reaction vessel followed by 10 mmol of C_2H_4 . The reaction mixture was allowed to warm to room temperature and react for 30 hours. After that time the volatile materials were removed and distilled through a series of traps cooled to -50 and -196°C . The -50°C trap contained 2.24 g (5.7 mmol) of a colorless liquid subsequently identified as $\text{SF}_5\text{N}(\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$.

$\text{SF}_5\text{N}(\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$ (nc): 73% yield; IR (gas): 3007 (w), 1254 (s), 1239 (s), 1224 (s), 1146 (m), 1113 (m), 1071 (w), 1017 (w), 917 (s), 897 (s), 816 (s), 699 (w), 604 cm^{-1} ; mass spectrum (70 eV): major m/z = 274 ($\text{SF}_5\text{N}(\text{CF}_2\text{CF}_3)\text{CH}_2^+$, 83%), 127 (SF_5^+ , 100%), 119 (CF_3CF_2^+ , 9%), 89 (SF_3^+ , 12%), 69 (CF_3 , 10%); chemical ionization mass spectrum (methane): major m/z = 324 (M+H^+ , 31%), 304 (M-F^+ , 100%), 288 (M-Cl^+ , 74%), 274 ($\text{SF}_5\text{N}(\text{CF}_2\text{CF}_3)\text{CH}_2^+$, 17%); ^{19}F NMR [$^{\text{A}}\text{SF}_4^{\text{B}}\text{N}(\text{CF}_2^{\text{M}}\text{CF}_3^{\text{X}})\text{CH}_2\text{CH}_2\text{Cl}$]: $\delta_{\text{A}} = 76.5$, $\delta_{\text{B}} = 70.7$, $\delta_{\text{M}} = -92.0$, $\delta_{\text{X}} = -80.9$ ($J_{\text{AB}} = 152.7$ Hz, $J_{\text{BM}} = 17.4$ Hz, $J_{\text{BX}} = 6.6$ Hz); ^1H NMR: δ 3.01 (bt, NCH_2), 2.82 (t, CH_2Cl) ($J_{\text{H-H}} = 7.9$ Hz).

Preparation of $\text{SF}_5\text{N}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$

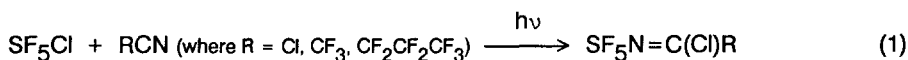
Both $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ (1.48 g, 3.7 mmol) and C_2H_4 (0.16 g, 5.7 mmol) were condensed at -196°C into a 70-mL glass reaction vessel. The mixture was then allowed to warm to room temperature, and 2 days later the volatile products were removed to the vacuum line and distilled through a series of traps at -30 and -196°C . The -30°C trap retained 1.41 g (3.3 mmol) of a colorless liquid later identified as $\text{SF}_5\text{N}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$.

$\text{SF}_5\text{N}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)\text{CH}_2\text{CH}_2\text{Cl}$ (nc): 89% yield; IR (capillary film): 3004 (w), 1475 (w), 1348 (m), 1245 (vsb), 1140 (vs), 945 (w), 920 (vsb), 885 (vsb), 844 (s), 787 (m), 726 (m), 703 (m), 690 (w), 600 (m), 585 (w) cm^{-1} ; chemical ionization mass spectrum (methane): major m/z = 424 (M+H^+ , 25%), 404 (M-F^+ , 65%), 388 (M-

Cl^+ , 59%), 374 ($\text{M}-\text{CH}_2\text{Cl}$, 35%), 354 ($\text{M}-\text{CF}_3^+$, 63%), 342 (40%), 338 (45%), 324 (24%), 250 (74%), 242 ($\text{SF}_5\text{NHC}_2\text{F}_4^+$, 100), 222 ($\text{SF}_5\text{NC}_2\text{F}_3^+$, 49%); ^{19}F NMR [$\text{F}^{\text{A}}\text{SF}_4^{\text{B}}\text{N}(\text{CF}_2^{\text{H}}\text{CF}_2^{\text{M}}\text{CF}_2^{\text{P}}\text{CF}_3^{\text{X}})\text{CH}_2\text{CH}_2\text{Cl}$]: $\delta_{\text{A}} = 75.1$, $\delta_{\text{B}} = 69.9$, $\delta_{\text{H}} = -87.0$, $\delta_{\text{M}} = -119.2$, $\delta_{\text{P}} = -128.1$, $\delta_{\text{X}} = -82.6$ ($J_{\text{AB}} = 152.8$ Hz); ^1H NMR: δ 3.80 (bm, NCH_2), 3.60 (t, CH_2Cl) ($J_{\text{H-H}} = 7.5$ Hz).

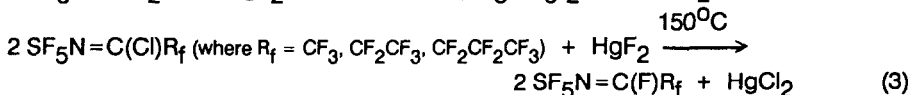
RESULTS AND DISCUSSION

In 1964 Tullock and co-workers reported the addition of SF_5Cl to nitriles under photolytic conditions [14]. This result was not unexpected since SF_5Cl had earlier



been found to add to olefins and acetylenes presumably under free radical conditions [16]. In the present study, it was necessary to prepare the new imine $\text{SF}_5\text{N}=\text{C(Cl)CF}_2\text{CF}_3$ from the reaction of SF_5Cl with perfluoropropionitrile in addition to preparing the other imines shown in equation 1. The yield of $\text{SF}_5\text{N}=\text{C(Cl)CF}_2\text{CF}_3$ was similar to that reported by Tullock for the other imines (approximately 30%), and the characteristic by-products were again found to be Cl_2 , S_2F_{10} , and $[\text{R(Cl)C}=\text{N}]_2$. Each product was identified minimally by its ^{19}F NMR and infrared spectra; additional characterization data is given for $\text{SF}_5\text{N}=\text{C(Cl)CF}_2\text{CF}_3$ in the Experimental Section.

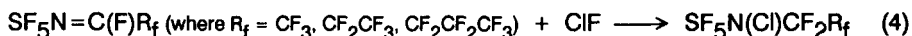
Having recently found that the mercurial $\text{Hg}[\text{N}(\text{CF}_3)\text{SF}_5]_2$ can be formed in virtually quantitative yield from the reaction of $\text{SF}_5\text{N}=\text{CCl}_2$ with excess HgF_2 at 150°C [1], we reacted the chloroimines $\text{SF}_5\text{N}=\text{C(Cl)R}_f$ with HgF_2 under similar conditions in an attempt to form the mercurials $\text{Hg}[\text{N}(\text{R}_f)\text{SF}_5]_2$ (eq 2). However, these reactions gave only the corresponding fluoroimine; presumably the mercurials are thermally unstable at the temperature required for reaction. Previously, this



metathesis had been effected by reacting the chloroimine with NaF in refluxing tetramethylene sulfone [14]. The method shown in equation 3 eliminates the need for a solvent and the separation problems thereby encountered.

The new fluoroimines were identified by ^{19}F NMR, infrared, and mass spectroscopy. The NMR spectrum of each compound exhibited a typical AB_4 pattern associated with the SF_5 group as well as the corresponding resonances in the carbon-fluorine region for the R_f group. Infrared analysis revealed the typical absorbances associated with the SF_5 group in the region of 925 to 800 cm^{-1} and around 600 cm^{-1} . Also present was the absorbance of the imine functionality, typically around 1760 cm^{-1} . It was possible to use this stretching frequency to monitor the progress of the metathesis reactions because the same stretch in the chloroimines appears at considerably lower wavenumbers due to the mass and electronic effects associated with chlorine versus fluorine substitution. Chemical ionization mass spectral analysis generally gave the molecular ion plus hydrogen and fragments such as $[\text{M-F}]^+$ and SF_5^+ .

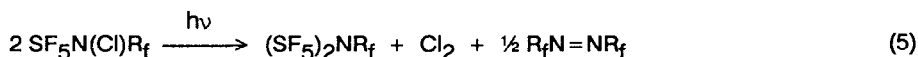
In the past, highly fluorinated *N*-chloroamines have been prepared by two general methods: (1) the reaction of mercurials such as $\text{Hg}[\text{N}(\text{CF}_3)_2]_2$ [17], $\text{Hg}[\text{N}(\text{CF}_3)\text{SF}_5]_2$ [1], and $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$ [10] with Cl_2 or ClF and (2) the reaction of unsaturated systems such as $\text{N}=\text{S}$ [18], $\text{N}=\text{C}$ [19], and nitriles [20] with ClF . The aforementioned lack of success in preparing new mercurials meant that we were limited to method 2. The fluoroimines were found to react with ClF in a nearly quantitative fashion to produce the corresponding *N*-chloroamines (eq 4). The



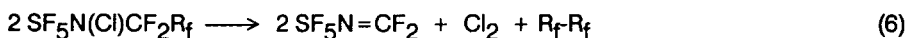
reactions go to completion at -78°C within a period of two hours. The resulting *N*-chloroamines are stable in glass at room temperature; no decomposition was noticed over a period of several months.

Each new *N*-chloroamine exhibited a typical ^{19}F NMR spectrum with an AB_4 pattern for the SF_5 group as well as the corresponding resonances for fluorine atoms attached to carbon. Infrared analysis was used for an initial check of purity following work-up as the amines no longer display a stretching frequency in the 1760 cm^{-1} region attributed to the $\text{N}=\text{C}$ stretch in the starting material. The identity of each product was further confirmed by chemical ionization mass spectrometry. The molecular ion plus hydrogen was generally observed along with the corresponding isotopic envelope associated with chlorine. Typical fragment ions included M^+ , $[\text{M-F}]^+$, $[\text{M+H}]\text{-ClF}^+$, and SF_5^+ as well as fragments associated with the perfluoroalkyl chain.

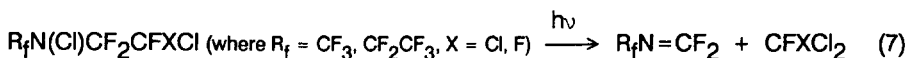
Gas phase UV photolysis of the *N*-chloroamines, $\text{SF}_5\text{N}(\text{Cl})\text{R}_f$ (where $\text{R}_f = \text{CF}_3$ [1], CF_2CF_3 , and $\text{CF}_2\text{CF}_2\text{CF}_3$), gave new perfluorinated tertiary amines (PTAs) of the formula type $(\text{R}_f)_3\text{-XN}(\text{SF}_5)_x$ where $X = 2$. The yield of the resulting PTAs in



equation 5 consistently dropped as the length of the perfluoroalkyl chain increased. When R_f was trifluoromethyl, the PTA was produced in over 90% yield along with a small amount (<5%) of the corresponding hydrazine $\text{SF}_5(\text{CF}_3)\text{N}-\text{N}(\text{CF}_3)\text{SF}_5$ [1]. In contrast, photolysis of $\text{SF}_5\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ gave only the PTA but the yield was reduced to 58%. When R_f was perfluoro-*n*-propyl, the yield of the PTA dropped to 8%, and no evidence for the corresponding PTA was found when R_f was perfluoro-*n*-butyl. The drop off in yield of the PTAs cannot be attributed to the increasing steric bulk of the perfluoroalkyl chain, cf. photolysis of $(\text{SF}_5)_2\text{NCl}$ gives $(\text{SF}_5)_3\text{N}$ in over 90% yield [21]. Instead, the explanation lies in a competing reaction pathway, namely β elimination of a perfluoroalkyl radical from the perfluoroalkyl chain as shown in equation 6. While



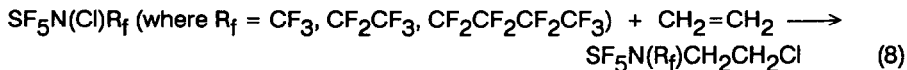
photolysis of bis(perfluoroalkyl)chloroamines has been shown to give rise to hydrazines [19,22], Peterman and Shreeve have observed an analogous β elimination of trifluoromethyl radicals in the photolysis of both $(\text{CF}_3\text{CF}_2)_2\text{NCl}$ and $(\text{CF}_3)_2\text{CFN}(\text{Cl})\text{CF}_2\text{CF}_3$ [19c] with production of the corresponding fluoroimines. It is interesting to note that a new PTA $(\text{CF}_3)_2\text{CFN}(\text{CF}_3)\text{CF}_2\text{CF}_3$ was also formed in the latter reaction [19c]. Additional examples of β elimination during the photolysis of *N*-chloroamines have appeared recently from Shreeve's laboratory (see equation 7) [23].



The ^{19}F NMR spectra of the new PTAs are characteristic of compounds containing geminal SF_5 groups [24]. They are minimally $\text{AB}_4\text{A}'\text{B}_4'$ spin systems which are further complicated by coupling to the fluorine atoms on carbon. The identity of the remaining R_f was further verified by ^{13}C NMR spectroscopy; the signs of the coupling constants were chosen on the basis of work by G. V. D. Tiers [25]. Although chemical ionization mass spectrometry did not give rise to molecular ions plus hydrogen, several characteristic fragment ions were observed such as $[\text{M}+\text{H}]-\text{SF}_6^+$ and $[\text{M}+\text{H}]-\text{SF}_6-\text{HF}^+$.

Several new $\text{SF}_5\text{N}(\text{R}_f)-$ derivatives were prepared from the insertion of ethylene and tetrafluoroethylene into the nitrogen-chlorine bond of the *N*-

chloroamines. The reactions with ethylene took place readily upon warming to room temperature, while a temperature of 60°C was required with tetrafluoroethylene. The



spectroscopic data were consistent with the proposed products. In related reactions of dichloro(perfluoroalkyl)amines with tetrafluoroethylene and trifluorochloroethylene, Shreeve and co-workers have found exclusively mono-insertion products at reaction temperatures of 65-70°C, while only di-insertion products were observed at temperatures of 95-100°C [23].

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