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Reactions of perfluoro(*N*-vinylmorpholine) and its derivatives with chlorine fluorosulfate

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Abstract

The vinyl amine $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$ and the tertiary amines $\overline{CF_2CF_2OCF_2CF_2N}CFXCF_2X$ (X = Cl, Br, OSO_2F) and $\overline{CF_2CF_2OCF_2CF_2N}CF_2Br$ have been reacted with $ClOSO_2F$ to give a number of interesting fluorosulfate-containing products. The reactivity of bromine (chlorine) α and β to the nitrogen in these amines is compared. The structure of the products has been confirmed by ^{19}F NMR, infrared and mass spectral studies, and by elemental analyses.

Introduction

The chemistry of perfluorinated vinyl amines has not been widely studied. This is particularly surprising in view of their potential use in the preparation of fluoropolymers expected to exhibit highly useful and unusual properties. Previously reported methods for the synthesis of perfluorovinyl amines require pyrolytic reaction conditions, and make use of starting materials which are not readily available, or result in difficult-to-separate mixtures [1]. Electrochemical fluorination has now been applied to the preparation of the precursors to several of these vinyl amines [2, 3]; their transformation to fluorovinyl amines has only recently been described [4–6].

Many literature reports describe the nucleophilic replacement of chlorine or bromine in perfluorochloro(bromo)alkanes and the addition reactions of perfluoroalkenes with $ClOSO_2F$. The reported regioselectivity of these additions or substitutions is however not consistent. A variety of mechanisms has been invoked to explain the products obtained. For example, regiospecific addition of chlorine fluorosulfate to $CF_3CF{=}CFR$ (R = CF_3, C_2F_5, C_3F_7 and $(CF_3)_2CF$) has been claimed, and later refuted [7]. In compounds of the type $R_fCFBrCF_2Br$, some studies indicate that attack gives a single compound, while other reports list multiple products [7–9]. The mechanisms used to explain the products formed range from classical S_N1 or S_N2 processes to direct halophilic attack on chlorine or bromine [10].

We report here the reactions of $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$ and its derivatives with chlorine fluorosulfate. Both the direction of addition of $ClOSO_2F$ to this vinyl amine, and the relative reactivity of bromine(chlorine) α and β to the nitrogen in the tertiary amine $\overline{CF_2CF_2OCF_2CF_2N}CFXCF_2X$ (X = Cl, Br, OSO_2F), are of considerable interest and are the subjects of this study.

Results and discussion

While perfluorinated vinyl amines have not previously been reacted with chlorine fluorosulfate, perfluorinated vinyl ethers which would be expected to give rise to similar chemistry have been studied [7]. Perfluoromethylvinyl ether reportedly reacts with either chlorine fluorosulfate or bromine fluorosulfate to give only a single addition product, i.e. $CF_3OCF(OSO_2F)CF_2Cl(Br)$. In our study, perfluoro(*N*-vinylmorpholine) reacts with only a 10% excess of $ClOSO_2F$ to give a mixture of three products:

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$$CF_2CF_2OCF_2CF_2NCF{=}CF_2 + ClOSO_2F \xrightarrow[24\ h]{RT}$$

$$CF_2CF_2OCF_2CF_2NCF(OSO_2F)CF_2Cl$$
(1a) (72%)

$$+\,CF_2CF_2OCF_2CF_2NCF(Cl)CF_2OSO_2F$$
(1b) (11%)

$$+\,CF_2CF_2OCF_2CF_2NCF(OSO_2F)CF_2OSO_2F$$
(2) (2%)

TABLE 1. Influence of reaction temperature on the products of the reaction between $ClOSO_2F$ and $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$

Reaction temperature (°C)	1:1 Adduct (%) (ratio of **1a**/**1b**)	1:2 Adduct (%) **(2)**
25	82.9 (87:13)	1.7
100	78.5 (100:0)	6.6
150	62.3 (100:0)	11.3

The major addition product is consistent with the product found in the perfluorovinyl ether reaction. The direction of addition of $XOSO_2F$ (X = Br, Cl) in the reaction with perfluoromethylvinyl ether and perfluoro(*N*-vinylmorpholine) is unexpected, particularly when compared with the addition product found in the reaction between $CF_3OCF{=}CF_2$ and the hypochlorite $ClOCH_2(CF_2)_2H$, where the only addition product observed is $CF_3OCF(Cl)CF_2OCH_2(CF_2)_2H$ [7]. The products of electrophilic attack by SO_3 on $R_fOCF{=}CF_2$ ($R_f = C_3F_7$ and C_4F_9) [11, 12] are however in accord with the direction of addition we find on reaction of chlorine fluorosulfate with perfluoro(*N*-vinylmorpholine). The product found is $R_f\overline{OCFCF_2SO_2O}$ (rather than $R_f\overline{CFCF_2OSO_2}$ as is the case in the absence of ether oxygen). This observation has been rationalized by the electronic influence of the ether oxygen electrons on the olefin π-system resulting in a partial negative charge on the CF_2 group, or by increased stabilization of adjacent positive charge by oxygen (over vinylic fluorine) in the addition intermediate (i.e. $^-OSO_2CF_2CF^+OR_f$ is more stable than $R_fOCF(SO_2O^-)CF_2^+$) [11–13].

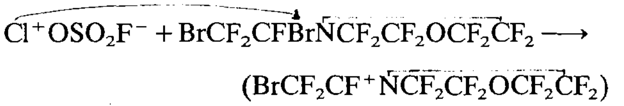
The reverse direction of addition, coupled with the fact that the reaction of perfluoro(*N*-vinylmorpholine) with chlorine fluorosulfate gives a low yield of $\overline{CF_2CF_2OCF_2CF_2N}CFOSO_2FCF_2OSO_2F$ and bidirectional 1:1 addition (compounds **1a** and **1b**) prompted a short study on the relative reactivity of halogen bound α and β to nitrogen in these tertiary amines. Interestingly, the products of the reaction between $ClOSO_2F$ and $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$ varied markedly with changes in the reaction temperature when the reactant stoichiometry was held constant at 6:5.3 of $ClOSO_2F$ to vinyl amine (see Table 1).

The formation of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2OSO_2F$ (**2**) results from the reaction of $ClOSO_2F$ with both compounds **1a** and **1b**, although since no **1b** was detected at either 100 °C or 150 °C the chlorine positioned α to the nitrogen is much more reactive towards $ClOSO_2F$ than the chlorine at a position β to the nitrogen. No catalyst was required for these reactions in contrast to the situation with perfluorochloroalkanes [14]. The FSO_3H-catalyzed reaction of chlorine fluorosulfate with $CF_3OCFClCF_2Cl$ at 40 °C reportedly gives a 97% yield of $CF_3OCF(OSO_2F)CF_2Cl$, while using FSO_3H/SbF_5 as a catalyst leads to the formation of both $CF_3OCF(OSO_2F)CF_2Cl$ (34%) and $CF_3OCF(OSO_2F)CF_2OSO_2F$ (37%) [14]. In the same study, chlorine fluorosulfate was found to react with $CF_3CFClCF_2Cl$ at 40 °C in the presence of FSO_3H to give an 84% yield of $CF_3CFClCF_2SO_3F$. Similarly, $S_2O_6F_2$ has been found to give $CF_3CFClCF_2OSO_2F$ in 80% yield at 70 °C from $CF_3CFClCF_2Cl$ in the presence of HSO_3F [15]. This is in contrast to the order of reactivity found for the reaction of the radical anion CO_2^- with $CF_3CFClCF_2Cl$, where the secondary chlorine is preferentially reduced [16].

Bromination of $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$ occurs readily to give $\overline{CF_2CF_2OCF_2CF_2N}CFBrCF_2Br$. At room temperature, a 1:1 molar ratio of chlorine fluorosulfate to $\overline{CF_2CF_2OCF_2CF_2N}CFBrCF_2Br$ reacts to give only a single product, $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Br$, in 91% yield. With an excess of chlorine fluorosulfate (2.5:1 molar ratio) and a reaction time of 2 weeks at room temperature, a 20% yield of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Br$ and a 67% yield of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2OSO_2F$ was found. Heating a mixture consisting of 7 mmol of $ClOSO_2F$ and 2 mmol of $\overline{CF_2CF_2OCF_2CF_2N}CFBrCF_2Br$ at 100 °C for 15 h gave a 92% isolated yield of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2OSO_2F$, a product which was isolated only in low yield even at 150 °C when the chlorinated derivative ($\overline{CF_2CF_2OCF_2CF_2N}CFClCF_2Cl$) was reacted with chlorine fluorosulfate. No product containing only a terminal fluorosulfate group was obtained from the amine containing bromine, regardless of reaction temperature or stoichiometry.

Attempts were made to examine what effect the structure of the *N*-fluoroalkyl group might have on the reactivity of the bromine α and β to the amine nitrogen by preparing $\overline{CF_2CF_2CF_2CF_2N}CFBrCF_2Br$ and $\overline{CF_2CF_2OCF_2CF_2N}CF_2Br$ [4]. However, $\overline{CF_2CF_2CF_2CF_2N}CFBrCF_2Br$ was obtained only in very low yield and was not further reacted. The reaction of $\overline{CF_2CF_2OCF_2CF_2N}CF_2Br$ proceeded readily at room temperature to give an 86% yield of $\overline{CF_2CF_2OCF_2CF_2N}CF_2OSO_2F$ (5 d at 25 °C).

All of the halogen-substitution data obtained in this study, as well as that taken from the literature, are consistent with halophilic attack by chlorine fluorosulfate at the halogen (chlorine or bromine) resulting in the formation of the most stable positively charged intermediate. For example,



$$Cl^+OSO_2F^- + BrCF_2CFBr\overline{NCF_2CF_2OCF_2C}F_2 \longrightarrow (BrCF_2CF^+\overline{NCF_2CF_2OCF_2C}F_2)$$

which is more stable than the competing intermediate, $[CF_2{}^+CFBr\overline{NCF_2CF_2OCF_2C}F_2]$. Similarly, from the literature [11],

$$FSO_3{}^-Cl^+ + CF_3CFClCF_2Cl \longrightarrow (CF_3CFClCF_2{}^+)$$

which is a more stable carbocation than $(CF_3CF^+CF_2Cl)$. While other mechanisms cannot be ruled out by the data obtained in this study, halophilic substitution is consistent with the products observed. It is also in accord with the fact that $ClOSO_2F$ is a ready source of positive chlorine [17].

Further studies of the reaction chemistry of perfluorinated vinyl amines and polyfluorinated tertiary amines with a variety of nucleophiles, electrophiles and interhalogens is currently underway in this laboratory.

Experimental

Materials

The starting materials $\overline{CF_2CF_2OCF_2CF_2N}CF_2Br$, $\overline{CF_2CF_2OCF_2CF_2N}CF=CF_2$, $\overline{CF_2CF_2CF_2CF_2N}CF=CF_2$ and $ClOSO_2F$ were prepared by known methods [4–6, 18]. All others, including ClF (Atochem, North America), SO_3 and bromine (Aldrich) were purchased as indicated and used as received.

General procedures

Infrared spectral data were obtained with a Hitachi EPI-G3 spectrometer. For ^{19}F NMR spectra, a Hitachi R-90F NMR spectrometer operating at a frequency of 84.68 MHz was used with CCl_3F as internal standard. Positive shifts are downfield from the reference. A Shimadzu GC/MS model 7000 instrument was used to record mass spectra. Gases were measured and manipulated using standard *PVT* techniques and a Pyrex glass vacuum line equipped with a Heise–Bourdon tube gauge. Elemental analyses were performed by Beller Laboratories in Göttingen, Germany.

Analytical gas chromatography was accomplished with 3-mm diameter stainless-steel columns containing 25% Kel F 90 on Chromosorb PAW on a Shimadzu model GC-2C gas chromatograph. A Gasukuro LL-75 modified gas chromatograph and 10-mm diameter stainless-steel columns packed with 25% Kel F 90 on Chromosorb PAW or 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW were used for semi-preparative gas chromatography.

Preparation and properties of $\overline{CF_2{}^ACF_2{}^BOCF_2CF_2N}CF^CBrCF_2{}^DBr$

When 15 mmol of bromine in Freon 113 (1:1 by weight) was combined in a dropwise manner with 14.7 mmol of $\overline{CF_2CF_2OCF_2CF_2N}CF=CF_2$ at room temperature in a 30 ml two-necked flask and allowed to stand at 25 °C in sunlight for several hours, an 83% yield of $\overline{CF_2CF_2OCF_2CF_2N}CFBrCF_2Br$ was obtained. The resulting mixture was washed with aqueous Na_2CO_3 and the product purified by semi-preparative gas chromatography. The spectral data obtained for $\overline{CF_2CF_2OCF_2CF_2N}CFBrCF_2Br$ are as follows. IR (KBr) (cm^{-1}): 1327 (ms); 1298 (s); 1286 (m, sh); 1260 (ms); 1215 (vs); 1203 (w); 1168 (vs); 1136 (s); 1120 (s); 1079 (m); 1044 (m); 967 (w); 921 (ms); 847 (m); 801 (w); 790 (w); 745 (m); 732 (ms); 657 (w); 612 (w); 598 (w). ^{19}F NMR δ: −88.0, −92.0 (A, ab, $J_{A-A'}=198$ Hz); −85.0, −86.3 (B, ab, $J_{B-B'}=172$ Hz); −99.3 (C, tp, $J_{C-D}=34.3$ Hz, $J_{C-A}=12.7$ Hz); −59.2 (D, m) ppm. MS (EI) *m/e* (species) intensity (correct isotope ratios were observed): 390 (M^+-Br) 22.1; 340 (M^+-CF_2Br) 9.2; 311 (M^+-2Br) 9.0; 243 ($C_3F_6BrN^+$) 10.0; 224 ($C_3F_5BrN^+$) 10.9; 179 ($C_2F_4Br^+$) 17.2; 145 ($C_3F_5N^+$) 36.9; 128 ($C_3F_4O^+$) 16.7; 119 ($C_2F_5{}^+$) 100; 100 ($C_2F_4{}^+$) 30.1; 69 ($CF_3{}^+$) 45.4.

Preparation and properties of $\overline{CF_2{}^ACF_2{}^BOCF_2CF_2N}CF^C(OSO_2F^D)CF_2{}^EBr$

At −196 °C, 1.0 mmol of $ClOSO_2F$ was condensed into a 30 ml stainless-steel Hoke vessel containing 1.0 mmol of $CF_2CF_2OCF_2CF_2NCFBrCF_2Br$. The reaction mixture was allowed to warm slowly to room temperature and then stood at room temperature for 5 d. The product was purified by semi-preparative gas chromatography (91% yield). The spectral data obtained for $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Br$ are as follows. IR (KBr) (cm^{-1}): 1493 (s); 1334 (m); 1305 (s); 1290 (sh); 1255 (s); 1222 (vs); 1210 (sh); 1175 (vs); 1161 (s); 1088 (s); 1050 (w); 970 (w); 933 (s); 850 (s); 797 (vw); 782 (w); 750 (w); 660 (vw); 625 (w); 575 (w). ^{19}F NMR δ: −93.0 (A, mult); −86.0 (B, mult); −102.9 (C, mult); −66.1 (D, mult); +52.1 (E, d, $J_{C-D}=9.2$ Hz) ppm. MS (EI) *m/e* (species) intensity (correct isotope ratios were observed): 410 (M^+-Br) 3.7; 360 (M^+-CF_2Br) 27.4; 311 ($M^+-Br-OSO_2F$) 5.6; 258 ($\overline{CF_2CF_2OCF_2CF_2N}$-$CO^+$) 9.3; 241 ($C_2F_4BrNSO^+$) 7.4; 224 ($C_2F_3BrSO_2{}^+$) 11.1; 179 ($C_2F_2Br^+$) 18.5; 144 ($NCFOSO_2F^+$) 20.4; 129 ($CF_2Br^+$) 24.1; 119 ($C_2F_5{}^+$) 100; 100 ($C_2F_4{}^+$) 33.3; 83 ($SO_2F^+$) 38.9; 69 ($CF_3{}^+$) 48.1 Analysis: Calc. for $C_6BrF_{12}NO_4S$: C, 14.69; F, 46.5%. Found: C, 14.82; F, 46.2%.

Preparation and properties of $\overline{CF_2{}^{A}CF_2{}^{B}OCF_2CF_2N}CF^{C}(OSO_2F^{D})CF_2{}^{E}(OSO_2F^{F})$

In a 30 ml stainless-steel Hoke vessel held at −196 °C were combined 2.06 mmol of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Br$ and 7.0 mmol of $ClOSO_2F$. The reaction mixture was warmed to 25 °C, and subsequently heated at 100 °C for 15 h. The product, $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2(OSO_2F)$, was obtained in 92% yield and was purified by removing all volatiles from the reaction mixture held at −78 °C, followed by semi-preparative gas chromatography. The spectral data obtained are as follows. IR (AgCl) (cm^{-1}): 1492 (s); 1403 (w); 1344 (m); 1310 (s); 1280 (s); 1250 (vs); 1215 (vs); 1175 (s); 1140 (s); 1125 (sh); 1085 (m); 1070 (m); 1035 (s); 935 (s); 892 (s); 845 (vs); 795 (w); 760 (s); 720 (w); 700 (vw); 674 (m); 629 (w); 595 (m); 565 (s); 544 (m); 496 (w); 481 (w). ^{19}F NMR δ: −90.5 (A, ab); −86.6 (B, ab); −109.4 (C, mult); +53.2 (D, d, $J_{C-D} = 12.4$ Hz); −83.2 (E, dd, $J_{E-F} = 7.4$ Hz); +50.8 (F, t) ppm. MS (EI) *m/e* (species) intensity: 410 ($M^+ - SO_3F$) 18.2; 360 ($M^+ - CF_2OSO_2F$) 28.1; 279 ($CF(OSO_2F)CF_2OSO_2F^+$) 5.2; 258 ($\overline{CF_2CF_2OCF_2CF_2N}CO^+$) 18.3; 199 ($C_2F_4OSO_2F^+$) 14.0; 164 ($C_3F_6N^+$) 44.7; 149 ($CF_2OSO_2F^+$) 8.3; 142 ($C_2F_4NCO^+$) 12.5; 119 ($C_2F_5{}^+$) 100; 114 ($C_2F_4N^+$) 24.9; 100 ($C_2F_4{}^+$) 41.6; 97 ($CF_2CFO^+$) 82.1; 83 ($SO_2F^+$) 96.7; 69 ($CF_3{}^+$) 47.5. Analysis: Calc. for $C_6F_{13}NO_7S_2$: C, 14.15; F, 48.5%. Found: C, 14.28; F, 48.8%.

Preparation and properties of $\overline{CF_2{}^{A}CF_2{}^{B}OCF_2CF_2N}CF_2{}^{C}OSO_2F^{D}$

After combining 5.0 mmol of $\overline{CF_2CF_2OCF_2CF_2N}CF_2Br$ with 11.4 mmol of $ClOSO_2F$ at −196 °C, the reaction mixture was allowed to warm slowly to room temperature and held at that temperature for 5 d. The mixture was then held at −78 °C and all volatile products removed under vacuum. On warming to room temperature, the product $\overline{CF_2CF_2OCF_2CF_2N}CF_2OSO_2F$ was obtained as a colorless liquid in 86% yield after purification by treatment with mercury and semi-preparative gas chromatography. The spectral data obtained are as follows. IR (KBr) (cm^{-1}): 1498 (s); 1407 (vw); 1351 (m); 1313 (vs); 1303 (sh); 1233 (vs); 1191 (s); 1152 (m); 1110 (vw); 1088 (m); 950 (sh); 933 (s); 843 (s); 722 (w); 680 (vw); 647 (vw); 618 (w); 578 (w); 550 (vw). ^{19}F NMR δ: −93.3 (A, t, $J_{A-C} = 15.5$ Hz); −85.8 (B, s); −54.6 (C, pd, $J_{C-D} = 7.9$ Hz); +48.8 (D, t) ppm. MS (EI) *m/e* (species) intensity: 280 ($M^+ - OSO_2F$) 63.2; 164 ($C_3F_6N^+$) 33.5; 149 ($CF_2OSO_2F^+$) 100; 119 ($C_2F_5{}^+$) 65.8; 114 ($C_2F_4N^+$) 76.6; 100 ($C_2F_4{}^+$) 53.2; 83 (SO_2F^+) 67.1; 69 ($CF_3{}^+$) 29.2. Analysis: Calc. for $C_5F_{11}NO_4S$: C, 15.83; F, 55.2%. Found: C, 15.53; F, 54.9%.

Preparation and properties of $\overline{CF_2CF_2OCF_2CF_2N}CF(Cl)CF_2OSO_2F$ and $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Cl$

The reactants ($ClOSO_2F$, 6 mmol; $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$, 5.3 mmol) were condensed into a 30 ml stainless-steel Hoke cylinder at −196 °C and allowed to warm slowly to room temperature. After standing at room temperature for 24 h, the reaction mixture was held at −78 °C and any volatile products removed under vacuum. The product remaining was warmed to room temperature and shaken with mercury for 5 min leading to the formation of a mixture containing 87 parts of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2Cl$ and 13 parts of $\overline{CF_2CF_2OCF_2CF_2N}CFClCF_2OSO_2F$ (82.9% yield), together with a 1.7% yield of $\overline{CF_2CF_2OCF_2CF_2N}CF(OSO_2F)CF_2(OSO_2F)$ which was separated by semi-preparative gas chromatography. The spectral data obtained for the mixture of $\overline{CF_2{}^{A}CF_2{}^{B}OCF_2CF_2N}CF^{C}(OSO_2F^{D})CF_2{}^{E}Cl$ and $\overline{CF_2{}^{F}CF_2{}^{G}OCF_2CF_2N}CF^{H}ClCF_2{}^{I}OSO_2F^{J}$ are as follows. IR (KBr) (cm^{-1}); 1500 (s); 1400 (w); 1346 (s); 1306 (m); 1280 (s); 1260 (s); 1230 (vs); 1220 (sh); 1199 (m); 1185 (m); 1132 (m); 1079 (m); 1036 (w); 1002 (vw); 983 (s); 970 (m); 954 (sh); 850 (s); 792 (w); 745 (vw); 622 (vw); 581 (m); 565 (m). ^{19}F NMR δ: −86.7, −90.3 (A, F, ab, $J_{A-A'} = 186$ Hz); −87.7, −84.2 (B, G, ab, $J_{B-B'} = 151$ Hz); −105.5 (C, mult); +52.1 (D, d, $J_{C-D} = 12.4$ Hz); −71.1 (E, p, $J_{A-E} = 12.4$ Hz); −103.6 (H, mult); −86.7 (I, mult); +49.5 (J, t, $J_{I-J} = 7.5$ Hz) ppm. MS (EI) *m/e* (species) intensity (correct isotope ratios were observed): 410 ($M^+ - Cl$) 3.4; 360 ($M^+ - CF_2Cl$) 25.9; 346 ($M^+ - OSO_2F$) 13.8; 296 ($M^+ - CF_2OSO_2F$) 5.2; 258 ($\overline{CF_2CF_2OCF_2CF_2N}CO^+$) 16.4; 215 ($FSO_3CFCF_2Cl^+$) 13.9; 199 ($C_2F_4OSO_2F^+$) 10.0; 180 ($C_3F_5NCl^+$) 18.1; 164 ($C_3F_6N^+$) 20.7; 135 ($C_2F_4Cl^+$) 18.6; 119 ($C_2F_5{}^+$) 100; 114 ($C_2F_4N^+$) 35.9; 113 ($CF_2ClCO^+$) 19.3; 85 ($CF_2Cl^+$) 37.9; 83 ($SO_2F^+$) 68.1; 69 ($CF_3{}^+$) 41.4. Analysis: Calc. for $C_6ClF_{12}NO_4S$: C, 16.16; F, 51.2%. Found: C, 16.26; F, 51.0%.

Preparation and properties of $\overline{CF_2CF_2CF_2CF_2N}CFBrCF_2Br$

A 7.5% yield of $\overline{CF_2CF_2CF_2CF_2N}CFBrCF_2Br$ was obtained when 11.2 mmol of $\overline{CF_2CF_2CF_2CF_2N}CF{=}CF_2$ was combined with 11.2 mmol of IBr in a 30 ml stainless-steel Hoke cylinder and the mixture heated at 100 °C for 24 h. The product was isolated and purified by semi-preparative gas chromatography. The spectral data obtained for $\overline{CF_2{}^{A}CF_2{}^{B}CF_2CF_2N}CF^{C}BrCF_2{}^{D}Br$ are as follows. IR (KBr) (cm^{-1}): 1348 (s); 1336 (s); 1292 (s); 1249 (s); 1219 (vs); 1194 (s); 1169 (vs); 1138 (ms); 1124 (s); 1088 (m); 1079 (m, sh); 1032 (ms); 977 (s); 871 (m); 847 (w, sh); 839 (w); 752 (s); 707 (w); 680 (w); 668 (w); 621 (w); 576 (w); 560 (m). ^{19}F NMR δ: −88.4, −94.1 (A, ab, $J_{A-A'} = 174$ Hz); −132.7, −134.7 (B, ab,

$J_{B-B'}=244$ Hz); -100.8 (C, mult); -58.3, -60.5 (D, $J_{D-D'}=176$ Hz) ppm. MS (EI) *m/e* (species) intensity (correct isotope ratios were observed): 374 (M^+-Br) 40.7; 324 (M^+-CF_2Br) 20.0; 295 ($C_6F_{11}N^+$) 11.9; 276 ($C_6F_{10}N^+$) 11.6; 243 ($C_6F_9{}^+$) 17.7; 179 ($C_2F_4Br^+$) 33.4; 176 ($C_4F_6N^+$) 33.7; 145 ($C_3F_5N^+$) 12.3; 131 ($C_3F_5{}^+$) 35.6; 129 ($C_6F_3{}^+$) 11.9; 119 ($C_2F_5{}^+$) 13.1; 100 ($C_2F_4{}^+$) 36.7; 76 ($C_2F_2N^+$) 13.8; 69 ($CF_3{}^+$) 100.

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