488 *Inorg. Chem.* **1992**, *31*, 488-491

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Synthesis and Reactions of Fluoroalkyl Polynitrogen Compounds

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Received August 13, 1991

Thermally induced insertions into a single nitrogen–chlorine bond of $(CF_3)_2NCF_2NCl_2$ (**1**) by the olefins $CF_2{=}CClF$, $CF_2{=}CHF$, and $CF_2{=}CH_2$ give rise to $(CF_3)_2NCF_2N(Cl)CF_2CCl_2F$ (**3**) and $(CF_3)_2NCF_2N(Cl)CX_1X_2CClF_2$ ($X_1 = F, X_2 = H$ (**4**); $X_1 = X_2 = H$ (**5**)), respectively. Photolysis of **3** with an excess of $CF_2{=}CH_2$ and $CF_2{=}CHF$ forms $(CF_3)_2NCF_2N(CF_2CCl_2F)CX_1X_2CClF_2$ ($X_1 = X_2 = H$ (**6**); $X_1 = F, X_2 = H$ (**7**)), and with excess $CF_2{=}ClF$, $(CF_3)_2NCF_2N(CF_2CCl_2F)CF_2CCl_2F$ (**8**) results. Photolysis of **3** neat results in the azaalkene $(CF_3)_2NCF_2N{=}CF_2$ (**10**) with loss of CCl_3F. Addition of ClF to **10** gives $(CF_3)_2NCF_2N(Cl)CF_3$ (**9**), which, when photolyzed with excess $CF_2{=}CHF$, forms $(CF_3)_2NCF_2N(CF_3)CF_2CHFCl$ (**11**) and, with excess $CF_2{=}CH_2$, forms $(CF_3)_2NCF_2N(CF_3)CH_2CClF_2$ (**12**). Small amounts of the possible structural isomers are formed as identified by proton NMR spectral studies or in the case of **3** as determined by the relative amounts of C-1 chlorofluorocarbons formed upon photolysis. Additionally, the reactivity of several azaalkenes was examined with nucleophiles, such as $(CH_3)_3SiN(CH_3)_2$, which, with $CF_3N{=}CF_2$, $CF_3N{=}C(F)N(CF_3)_2$, $(CF_3)_2NN{=}CCl_2$ (**13**), $CF_3CF_2(CF_3)NN{=}C(Cl)CF_3$ (**14**), $(CF_3)_2N{-}N{=}C(Cl)CF_3$ (**15**), and $SF_5N{=}CCl_2$, gives $CF_3N{=}C[N(CH_3)_2]_2$ (**16**), $(CF_3)_2NC[N(CH_3)_2]{=}NCF_3$ (**17**), $(CF_3)_2NN{=}C[N(CH_3)_2]_2$ (**18**), $C_2F_5(CF_3)NN{=}C(CF_3)N(CH_3)_2$ (**19**), $(CF_3)_2NN{=}C(CF_3)N(CH_3)_2$ (**20**), and $SF_5N{=}C[N(CH_3)_2]_2$ (**21**), respectively. With cyanotrimethylsilane, $CF_3N{=}CF_2$ gives $CF_3N{=}C(CN)_2$ (**22**), and with hexamethyldisilazane, $CF_3N{=}C(NH_2)N(CN)CF_3$ (**23**) forms. Most compounds form in high yield and are stable at ambient conditions. The densities of **8**, **11**, and **12** are 2.19, 1.80, and 1.76 g/cm^3, respectively.

Introduction

The relatively high thermal and hydrolytic stabilities of polyfluoro and perfluoroalkyl amines, diazanes, diazenes, and tetrazanes have tweaked our interest in continuing our studies of highly fluorinated polynitrogen compounds.[1-7] On the basis of these attractive properties and on the fact that these compounds tend to be more dense on average than simple fluorocarbons, the possible real world applications are rather broad, including use as lubricants, hydraulic fluids and refrigerants and in biological systems. There are a variety of synthetic routes to these materials.[1] In this work, we have taken advantage of the ease of insertion of olefinic or nitrilic groups into the nitrogen–chlorine bonds of *N,N*-dichloro(fluoroalkyl)amines or *N*-chlorobis(fluoroalkyl)amines in order to form the polynitrogen compounds.

Additionally, we have utilized the nucleophilic nature of (trimethylsilyl)dialkylamines with a variety of fluorinated electrophiles to displace a halogen bonded to an sp^2 carbon, thus introducing the dialkylamine functionality while concomitantly increasing the percentage of nitrogen in the molecule and increasing solubility in hydrocarbon solvents. Although this is a widely used methodology in organic chemistry, there are fewer examples in the case of fluorinated electrophiles.[8-17] Some of the imine derivatives that have been reported are $CF_3N{=}C[N(CH_3)_2]_2$ (from $CF_3N{=}CFN(CH_3)_2$ with $(CH_3)_2NH$)[17] and those that contain the *N*-pentafluorosulfanyl group, e.g., $SF_5N{=}C[N(C_2H_5)_2]_2$ and $SF_5N{=}C(R)N(C_2H_5)_2$ where R = Cl, CH_3 CF_3, C_2H_5, and OCH_3.[18]

Results and Discussion

In our earlier work to prepare diamines, we took advantage of the photolytically induced decomposition of appropriately substituted secondary *N*-chloroamines to form perfluoroazaalkenes, e.g., $CF_3N(Cl)CF_2CFCl_2 \xrightarrow{h\nu} CF_3N{=}CF_2 + CFCl_3$,[1,6] which in this case can be dimerized in the presence of CsF to form $(CF_3)_2NCF{=}NCF_3$.[19] With subsequent saturation of the double bond with chlorine fluoride, the reactive *N*-chlorodiamine $(CF_3)_2NCF_2N(Cl)CF_3$ was obtained. In our present study, we were interested in preparing more diversely substituted secondary and tertiary amines, which can be accomplished via the use of *N,N*-dichloroamines. To that end, the previously reported diamine $(CF_3)_2NCF_2NCl_2$ (**1**) was an attractive model compound.[20,21] However, its precursor, $(CF_3)_2NCN$ (**2**), was difficult to obtain pure in good yield largely due to the ease with which $CF_3N{=}CF_2$ dimerizes to $(CF_3)_2NCF{=}NCF_3$. By modifying the literature method,[21] it is now possible to obtain **2** essentially free of the dimer and to accomplish the addition of chlorine fluoride to the nitrile functionality to form **1** in 65–80% yield on a 25–30 mmol scale, viz.

$$CF_3N{=}CF_2 + ClCN \xrightarrow[50\ °C/10\ h]{KF/CH_3CN} \mathbf{2}$$

To preclude dimer formation, it is important to use equimolar amounts of ClCN and KF, to use a large excess of solvent, and to shake the mixture for several hours at 25 °C before heating. In the chlorofluorination of **2**, only a small excess of ClF should be used and the mixture held at −60 °C for ~12 h before allowing slow warm-up to 0 °C.

$$\mathbf{2} + ClF \xrightarrow[(2)\ slowly \to 0°C]{(1)\ -60\ °C/12\ h} \underset{65-80\%}{(CF_3)_2NCF_2NCl_2}$$

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Table I. Isomer Distributions (%) of Insertion Products of $CF_2{=}CHF$ and $CF_2{=}CH_2$ into >N—Cl and $-NCl_2$ Bonds (R_fNXCl)[a]

X	R_fNXC-$FHCClF_2$	R_fNXCF_2-$CHClF$	R_fNXCH_2-$CClF_2$	R_fNXCF_2-CH_2Cl
Cl	63	37	98	2
CF_3	83	17	75	25
CF_2Cl_2F	95	5	99	1

[a] $R_f = (CF_3)_2NCF_2$.

The ease of stepwise insertion of a variety of olefins into the nitrogen–chlorine bond(s) is similar to that of *N*-dichloromonoamines[3] with the formation of one predominant isomer.

$$\mathbf{1} + CF_2{=}CClF \xrightarrow[12\text{–}16\ \text{h}]{65\text{–}70\ ^\circ\text{C}} \underset{\mathbf{3}}{(CF_3)_2NCF_2N(Cl)CF_2CCl_2F}$$

$$\mathbf{1} + CF_2{=}CX_1X_2 \xrightarrow[12\text{–}16\ \text{h}]{65\text{–}70\ ^\circ\text{C}} \underset{\mathbf{4,\ 5}}{(CF_3)_2NCF_2N(Cl)CX_1X_2CClF_2}$$

$$X_1 = F,\ X_2 = H\ (\mathbf{4});\ X_1 = X_2 = H\ (\mathbf{5})$$

Compounds **3**–**5** are stable, slightly volatile materials that can be photolyzed with olefins to form the di(tertiary amines), e.g.

$$\mathbf{3} + CF_2{=}CX_1X_2 \xrightarrow[5\text{–}7\ \text{h}]{3000\ \text{Å}} \underset{\mathbf{6,\ 7}}{(CF_3)_2NCF_2N(CF_2CCl_2F)CX_1X_2CClF_2}$$

$$X_1 = X_2 = H\ (\mathbf{6});\ X_1 = F,\ X_2 = H\ (\mathbf{7})$$

$$\mathbf{3} + CF_2{=}CClF \xrightarrow[5\text{–}7\ \text{h}]{3000\ \text{Å}} \underset{\mathbf{8}}{(CF_3)_2NCF_2N(CF_2CCl_2F)CF_2CCl_2F}$$

These reactions are carried out by using a 3-fold excess of olefin to preclude formation of the diazane, $[(CF_3)_2NCF_2NCF_2CCl_2F]_2$, or azaalkene.

It is interesting to compare the products obtained from the photolysis of **3** with those from $(CF_3)_2NCF_2N(Cl)CF_3$ (**9**).[1] As we have demonstrated earlier, photolysis of $R_fN(CF_2CFXCl)Cl$ (X = F, Cl) provides a facile, nearly quantitative route to azaalkenes.[3,5,6] Thus, when **3** is irradiated neat, the azaalkene is formed in high yield whereas with **9** only coupling occurs to form the diazane with concomitant loss of chlorine.

$$\mathbf{3} \xrightarrow[2\ \text{h}]{3000\ \text{Å}} \underset{\mathbf{10}}{(CF_3)_2NCF_2N{=}CF_2} + CCl_3F$$

$$\mathbf{9} \xrightarrow[2\ \text{h}]{3000\ \text{Å}} [(CF_3)_2NCF_2NCF_3]_2{}^{1} + Cl_2$$

With more complex bis(secondary chloroamines), e.g., $CFCl_2CF_2N(Cl)CF_2CF_2N(Cl)CF_2CCl_2F$, photolysis gives 2 mol of the azaalkene, $CF_2{=}NCF_2CCl_2F$, with loss of chlorine. Gas-phase photolysis of neat chloro(perfluoroalkyl)(polyfluoroethyl)amines $(R_fN(Cl)C_2F_{5-x}Cl_x)$ gives rise to azaalkenes with concomitant formation of C-1 chlorofluorocarbons. However, if the polyhalogen alkyl is C-1, normally diazane formation occurs with loss of chlorine. In both cases, photolysis of the chloroamine in the presence of a severalfold excess of olefin results in insertion into the nitrogen–chlorine bond to form the tertiary alkylamine, as is the case for the formation of compounds **6**–**8**, **11**, and **12**.

The addition of chlorine fluoride to **10** gives rise to **9**.[1] Earlier we had demonstrated the insertion of $CF_2{=}CFCl$ into the N—Cl bond of **9** using photolytic conditions. In an effort to introduce hydrogen into the products, we can now report the synthesis of **11** and **12**, where the terminal ethyl groups have one or two

$$\mathbf{9} + CF_2{=}CHF \xrightarrow[5\text{–}7\ \text{h}]{3000\ \text{Å}} \underset{\mathbf{11}}{(CF_3)_2NCF_2N(CF_3)CF_2CHFCl}$$

$$\mathbf{9} + CF_2{=}CH_2 \xrightarrow[5\text{–}7\ \text{h}]{3000\ \text{Å}} \underset{\mathbf{12}}{(CF_3)_2NCF_2N(CF_3)CH_2CClF_2}$$

hydrogen atoms, respectively. An excess of olefin is necessary to prevent diazane formation.

Earlier workers[22,23] have shown that insertion reactions similar to ours did give rise to mixtures of isomers where one was much preferred over the other. We did not attempt to separate any structural isomers, but it was possible to observe that bidirectional addition had occurred and the relative amounts of each based on proton NMR spectra, on mass spectral data, or on the azaalkene generated. The results are given in Table I. This is corroborated in the mass spectra by observing, e.g., $(CF_3)_2NCF_2N(CF_3)CH_2{}^+$ and not $(CF_3)_2NCF_2N(CF_3)CF_2{}^+$, which supports the predominance of the isomer $(CF_3)_2NCF_2N(CF_3)CH_2CClF_2$.

The relative amounts of structural isomers from the insertion reactions of **1** and chlorotrifluoroethene were determined by measuring the ratio of $CCl_3F{:}CCl_2F_2$ which is greater than 8:1 after photolytic decomposition.

$$(CF_3)_2NCF_2N(Cl)CF_2CCl_2F \xrightarrow{3000\ \text{Å}} (CF_3)_2NCF_2N{=}CF_2 + CCl_3F$$

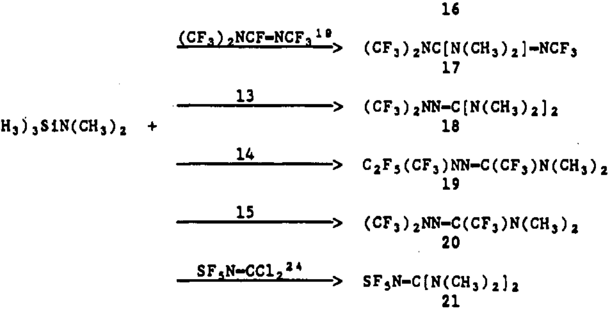
$$(CF_3)_2NCF_2N(Cl)CClFCClF_2 \xrightarrow{3000\ \text{Å}} (CF_3)_2NCF_2N{=}CClF + CCl_2F_2$$

This straightforward route to form azaalkenes, e.g., $CF_3N{=}CF_2$[5] and $C_2F_5N{=}CF_2$,[5] and then via chlorine fluoride addition to form *N*-chlorobis(perfluoroalkyl)amines, $(CF_3)_2NCl$ and $CF_3(C_2F_5)NCl$, respectively, enhances the further study of this chemistry and the synthesis of new polynitrogen compounds. The insertion of the nitrile functionality into the N–Cl bond occurs readily to form carbimide in high yield.[3,24,25]

$$R_f(CF_3)NCl + RC{\equiv}N \xrightarrow{h\nu} \underset{\mathbf{13\text{–}15}}{R_f(CF_3)NN{=}CClR}$$

$$\begin{array}{cccc} & \mathbf{13} & \mathbf{14} & \mathbf{15} \\ R_f = & CF_3 & CF_3CF_2 & CF_3 \\ R = & Cl & CF_3 & CF_3 \end{array}$$

These variously substituted carbimides are remarkably susceptible to nucleophilic attack by silylated compounds. This method has been utilized to introduce additional nitrogen-containing groups into these compounds and to increase their solubilities in hydrocarbon solvents. The reactions proceed neat at 25 °C. **16** was obtained earlier by treating $CF_3N{=}CF[N(CH_3)_2]$ with $(CH_3)_2NH$.[17]



With cyanotrimethylsilane, $CF_3N{=}CF_2$ can be reacted to form a new class of dicyano compound: $CF_3N{=}C(CN)_2$ (**22**). However, in the reaction of hexamethyldisilazane with perfluoroazapropene, initial elimination of $(CH_3)_3SiF$ occurs to form a carbodiimide which subsequently undergoes rearrangement, i.e.

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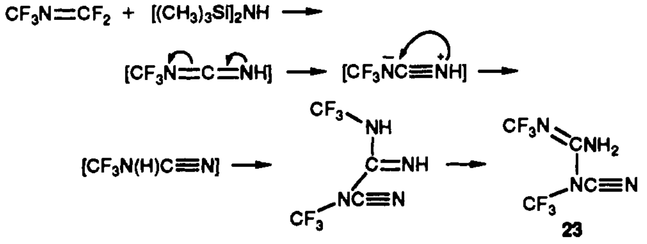

Compounds **13–15** are obtained in nearly quantitative yield, and their subsequent reactions and those of other imines with the silylated reagents proceed smoothly in excellent yields. Purification is accomplished via trap-to-trap distillation.

Experimental Section

Materials. The reagents $(CF_3)_2NCN$,[21] $(CF_3)_2NCF_2NCl_2$,[20] $CF_3N{=}CF_2$,[5] $C_2F_5N{=}CF_2$,[5] $(CF_3)_2NCF{=}NCF_3$,[19] $(CF_3)_2NN{=}CCl_2$,[25] $C_2F_5N(CF_3)N{=}CCl_2$,[3] $SF_5N{=}CCl_2$,[24] and SF_5Cl[26] were prepared according to the literature methods. All other materials were purchased as indicated: ClF (Ozark-Mahoning); ClCN (K&K Laboratories); CF_3CN $CF_2{=}CFCl$, $CF_2{=}CFH$, $CF_2{=}CH_2$ (PCR), $(CH_3)_3SiN(CH_3)_2$, $(CH_3)_3SiCN$, $[(CH_3)_3Si]_2NH$ (Aldrich).

General Procedures. A conventional Pyrex vacuum system equipped with Heise Bourbon tube and Televac thermocouple gauges was used to handle gases and volatile liquids. Standard *PVT* techniques were used to quantify volatile products and starting materials, and trap-to-trap distillation was used for purification. Infrared spectra were recorded by using a Perkin-Elmer Model 1710 Fourier transform spectrometer using 10-cm gas cells equipped with KBr windows. ^1H and ^{19}F NMR and mass spectral data were obtained with a JEOL FX90Q or Bruker AC200 NMR spectrometer and a VG 7070HS mass spectrometer. Chlorine isotope ratios supported fragment assignments. Elemental analyses were performed by Beller Microanalytisches Laboratorium, Göttingen, Germany.

Preparation of 3–5. In a typical reaction, 13 mmol of **1** and 15 mmol of olefin, $CF_2{=}CClF$, $CF_2{=}CHF$, or $CF_2{=}CH_2$, were condensed at −196 °C into a 75-mL stainless steel cylinder fitted with a Whitey valve. After warming to 25 °C, the cylinder was placed in a 70–75 °C oven for 16–20 h. The resulting mixture was fractionated by trap-to-trap distillation under dynamic vacuum. Compound **3** was obtained as a colorless liquid in 65% yield in a trap at −35 °C having passed through a trap at −10 °C. Spectral data obtained are as follows. IR (gas): 1355 vs, 1327 vs, 1255 s, 1225 vs, 1192 s, 1161 s, 1137 s, 1123 s, 1106 s, 1039 s, 994 s, 909 s, 848 m, 770 m, 727 m cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(Cl)$-$CF_2{}^CCF^DCl_2$: ^{19}F ϕ −54.28 (A, tr, $J_{A-B} = 11.29$ Hz), −65.16 (B, mult), −90.88 (C, tr of d, $J_{B-C} = 18.83$ Hz, $J_{C-D} = 6.34$ Hz), −70.46 (D, mult). MS (CI^+) [*m/e* (species) intensity]: 247 ($M^+ - CF_2Cl_3$) 0.85, 202 ($(CF_3)_2NCF_2{}^+$) 1.15, 180 ($CF_2{=}NCF_2CFCl^+$) 1.15, 114 ($CF_2{=}NCF_2{}^+$) 4.95, 86 (CF_2HCl^+) 100, 69 ($CF_3{}^+$) 4.47. Compound **4** was obtained as a colorless liquid in 55% yield in a −50 °C trap having passed a trap at −20 °C. Spectral data obtained are as follows. IR (gas): 1391 s, 1354 vs, 1228 vs, 1191 s, 1144 s, 1029 s, 998 vs, 948 m, 914 m, 866 m, 828 w, 732 s, 592 w, 578 m, 568 w, 559 w, 550 w, 482 w cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(Cl)CF^CH^DCClF_2{}^E$: ^{19}F ϕ −54.52 (A, m), −56.14 (B, m), −56.69 (C, m) −66.82 (E, m); ^1H δ 5.88 (D, m). MS (CI^+) [*m/e* (species) intensity]: 349 ($M^+ - 19$) 4.76, 329 ($M^+ - 2HF + 1$) 8.18, 315 ($M^+ - ClF + 1$) 14.72, 295 ($M^+ - HClF_2 + 1$) 31.52, 247 ($(CF_3)_2NCF_2NCF^+$) 46.43, 216 ($CF_2N(Cl)CFHCF_2Cl^+$) 17.97, 202 ($(CF_3)_2NCF_2{}^+$) 100, 182 ($CF_2NCF_2CFHCl^+ + 1$) 33.76, 162 ($CFNCFHCClF_2{}^+$) 97.66, 69 ($CF_3{}^+$) 100. Compound **5** was obtained as a colorless liquid in 30% yield in a trap at −40 °C having passed through a −10 °C trap. Spectral data obtained are as follows. IR (gas): 1355 vs, 1274 s, 1228 s, 1198 s, 1157 s, 1132 s, 1073 s, 1028 m, 991 vs, 814 w, 787 w, 761 w, 731 m, 664 w cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN$-$(Cl)CH_2{}^DCF_2{}^CCl$: ^{19}F ϕ −54.38 (A, tr of tr, $J_{A-B} = 11.29$ Hz, $J_{A-C} = 3.76$ Hz), −72.79 (B, heptet), −59.18 (C, m); ^1H δ 3.97 (D, tr, $J_{C-D} = 10.35$ Hz). MS (CI^+) [*m/e* (species) intensity]: 331 ($M^+ - F$) 3.23, 315 ($M^+ - Cl$) 5.76, 297 ($M^+ - ClF + 1$) 5.65, 277 ($M^+ - HClF_2 + 1$) 10.79, 227 ($CF_2NCF_2NCH_2CF_2Cl^+$) 4.69, 164 ($CF_2NCH_2CF_2Cl^+ + 1$) 13.31, 128 ($CF_2NCH_2CF_2{}^+$) 56.3, 99 ($CH_2CF_2Cl^+$) 10.55, 69 ($CF_3{}^+$) 100.

Preparation of 6–8. In a typical reaction, 5 mmol of **3** and 20 mmol of $CF_2{=}CH_2$, $CF_2{=}CHF$, or $CF_2{=}CClF$ were condensed into a 500-mL quartz vessel at −196 °C and photolyzed at 3000 Å for 5–7 h. The resulting products were separated and purified by trap-to-trap distillation. Compound **6** was found as a colorless nonvolatile liquid in the quartz vessel in 85% yield. Spectral data obtained are as follows. IR (liquid film/KBr): 1353 s, 1255 s, 1229 vs, 1191 s, 1105 w, 1030 w, 991 w, 911 vw, 810 vw, 732 vw, 713 vw, 569 vw, 482 vw cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(CF_2{}^CCF^ECl_2)CH_2{}^FCF_2{}^DCl$: ^{19}F ϕ −55.03 (A, m), −59.61 (B, m), −57.73 (C, m), −87.10 (D, m), −72.22 (E, m); ^1H δ 4.14 (F, m, $J_{D-F} = 11.74$ Hz). MS (CI^+) [*m/e* (species) intensity]: 447 ($M^+ - F$) 19.85, 431 ($M^+ - Cl$) 38.40, 381 ($M^+ - CF_2Cl$) 14.35, 365 ($M^+ - CCl_2F$) 1.05, 343 ($CF_2NCF_2N(CH_2CF_2Cl)CF_2CClF^+$) 3.86, 202 ($(CF_3)_2NCF_2{}^+$) 100. Anal. Calcd for $C_7H_2Cl_3F_{13}N_2$: C, 18.03; H, 0.43; F, 53.0. Found: C, 18.00; H, 0.45; F, 52.8. Density: 1.92 g/cm^3. Compound **7** was obtained as a colorless nonvolatile liquid in the quartz vessel in 75% yield. Spectral data obtained are as follows. IR (liquid film/KBr): 1447 vw, 1343 s, 1294 s, 1231 s, 1211 s, 1195 s, 1160 m, 1126 m, 1104 m, 1080 w, 985 s, 910 s, 832 w, 782 w, 736 s, 693 w, 651 w, 602 w, 470 vs cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(CF_2{}^CCF^ECl_2)$-$CH^GF^FCF_2{}^DCl$: ^{19}F ϕ −54.90 (A, m), −57.40 m (B, m), −64.46 (C, m), −73.90 (D, m), −63.59 (E, m), −86.09 (F, m); ^1H δ 5.92 (G, m, $J_{F-G} = 40.03$ Hz). MS (CI^+) [*m/e* (species) intensity]: 465 ($M^+ - F$) 6.57, 449 ($M^+ - Cl$), 8.98, 431 ($M^+ - ClF + 1$) 0.80, 361 (CF_2NCF_2N-$(CF_2CFCl_2)CF_2CHF^+$) 4.71, 332 ($CF_2N(CF_2CFCl_2)CF_2CHClF^+$) 31.10, 313 ($CF_3(CF_2)NCF_2NCF_2CClF^+$) 11.89, 295 ($CF_2NCF_2N$-$(CF_2CHClF)CF_2{}^+$) 10.55, 202 ($(CF_3)_2NCF_2{}^+$) 100. Anal. Calcd for $C_7HCl_3F_{14}N_2$: C, 17.35; H, 0.21; F, 54.96. Found: C, 17.12; H, 0.23; F, 55.0. Density: 2.01 g/cm^3. Compound **8** was found as an involatile colorless liquid in the quartz vessel in 77% yield. Spectral data obtained are as follows. IR (liquid film/KBr): 1345 vs, 1334 vs, 1318 vs, 1280 vs, 1248 vs, 1196 vs, 1156 s, 1127 s, 1098 s, 1004 vw, 984 s, 970 w, 902 s, 862 vw, 806 w, 787 w, 766 s, 730 s, 687 vw, 644 vw, 614 vw, 463 vs cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(CF_2{}^CCF^DCl_2)_2$: ^{19}F ϕ −55.08 (A, m), −81.37 (B, m), −54.69 (C, m), −69.23 (D, m). MS (CI^+) [*m/e* (species) intensity]: 499 ($M^+ - F$) 0.66, 395 ($CF_2NCF_2N(CF_2CFCl_2)CF_2CFCl^+$) 2.76, 366 ($CF_2N(CF_2CCl_2F)_2{}^+$) 14.04, 349 ($CF_3NCF_2N(CF_2CCl_2F)$-$CF_2{}^+ + 1$) 0.98, 329 ($CF_2NCF_2N(CF_2CCl_2F)CF_2{}^+$) 11.32, 151 ($CF_2CCl_2F^+$) 100. Anal. Calcd for $C_7Cl_4F_{14}N_2$: C, 16.22; F, 51.35; Cl, 27.02. Found: C, 16.29; F, 50.7; Cl, 27.02. Density: 2.19 g/cm^3.

Photolysis of 3. A 14-mmol sample of **3** was condensed into a 500-mL quartz vessel at −196 °C and was photolyzed at 3000 Å for 2–3 h. Compound **10**, $(CF_3)_2NCF_2N{=}CF_2$, was obtained in 80% yield in a trap at −85 °C having passed through a trap at −55 °C. Spectral data obtained are as follows. IR (gas): 1801 vs, 1340 vs, 1280 s, 1228 s, 1160 s, 1117 m, 1028 s, 990 s, 901 s, 848 w, 762 s, 732 s, 604 w, 556 w, 535 w, 523 w, 481 w cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BNCF^CF^D$: ^{19}F ϕ −54.46 (A, tr, $J_{A-B} = 11.29$ Hz), −59.83 (B, heptet), −28.05 (C, d, $J_{C-D} = 90.39$ Hz), −45.77 (D, d). MS (CI^+) [*m/e* (species) intensity]: 267 ($M^+ + 1$) 10.64, 247 ($M^+ - F$) 52.15, 202 ($(CF_3)_2NCF_2{}^+$) 22.51, 159 ($CF_2NCF_2NCF^+$) 4.03.

Preparation of Compound 9. In a typical reaction, 9 mmol of **10** and 11 mmol of ClF were condensed at −196 °C into a 75-mL stainless steel cylinder fitted with a Whitey valve. The cylinder was allowed to warm slowly to and remain at 25 °C for 2 h. Compound **9** was obtained in 87% yield in a trap at −88 °C having passed through a trap at −60 °C. Spectral data obtained are in agreement with those in the literature.[1]

Preparation of 11 and 12. In a typical reaction, 5 mmol of **9** and 15 mmol of $CF_2{=}CFH$ or $CF_2{=}CH_2$ were condensed into a 500-mL quartz vessel and photolyzed at 3000 Å for 5–7 h. The resulting product, **11** or **12**, was separated and purified by trap-to-trap distillation. Compound **11** was found as a colorless liquid in 50% yield in a trap at −70 °C having passed a trap at −30 °C. Spectral data obtained are as follows. IR (gas): 1337 vs, 1268 vs, 1220 vs, 1171 s, 1142 vs, 1089 s, 1018 s, 992 vs, 906 m, 882 m, 847 m, 821 m, 787 m, 757 s, 733 s, 681 w, 649 w, 580 vw, 571 vw, 553 w, 509 vw cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN$-$(CF_3){}^CCF_2{}^DCH^FClF^E$: ^{19}F ϕ −55.29 (A, tr, $J_{A-B} = 1.22$ Hz), −65.74 (B, m), −53.85 (C, m), −61.29 (D, m), −164[23] (E, d, $J_{E-F} = 30.13$ Hz); ^1H δ 5.8 (F, m). MS (CI^+) [*m/e* (species) intensity]: 383 ($M^+ - F$) 8.79, 367 ($M^+ - Cl$) 1.85, 316 ($(CF_3)_2NCF_2N(CF_2)_2$) 0.32, 250 (CF_2N-$(CF_3)CF_2CHClF^+$) 49.85, 114 ($CF_2NCF_2{}^+$) 100, 69 ($CF_3{}^+$) 100. Anal. Calcd for $C_6HClF_{14}N_2$: C, 17.91; H, 0.25; F, 66.17. Found: C, 18.01; H, 0.38; F, 65.60. Density: 1.80 g/cm^3. Compound **12** was found in 70% yield in a trap at −35 °C having passed through a trap at −10 °C. Spectral data obtained are as follows. IR (gas): 1358 vs, 1307 vs, 1271 s, 1212 vs, 1167 s, 1136 s, 1111 s, 1076 m, 1029 m, 990 s, 915 m, 848 m, 807 w, 794 w, 774 w, 734 s, 673 w, 648 w, 568 w, 550 w, 491 vs cm^{-1}. NMR for $(CF_3)_2{}^ANCF_2{}^BN(CF_3){}^CCH_2{}^ECF_2{}^DCl$: ^{19}F ϕ −55.43 (A, m), −61.94 (B, m), −56.47 (C, m), −60.54 (D, m); ^1H δ 3.95 (E, m, $J_{D-E} = 11.60$ Hz). MS (CI^+) [*m/e* (species) intensity]: 365 ($M^+ - F$) 67.63, 349 ($M^+ - Cl$) 69.97, 316 ($M^+ - CF_3 + 1$) 6.86, 299 ($(CF_3)_2NCF_2N$-$(CF_3)CH_2{}^+$) 23.34, 277 ($M^+ - CF_5$) 1.56, 261 ($CF_2NCF_2N(CF_3)$-$CH_2CF_2{}^+$) 28.27, 232 ($CF_2N(CF_3)CH_2CF_2Cl^+$) 98.24, 216 ($(CF_3)_2NCH_2CF_2{}^+$) 10.03, 202 ($(CF_3)_2NCF_2{}^+$) 100. Anal. Calcd for $C_6H_2ClF_{13}N_2$: C, 18.75; H, 0.52; F, 64.32. Found: C, 18.81; H, 0.64; F, 64.00. Density: 1.76 g/cm^3.

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(26) Nyman, F.; Roberts, H. L. *J. Chem. Soc.* **1962**, 3180.

Preparation of 16–21. $(CH_3)_2NSi(CH_3)_3$ (6 mmol) and $CF_3N{=}CF_2$ (3 mmol), $(CF_3)_2NCF{=}NCF_3$ (6 mmol), $(CF_3)_2NN{=}CCl_2$ (3 mmol), $(CF_3)_2NN{=}C(Cl)CF_3$ (6 mmol), $CF_3(C_2F_5)NN{=}C(Cl)CF_3$ (6 mmol), or $SF_5N{=}CCl_2$ (3 mmol) were condensed into a Pyrex glass vessel equipped with a Teflon stopcock. The reaction mixture was warmed slowly to 25 °C and allowed to remain for 12–14 h. The resulting mixtures were separated by trap-to-trap distillation to give the products. Compound **16** was isolated in a cold trap at −60 °C in 70% yield. Spectral data obtained are as follows. IR (gas): 2955 s, 2829 w, 1708 vs, 1510 m, 1453 m, 1420 m, 1384 s, 1297 s, 1233 m, 1210 m, 1099 s, 1000 s, 872 s, 830 m, 729 s, 693 m, 611 m, 531 w cm^{-1}. NMR: ^{19}F ϕ −48.5 (CF_3N, s); ^1H δ 3.01 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 159 ($M^+ - HF_2 + 15$) 97.9, 158 ($M^+ - H_2F_2 + 15$) 93.6, 139 ($M^+ - N(CH_3)_2$) 100, 123 ($M^+ - 4CH_3$) 14.8, 89 ($FCN_2(CH_3)_2^+$) 30.3, 69 (CF_3^+) 25.2. Anal. Calcd for $C_6H_{12}F_3N_3$: C, 39.34; H, 6.55. Found: C, 38.79; H, 6.72. Compound **17** was isolated in a trap at −35 °C in 65% yield. Spectral data obtained are as follows. IR (gas): 2970 s, 1734 s, 1305 w, 1263 s, 1214 m, 1180 m, 1118 m, 1076 s, 1050 m, 1006 w, 912 s, 849 s, 817 m, 757 m, 736 w cm^{-1}. NMR: ^{19}F ϕ −48.12 ($(CF_3)_2N$, s), −48.53 (CF_3N, s); ^1H δ 3.00 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 291 (M^+) 1.61, 159 ($M^+ - CF_4 - N(CH_3)_2$) 18.6, 139 ($CF_3NCN(CH_3)_2^+$) 100, 123 ($CF_3NCNCH_2^+$) 4.64, 85 ($M^+ - 3CF_3 + 1$) 2.57, 78 ($C_4N_2H_2^+$) 3.8. Anal. Calcd for $C_6H_6F_9N_3$: C, 24.74; H, 2.06; N, 14.43. Found: C, 24.69; H, 2.77; N, 13.47. Compound **18** was collected in a trap at −40 °C in 64% yield. Spectral data obtained are as follows. IR (gas): 2915 s, 2823 w, 1708 s, 1592 m, 1459 s, 1386 m, 1338 s, 1296 s, 1261 s, 1207 m, 1178 m, 1058 s, 1000 m, 966 m, 926 m, 763 s, 710 m, 630 m, 531 m cm^{-1}. NMR: ^{19}F ϕ −64.11 (CF_3, s); ^1H δ 2.8 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 238 ($M^+ - 2CH_3 + 2$) 29.5, 222 ($M^+ - N(CH_3)_2$) 20.2, 159 ($M^+ - CF_3 - 2F$) 3.22, 158 ($M^+ - CF_3 - HF_2$) 6.3, 139 ($CF_3NNCNCH_3^+ + 1$) 17.6, 85 ($M^+ - 2CF_3 - N(CH_3)_2 + 1$) 1.7, 71 ($NCN(CH_3)_2^+ + 1$) 100. Compound **19** was isolated in a trap at −35 °C in 72% yield. Spectral data obtained are as follows. IR (gas): 2953 s, 2838 w, 1628 vs, 1581 m, 1488 m, 1449 m, 1408 m, 1377 m, 1354 m, 1273 vs, 1229 vs, 1196 s, 1151 s, 1084 s, 1025 m, 998 m, 963 m, 917 m, 891 m, 798 w, 753 w, 718 m, 693 w, 653 w, 640 w, 613 w, 568 w, 546 w, 521 w cm^{-1}. NMR: ^{19}F ϕ −60.75 (CF_3N, tr of q, $J_{CF_3N-CF_3CF_2}$ = 2.91 Hz), −64.86 (CF_3C, s), −79.57 ($C\mathit{F}_3CF_2$, q), −101.1 (CF_2, q); ^1H δ 3.11 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 342 ($M^+ + 1$) 56.7, 341 (M^+) 32.9, 322 ($M^+ - F$) 94, 139 ($NC(CF_3)N(CH_3)_2^+$) 100, 110 ($NC(CF_3)N^+ + 1$) 41, 69 (CF_3^+) 27.9. Anal. Calcd for $C_7H_6F_{11}N_3$: C, 24.63; H, 1.75; F, 61.2. Found: C, 24.65; H, 1.86; F, 60.9. Compound **20** was isolated in a trap at −50 °C in 55% yield. Spectral data obtained are as follows. IR (gas): 2958 s, 2894 m, 1699 m, 1654 w, 1635 w, 1576 w, 1507 w, 1467 s, 1450 s, 1284 vs, 1254 s, 1175 s, 1101 m, 1060 s, 986 s, 934 m, 844 s, 756 m, 675 m, 620 m cm^{-1}. NMR: ^{19}F ϕ −67.29 (CF_3N, s), −71.4 (CF_3C, s); ^1H δ 2.43 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 229 ($M^+ - N(CH_3)_2 - F + 1$) 2.0, 160 ($M^+ - N(CH_3)_2 - CF_4 + 1$) 5.54, 147 ($C_2F_5N_2^+$) 100, 131 ($C_2F_2N_3C_2H_3^+$) 5.3, 103 ($C_2F_2NC_2H_3^+$) 8.4, 59 ($CFN_2^+$) 100. Compound **21** was found in a trap at −20 °C in 66% yield. Spectral data obtained are as follows. IR (gas): 2948 s, 2906 m, 1608 vs, 1559 vs, 1533 vs, 1474 s, 1427 s, 1410 s, 1397 s, 1336 m, 1251 m, 1233 m, 1199 m, 1158 s, 1146 m, 1066 m, 973 w, 930 w, 906 w, 872 vs, 835 vs, 801 vs, 771 m, 731 s, 662 m, 634 m, 586 m, 555 m, 531 w, 483 w cm^{-1}. NMR: ^{19}F ϕ 83.34, 81.48 (SF_4, d, J_{F-F} = 156.2 Hz), 105.4 (SF, p); ^1H δ 2.9 (CH_3, s). MS (CI^+) [*m/e* (species) intensity]: 242 ($M^+ + 1$) 6.7, 222 ($M^+ - F$) 100, 197 ($M^+ - N(CH_3)_2$) 17.8, 127 (SF_5^+) 3, 114 ($M^+ - SF_5$) 13, 85 ($SF_2N^+ + 1$) 9, 71 ($SF_2^+ + 1$) 27, 70 (SF_2^+) 17.4. Anal. Calcd for $C_5H_{12}F_5N_3S$: C, 24.89; H, 4.97; N, 17.42. Found: C, 24.75; H, 4.83; N, 17.44.

Reaction of Cyanotrimethylsilane with $CF_3N{=}CF_2$. A 3-mmol sample of $CF_3N{=}CF_2$ and 6 mmol of $(CH_3)_3SiCN$ were condensed at −196 °C into a Pyrex glass vessel equipped with a Teflon stopcock. The reaction mixture was warmed slowly to and allowed to remain at 25 °C for 12–14 h. All of the volatile materials were removed from the reaction vessel to leave **22** as a yellow solid (mp 190–192 °C). Spectral data obtained are as follows. IR (KBr disk): 2260 s, 2232 m, 1620 vs, 1400 w, 1201 s, 1136 m, 1107 vs, 1047 m, 900 vs, 858 m, 724 m, 673 w, 571 m cm^{-1}. NMR: ^{19}F ϕ −55.31 (CF_3N, s). MS (CI^+) [*m/e* (species) intensity]: 148 ($M^+ + 1$) 22.1, 147 (M^+) 16.1, 103 ($CF_2NC_2N^+ + 1$) 66.6, 102 ($CF_2NC_2N^+$) 1.7, 79 ($M^+ - CF_3 + 1$) 18.3, 69 (CF_3^+) 5.3.

Reaction of Hexamethyldisilazane with $CF_3N{=}CF_2$. A 4-mmol sample of $CF_3N{=}CF_2$ and 4 mmol of $(CH_3)_3SiN(H)Si(CH_3)_3$ were condensed at −196 °C into a Pyrex glass reaction vessel equipped with a Teflon stopcock. The mixture was warmed slowly to 25 °C. At this temperature a white solid appeared. After remaining for 2 h, the mixture was filtered to give **23** as a white solid (mp 121–123 °C dec). Spectral data obtained are as follows. IR (KBr disk): 3250 br, 3048 s, 2271 m, 2154 s, 1640 s, 1580 m, 1407 s, 1328 s, 1252 s, 926 m, 852 m, 741 s, 581 m, 562 w, 521 w cm^{-1}. NMR: ^{19}F ϕ −53.5 and −53.8 (CF_3N, 2 s); ^1H δ 3.82 (NH_2, br). MS (CI^+) [*m/e* (species) intensity]: 219 ($M^+ - H$) 10.2, 149 ($M^+ - CF_3 - 2H$) 42.3, 131 ($M^+ - CF_3 - HF$) 8.3, 91 ($CF_2NCN^+ + 1$) 10.6, 69 (CF_3^+) 100.

Acknowledgment. We are grateful for the support of the National Science Foundation (Grant CHE-9003509), the Air Force Office of Scientific Research (Grant 91-0189), and Daikin Industries, Ltd.

Registry No. **1**, 123837-31-0; **2**, 54657-79-3; **3**, 137719-85-8; **4**, 137719-86-9; **5**, 137719-87-0; **6**, 137719-88-1; **7**, 137742-06-4; **8**, 137719-89-2; **9**, 130229-97-9; **10**, 137719-90-5; **11**, 137719-91-6; **12**, 137742-07-5; **13**, 13105-65-2; **14**, 122540-49-2; **15**, 137719-92-7; **16**, 69538-01-8; **17**, 137719-93-8; **18**, 137719-94-9; **19**, 137719-95-0; **20**, 137719-96-1; **21**, 137742-08-6; **22**, 137719-97-2; **23**, 137719-98-3; chlorotrifluoroethylene, 79-38-9; trifluoroethylene, 359-11-5; 1,1-difluoroethylene, 75-38-7; dimethyl(trimethylsilyl)amine, 2083-91-2; (difluoromethylene)(trifluoromethyl)amine, 371-71-1; perfluoro[methyl(dimethylamino)methylenimine], 686-39-5; [(dichloromethylene)amino]pentafluorosulfur, 1801-00-9; cyanotrimethylsilane, 7677-24-9; hexamethyldisilazane, 999-97-3.