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Perfluoroalkyl(*N*-pentafluorosulfanyl)azidoazomethines and Perfluoroalkyl(*N*-pentafluorosulfanyl)carbodiimides

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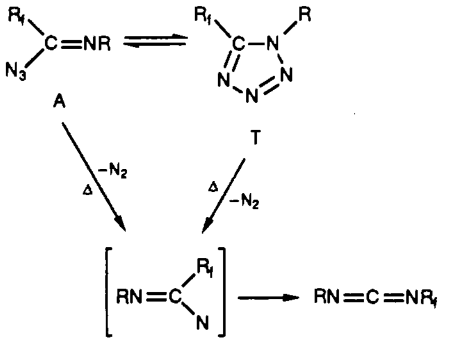
Photolytic addition of SF_5Cl to $NF_2CF_2C{\equiv}N$ gives the imine $NF_2CF_2C(Cl){=}NSF_5$ and to $CF_3C(C{\equiv}N){=}NF$ results in an isomeric mixture of $CF_3C({=}NF)C(Cl){=}NSF_5$ and $CF_3CCl(C{\equiv}N)NFSF_5$. With azide ion, $R_fC(Cl){=}NSF_5$ [$R_f = CF_3, C_2F_5, NF_2CF_2, (CF_3)_2N$] form the perfluoroalkyl (*N*-pentafluorosulfanyl)azidoazomethines, $R_fC(N_3){=}NSF_5$. The latter rearrange under pyrolytic conditions to $R_fN{=}C{=}NSF_5$ ($R_f = CF_3, C_2F_5, NF_2CF_2$). A gas electron diffraction analysis provides structural information for $CF_3N{=}C{=}NSF_5$ where the $\angle N{=}C{=}N$ of 171 (4)° brings the CF_3 and SF_5 groups into closer proximity. Both $C_2F_5C(Cl){=}NSF_5$ and $C_2F_5C(N_3){=}NSF_5$ undergo controlled hydrolysis to the white crystalline solid $C_2F_5C(O)N(H)SF_5$.

Introduction

Carbodiimides are versatile and useful precursors to materials with industrial applications.[2-4] Nonfluorinated carbodiimides have resulted from reactions of a variety of nitrogen-containing compounds, including ureas and thioureas, isocyanates, oxazetidines, and oxadiazetidines as well as tetrazoles and azidoazamethines. The latter two compounds, which when heated lose nitrogen to give carbodiimides, often exist in equilibrium.[5-9] The predominant species is a function of the substituent(s) at nitrogen, e.g.



when R is an electron-donating group the tetrazole (T) is favored, while the azide (A) tends to be more stable when R is an electron-withdrawing group.[10] This is illustrated by comparison of the compounds $CF_3(N_3)C{=}NR$, which, when R = SF_5, exists as A,[11] and, when R = CH_3, exists as T.[12] More recently, workers who synthesized several perfluoroazidoazomethines report no evidence for cyclization to tetrazole tautomers.[13]

$$CF_3N{=}CFR + Me_3SiN_3 \rightarrow CF_3N{=}C(N_3)R$$

$$R = F, CF_3, C_2F_5, n\text{-}C_3F_7, CF(CF_3)_2, C(CF_3)_3$$

However, earlier work in our laboratory showed that an equilibrium mixture of A and T results when R = $CF(CF_3)_2$ with T the predominant species.[14] Others have made similar observations.[15-21] Regardless of the species present, rearrangement occurs on gas phase pyrolysis at 270-300 °C in helium to form perfluorodialkylcarbodiimides in 71-85% yield.[13,22]

Unsymmetric alkyl(perfluoroalkyl)carbodiimides result from the reaction of perfluoroazaalkenes, $R_fN{=}CF_2$, with primary amines

$$R_fN{=}CF_2 + RNH_2 \xrightarrow{-HF} RN{=}CFNHR \xrightarrow[BF_3\cdot NEt_3]{-HF} R_fN{=}C{=}NR$$

$$R_f = CF_3;\ R = CH_3, C_2H_5, c\text{-}C_6H_{11}, (CF_3)_2CH^{23}$$

Also, perfluoro-α,ω-bis(azomethines) undergo 1,3-fluoride ion migration in the presence of fluoride ion to form the diimide, e.g.

$$CF_2{=}NCF_2N{=}CF_2 \xrightarrow{F^-} CF_3N{=}C{=}NCF_3^{24}$$

Now we can report new perfluoroazidoazomethines and perfluoroalkylcarbodiimides which contain the SF_5 moiety. The

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latter compounds may be useful in imparting oil and water repellency to nylon, polyester, and other fibers.[25-27]

Results and Discussion

Certain compounds that contain the $-SF_5$ group exhibit excellent dielectric properties as exemplified by SF_6, which is used as a gaseous insulator in high voltage generators and other electric equipment. Although a large number of simple *N*-pentafluorosulfanyl(VI) derivatives, such as SF_5NCO, SF_5NF_2, SF_5NCl_2, $SF_5N{=}CF_2$, $SF_5N{=}CCl_2$, $(SF_5)_3N$, SF_5NH_2 and $(SF_5)_2NR$, and, more recently, SF_5NC,[28-33] have been synthesized, until this time no *N*-chalcogenopentafluoride diimide has been reported.

The straightforward, high yield route to F_2NCF_2CN and $CF_3C(CN){=}NF$ provides a ready source of reactive starting materials.[34,35] The reactions proceed via the addition of the NF_2 radical across appropriate olefins

$$CF_2{=}CH_2\ (CF_3CH{=}CH_2) + N_2F_4 \xrightarrow[-HF]{KF} \underset{I}{F_2NCF_2CN}\ (\underset{II}{CF_3C(CN){=}NF})$$

Bis(trifluoromethyl)aminoacetonitrile is formed readily.

$$ClCN + SF_4 \xrightarrow{CsF} CF_3N{=}SF_2 \xrightarrow{ClF} \underset{III}{CF_3NCl_2} + SF_4{}^{36}$$

$$III + CF_2{=}CFCl \rightarrow CF_3N(Cl)CF_2CFCl_2 \xrightarrow{h\nu} \underset{IV}{CF_3N{=}CF_2} + CFCl_3$$

$$IV + CsF/AgF + ClCN \rightarrow \underset{V}{(CF_3)_2NCN}{}^{37}$$

The discovery of SF_5Cl and SF_5Br opened the door to the free radical addition chemistry of $SF_5{}^{\bullet}$.[28,31,38,39] Photolysis of SF_5Cl with nitriles gives the respective imines, $R_fC(Cl){=}NSF_5$.

$$SF_5Cl + R_fCN \xrightarrow{h\nu} R_fC(Cl){=}NSF_5$$

	R_f	
I	NF_2CF_2	VIII
V	$(CF_3)_2N$	IX[40]
VI	CF_3	X[39]
VII	C_2F_5	XI[31]

Table I. IR Absorption Frequencies (cm^{-1})

compd	$\nu_{X{=}Y{=}Z}$[a]	$\nu_{C{=}N}$
$SF_5N{=}C(N_3)CF_3$ (XIV)[b]	2159	1680
$SF_5N{=}C(N_3)C_2F_5$ (XV)[b]	2149	1666
$SF_5N{=}C(N_3)CF_2NF_2$ (XVI)[b]	2151	1671
$SF_5N{=}C(N_3)N(CF_3)_2$ (XVII)[b]	2159	1661
$F_2NCF_2CF_2N(CF_3)N{=}C(N_3)CF_2NF_2$[c]	2162	1540
$CF_3N{=}C{=}NCF_3$[d,e]	2212	
$SF_5N{=}C{=}NCF_3$ (XIX)[b]	2183, 2158	
$SF_5N{=}C{=}NC_2F_5$ (XX)[b]	2180	
$SF_5N{=}C{=}NCF_2NF_2$ (XXI)[b]	2180, 2159	
$F_2NCF_2CF_2N(CF_3)N{=}C{=}NCF_2NF_2$[c]	2270	

[a] $N{=}N{=}N$ or $N{=}C{=}N$. [b] This work. [c] Unpublished work, University of Idaho. [d] Reference 13. [e] Reference 24.

An isomeric mixture of compounds is obtained when SF_5Cl is reacted with II with partial saturation of either the nitrile or the imine functionality occurring.

$$SF_5Cl + \underset{II}{CF_3C(CN){=}NF} \rightarrow \underset{XII}{CF_3C(CCl{=}NSF_5){=}NF} + \underset{XIII}{CF_3CCl(CN)NFSF_5}$$

Complete separation of XII and XIII was not possible because of similar boiling points. The infrared spectrum of the isomeric mixture shows stretching frequencies for carbon–nitrogen bonds at 1743 and 1667 cm^{-1} and at 2269 cm^{-1}, respectively.

Moderately stable *N*-pentafluorosulfanyl(perfluoroalkyl)azidomethines, $R_fC(N_3)NSF_5$, were obtained with NaN_3 in reaction with VIII–XI.

$$NaN_3 + R_fC(Cl){=}NSF_5 \longrightarrow R_fC(N_3){=}NSF_5$$

	R_f	
X	CF_3	XIV
XI	C_2F_5	XV
VIII	NF_2CF_2	XVI
IX	$(CF_3)_2N$	XVII

Unlike the nonfluorinated analogs, these azidomethines showed no tendency to cyclize to give tetrazole tautomers. The infrared bands assigned to $\nu_{C{=}N}$ and ν_{N_3} for XIV–XVII are given in Table I. The molecular ion peaks for these compounds were observed at *m/e* 264, 314, 298, and 384, respectively. The ^{19}F NMR spectrum of XIV showed a typical AB_4X_3 spin system with a SF_5 group having a total of nine lines for the axial fluorine atom (A) and two multiplets for equatorial fluorine atoms (B). Coupling between the equatorial fluorine atoms and the CF_3 group occurs ($J_{CF_3\text{-}SF_4} = 10.6$ Hz). It was possible to simulate the spectrum by using the parameters for chemical shifts and coupling constants: B, δ 74.5; A, δ 56.8 ($J_{A\text{-}B} = 162.9$ Hz; $J_{B\text{-}B'} = 2$ Hz); X, δ −61 ($J_{BX} = 10.6$ Hz). Elemental analyses are reported for all of the new compounds except for XVII, which, because of its possible shock sensitivity, was not able to be transported to Germany for analysis.

Controlled hydrolysis of XI and XV gives rise to the sublimable crystalline compound XVIII

$$\begin{matrix} C_2F_5C(Cl){=}NSF_5 \\ C_2F_5C(N_3){=}NSF_5 \end{matrix} \xrightarrow{H_2O} \underset{XVIII}{C_2F_5C(O)N(H)SF_5}$$

with infrared bands at 3272 cm^{-1} (ν_{NH}) and 1752 cm^{-1} $\nu_{(C{=}O)}$.

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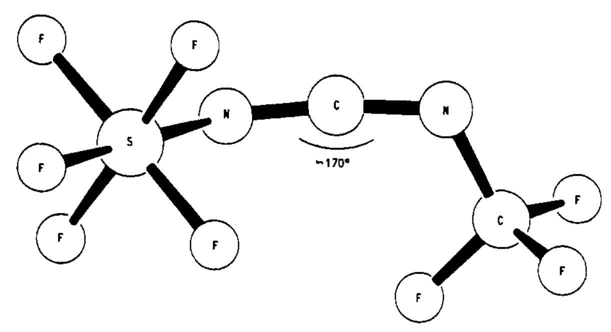


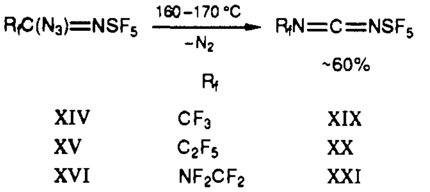
Figure 1. Electron diffraction structure of $CF_3N{=}C{=}NSF_5$.

Table II. Geometric Parameters for $CF_3N{=}C{=}NSF_5$[a]

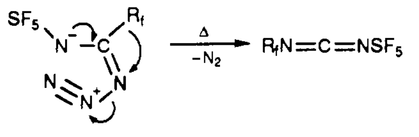
bond lengths (Å)		bond angles (deg)	
N=C	1.228 (6)	F—C—F	108.3 (5)
S—N	1.690 (7)	F—S—F	88.3 (3)
C—F	1.330 (4)	C=N—C	115.7 (28)
N—C	1.420 (10)	C=N—S	130.6 (21)
S—F	1.567 (2)	C=N=C	171.1 (38)

[a] r_a values, error limits are 3σ values.

Each of the perfluoroazidoazomethines rearranged upon gas-phase pyrolysis in sealed tubes at 160–170 °C to produce the appropriate perfluoroalkyl(*N*-pentafluorosulfanyl)carbodiimide.



This type of behavior is not unusual, often being reported as a Beckmann[41] or an azide analog of a Tiemann rearrangement,[4] and perhaps occurs as follows.[42]



Compounds XIX–XXI have characteristic antisymmetric N=C=N stretching vibrations in the infrared spectrum at 2181, 2158; 2180; and 2180, 2159 cm^{-1}, respectively. These are compared with similar compounds in Table I. The chemical ionization mass spectrum of XIX and XX showed a peak for M$^+$ + 1 at *m/e* 237 and 287 while for XXI a peak for M$^+$ – F at *m/e* 250 was observed.

The gas-phase electron diffraction intensities of XIX have been recorded. The resulting structure is displayed in Figure 1, and the geometric parameters are given in Table II. In the structure refinement both C=N bond lengths were set equal and local C_{3v} and C_{4v} symmetry was assumed for the CF$_3$ and SF$_5$ groups, respectively. Both groups stagger the lone pair of the adjacent nitrogen atoms. This implies that SF$_5$ staggers, but CF$_3$ eclipses the N=C bonds. X-ray crystallographic studies for both aromatic and mixed aliphatic–aromatic species have shown that the carbodiimide bonds deviate slightly from linearity, with the N=C=N angle varying between 166 and 170°.[4] For $CF_3N{=}C{=}NSF_5$, both the N=C=N angle, which was found at ~170°, and the direction of the bend (see Figure 1) are in keeping with similar data for other carbodiimides. While in some cases the apparent anomalous direction of the bend has been rationalized based on crystal packing effects, in fact it may result from an electronic effect such as nitrogen–nitrogen lone pair repulsion. Even when the carbodiimide is symmetrically substituted, it may be nonlinear, e.g., $H_3GeN{=}C{=}NGeH_3$, or linear, e.g., $(C_6H_5)_3SiN{=}C{=}NSi(C_6H_5)_3$.[43–45] Steric repulsions between the substituents in XIX are negligible since the shortest F···F contact between the CF$_3$ and SF$_5$ groups is 3.50 Å, i.e., much longer than the van der Waals distance (2.70 Å). Some of the angles and the dihedral angle are not well determined, but the dihedral angle of ~99° is definitely much larger than that in $PF_2N{=}C{=}NPF_2$ at ~55°.[46]

Experimental Section

Materials. Reagents were purchased as indicated: sodium azide (EM Science); CF$_3$CN, C$_2$F$_5$CN (PCR); ClF (AtoChem North America). F_2NCF_2CN, $CF_3CF(CN){=}NF$,[34] $(CF_3)_2NCN$,[37] $CF_3C(Cl){=}NSF_5$,[39] and $C_2F_5C(Cl){=}NSF_5$[33] were prepared according to the literature methods.

Instrumentation. For infrared, ^{1}H and ^{19}F nuclear magnetic resonance, and mass spectral analysis, Perkin-Elmer 1710 Fourier transform infrared, Bruker AC200 FT NMR, and VG 7070HS mass spectrometers were employed. ^{19}F NMR resonances are reported as positive when downfield from CFCl$_3$. The electron diffraction intensities were recorded with a Balzers Gasdiffractograph[47] at two camera distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. A conventional Pyrex vacuum system equipped with Heise Bourdon tube and Televac thermocouple gauges was used to handle gases and volatile liquids. Elemental analyses were performed by Beller Microanalytisches Laboratorium, Göttingen, Germany.

Synthesis of VIII, XII, and XIII. At –195 °C, compound I or II (12 mmol) and SF$_5$Cl (15 mmol) were condensed into a quartz vessel. Each mixture was photolyzed for 24 h at 3000 Å by using a Rayonet chemical reactor. By using trap-to-trap separation, VIII or a mixture of XII and XIII were stopped in a trap cooled at –78 °C in approximately 33% yield.

Characterization of Compound VIII. Spectral data obtained for VIII are as follows. IR (gas): 1678 m, 1376 w, 1360 w, 1278 s, 1236 vs, 1172 m, 1130 m, 1029 vs, 939 s, 912 vs, 891 s, 873 vw, 831 vw, 782 vw, 733 vs, 659 w, 632 vw, 606 s, cm^{-1}. NMR: ^{19}F δ 64.8 (two sets of complex mult), SF$_5$ (J_{AB} = 127 Hz); 19.8 (br), NF$_2$; –101.8, –103.0, CF$_2$ (E, Z). MS EI [*m/e* (species), intensity]: 291 (M$^+$ + 1), 0.14; 271 (M$^+$ – F), 0.64; 255 (M$^+$ – Cl), 0.1; 238 (M$^+$ – NF$_2$), 0.3; 165 (C$_2$NSF$_5^+$), 0.7; 127 (SF$_5^+$), 100; 102 (NF$_2$CF$_2^+$), 0.4; 52 (NF$_2^+$), 0.7; 50 (CF$_2^+$), 0.8. Anal. Calcd for C$_2$ClF$_9$N$_2$S: C, 8.28; Found: C, 8.33.

Characterization of Compounds XII and XIII. Spectral data obtained for the mixture of isomers are as follows. IR: 2269 w, 1743 m, 1677 w, 1641 vw, 1528 vw, 1460 vw, 1347 vw, 1308 vw, 1262 s, 1234 vs, 1216 vs, 1161 vw, 1120 w, 1064 m, 1016 m, 972 vs, 891 m, 873 vs, 837 w, 764 vw, 736 vw, 697 w, 607 m, 563 vw, 516 vw, cm^{-1}. NMR: ^{19}F δ 61.73 (complex mult), SF$_5$, 71.15 (br), =NF; –32.1 (br), NF; –71.69, –71.92, (CF$_3$). MS CI [*m/e* (species), intensity]: 303 (M$^+$ + 1), 0.2; 283 (M$^+$ – F), 1.3; 276 (M$^+$ – CN), 0.8.

Synthesis of $SF_5N{=}C(N_3)R_f$, Compounds XIV, XV, XVI, and XVII. The respective chloroamines X, XI, VIII, or IX were condensed at –196 °C over NaN$_3$ in CH$_3$CN/C$_6$H$_5$CN. The temperature was slowly raised to –5 °C. After 3 h of constant stirring at this temperature and subsequent stirring at 25 °C for 24 h, each mixture was subjected to fractional condensation with the azido compound being held at –40, –25, –30, and –15 °C in yields of 56, 42, 30, and 25%, respectively.

Characterization of Compounds XIV, XV, XVI, and XVII. Spectral data obtained for XIV are as follows. IR (gas): 2159 w, 1680 m, 1380 m, 1268 m, 1228 vs, 1196 vs, 1166 w, 1102 s, 1070 s, 966 w, 940 vs, 904 m, 866 vvs, 802 vw, 758 w, 734 w, 607 m, 481 w, cm^{-1}. NMR: ^{19}F δ 74.5, SF$_{eq}$; 56.8, SF$_{ax}$ (J_{SF_4-SF} = 162.9 Hz); –49.9, CF$_3$ ($J_{SF_4-CF_3}$ = 10.6 Hz). MS CI [*m/e* (species), intensity]: 264 (M$^+$), 5.4; 245 (M$^+$ – F), 5.0; 195 (CF$_5$N$_4$S$^+$), 3.0; 153 (CF$_5$NS$^+$), 15; 127 (SF$_5^+$), 45; 89 (SF$_3^+$), 100; 69 (CF$_3^+$), 38. Anal. Calcd for C$_2$F$_8$N$_4$S: C, 9.09; N, 21.21.

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Found: C, 10.69; N, 21.76. Spectral data obtained for XV are as follows. IR: 2149 m, 1666 m, 1384 m, 1325 s, 1252 vs, 1237 s, 1205 s, 1163 s, 1124 s, 1072 w, 1045 m, 986 w, 970 m, 940 vs, 903 s, 860 vs, 835 m, 754 m, 734 w, 607 m, cm^{-1}. NMR: ^{19}F δ 75.0, SF_{eq}; 56.4, SF_{ax} ($J_{SF_4\text{-}SF}$ = 148.7 Hz); –110 (mult), CF_2; –82.1 (s), CF_3. MS CI [*m/e* (species), intensity]: 315 ($M^+ + 1$), 6.0; 296 ($M^+ - F + 1$), 1.0; 146 ($C_3F_5N^+ + 1$), 35; 127 (SF_5^+), 55; 119 ($C_2F_5^+$), 22; 89 (SF_3^+), 100; 69 (CF_3^+), 27. Anal. Calcd for $C_3F_{10}N_4S$: C, 11.46; N, 17.83. Found: C, 11.58; N, 17.89. Spectral data obtained for XVI are as follows. IR (gas): 2152 m, 1665 m, 1485 vw, 1475 vw, 1377 vw, 1342 vw, 1332 vw, 1267 vw, 1233 vs, 1146 s, 1068 vw, 1029 s, 940 vs, 904 s, 863 vs, 796 vw, 762 vw, 732 vw, 687 vvw, 633 vvw, 607 m, 573 vvw, 563 vw, cm^{-1}. NMR: ^{19}F δ 75.1, 68.4 (mult), SF_{eq}; 56.4, SF_{ax} (mult); +20.85, +19.33 (br), NF_2; –98.5, –103.7, (CF_2). MS CI [*m/e* (species), intensity]: 297 (M^+), 0.4; 250 ($M^+ - N_2F$), 6.6; 236 ($M^+ - N_3F$), 2.5; 217 ($M^+ - N_3F_2$), 5.5; 203 ($M^+ - N_4F_2$), 2.7; 195 ($CN_4SF_5^+$), 4.3; 170 ($C_2F_4N_5^+$), 12.5; 153 (CF_5NS^+), 4.1; 141 (SF_5N^+), 4.0; 127 (F_5S^+), 100; 114 ($C_2F_4N^+$), 2.2; 108 (F_4S^+), 31; 102 (CF_4N^+), 50.8; 89 (F_3S^+), 98; 84 (F_2NS^+), 30; 70 (F_2S^+), 61. Spectral data obtained for XVII are as follows. IR (gas): 2159 s, 1662 m, 1611 vw, 1536 vw, 1481 vw, 1450 vw, 1294 vs, 1229 vs, 1189 vs, 1069 s, 961 w, 939 s, 903 vw, 865 w, 735 s, 607 vw, 570 vw, 481 w, cm^{-1}. NMR: ^{19}F δ 80.4, SF_{ax} (nine signal pattern); 70.06 (d, mult), SF_{eq} ($J_{SF_{ax}\text{-}SF_{eq}}$ = 154.9 Hz); –56.26, –57.26, (CF_3). MS CI [*m/e* (species), intensity]: 348 ($M^+ + 1$), 7.86; 347 (M^+), 11.0; 305 ($M^+ - N_3$), 98.0; 286 ($M^+ - N_3F$), 33.0; 278 ($M^+ - CF_3$), 21.0; 267 ($M^+ - N_3F_2$), 98.0; 248 ($M^+ - N_3F_3$), 14.9; 229 ($M^+ - N_3F_4$), 42.0; 210 ($M^+ - N_3F_5$), 19.1; 178 ($M^+ - N_3F_5S$), 98.9; 152 ($C_2F_6N^+$), 99.0; 127 (SF_5^+), 100; 69 (CF_3^+), 69.8.

Synthesis of XVIII. An acetonitrile solution of XI or XV with H_2O (1:1) at 25 °C produced $SF_5N(H)C(O)C_2F_5$. The white crystalline material was dried over P_4O_{10} and was sublimed on a cold finger (80% yield).

Characterization of Compound XVIII. Spectral data obtained for XVIII are as follows. IR (solid, KBr): 3272 ($\nu_{N\text{-}H}$), 1752 vs, 1501 s, 1340 m, 1277 m, 1213 vs, 1195 vs, 1152 vs, 1039 s, 902 vs, 859 vs, 769 m, 758 m, 728 m, 665 m, cm^{-1}. NMR: ^{19}F δ 71.6 (mult), SF_5; –83.3 (t), CF_3; –112.95 (q), CF_2; ^{1}H δ 2.18, NH. MS CI [*m/e* (species), intensity]: 290 ($M^+ + 1$), 6.0; 289 (M^+), 1.0; 270 ($M^+ - F$), 1.9; 251 ($M^+ - 2F$), 2.1; 250 ($M^+ - HF_2$), 73.0; 149 ($C_3H_2F_5O^+$), 100; 119 ($C_2F_5^+$), 71.8; 100 ($C_2F_4^+$), 28.0; 89 (SF_3^+), 59.8; 69 (CF_3^+), 79.9. Anal. Calcd for $C_3HF_{10}NOS$: C, 12.46; H, 0.35; N, 4.84. Found: C, 12.94; H, 0.42; N, 5.28.

Synthesis of XIX, XX, and XXI. Compound XIV, XV, and XVI (0.5 mmol) were respectively pyrolyzed in a sealed tube at 160–170 °C for 12 h. The resulting carbodiimides were held in a trap cooled to –78 °C (~60% yield).

Characterization of Compounds XIX, XX and XXI. Spectral data obtained for XIX are as follows. IR (gas): 2183 vs, 2158 vs, 1692 w, 1454 w, 1384 w, 1335 w, 1232 s, 1162 s, 1051 vw, 969 w, 917 vs, 880 vs, 853 vs, 808 m, 725 vw, 681 m, 604 s, 589 s, 544 m, 502 vw, cm^{-1}. NMR: ^{19}F δ 83.4 (mult), SF_{eq}; 68.5 (mult), SF_{ax}; –49.9 (s), CF_3. MS CI [*m/e* (species), intensity]: 238 ($M^+ + 2$), 9.0; 237 ($M^+ + 1$), 15.8; 236 (M^+), 0.2; 217 ($M^+ - F$), 3.8; 199 ($M^+ - 2F + 1$), 17.5; 198 ($M^+ - 2F$), 0.3; 153 (CF_5NS^+), 2.3; 141 (F_5SN^+), 4.5; 89 (SF_3^+), 100; 70 (SF_2^+), 41.0; 69 (CF_3^+), 60.0. Anal. Calcd for $C_2F_8N_2S$: C, 10.17; N, 11.86. Found: C, 9.49; N, 10.52. Spectral data obtained for XX are as follows. IR (gas): 2181 vs, 1463 m, 1335 s, 1240 vs, 1196 vs, 1151 vs, 1054 vs, 934 m, 915 vs, 867 vs, 820 m, 809 m, 732 m, 682 m, 605 vs, 590 m, 544 vw, 530 vw, 481 vw, cm^{-1}. NMR: ^{19}F δ 83.52 (d, mult), SF_{eq}; 67.3 (mult, nine peak pattern), SF_{ax} ($J_{SF_4\text{-}SF}$ = 161.6 Hz); –86.24, CF_3; –89.72, CF_2. MS CI [*m/e* (species), intensity]: 287 ($M^+ + 1$), 20.0; 267 ($M^+ - F$), 69.8; 217 ($M^+ - CF_3$), 20.9; 127 (SF_5^+), 100; 89 (SF_3^+), 55.1; 84 (F_2NS^+), 98.2; 69 (CF_3^+), 50.1. Anal. Calcd for $C_3F_{10}N_2S$: C, 12.59; N, 9.79. Found: C, 12.67; N, 9.70. Spectral data obtained for XXI are as follows. IR (gas): 2159 vs, 1757 w, 1439 w, 1330 m, 1247 s, 1193 s, 1127 s, 994 s, 938 vs, 918 vs, 871 vs, 854 vs, 831 s, 783 w, 725 w, 680 w, 604 s, 589 vs, 564 w, 544 w, cm^{-1}. NMR: ^{19}F δ 83.6, SF_{eq}; 68.1, SF_{ax} ($J_{SF_4\text{-}SF}$ = 157.2 Hz); 21.1, NF_2; –106.27, –119.36 (mult), CF_2. MS CI [*m/e* (species), intensity]: 250 ($M^+ - F$), 0.4; 143 ($M^+ - SF_5 + 1$), 0.4; 127 (SF_5^+), 7.1. Anal. Calcd for $C_2F_9N_3S$: C, 8.92. Found: C, 7.04.

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