Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Reactions of *F*-Ethyl- and *F*-*n*-Propylsulfur Imide Dihalides with Nucleophiles. Chlorofluorination of *F*-Ethyl- and *F*-*n*-Propylsulfinylimines

TAKASHI ABE[1] and JEAN'NE M. SHREEVE*

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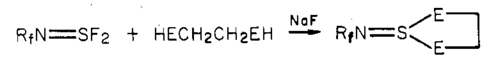
Nucleophilic displacement reactions between $C_2F_5N{=}SF_2$ and $LiOCH_2CF_3$, $NaOCH_3$, or $(CH_3)_2NSi(CH_3)_3$ produce $C_2F_5N{=}SX_2$ (X = OCH_2CF_3, OCH_3, $N(CH_3)_2$) and also in the latter case $C_2F_5N{=}S(F)N(CH_3)_2$ which could be reacted further with $NaOCH_3$ to give $C_2F_5N{=}S(OCH_3)N(CH_3)_2$. However, with $LiN{=}C(CF_3)_2$, extensive rearrangement occurs to give $i\text{-}C_3F_7N{=}S{=}NC_3F_7\text{-}i$ and CF_3CN. With chlorinating reagents, such as $AlCl_3$ or PCl_5, $R_fN{=}SF_2$ (R_f = C_2F_5, $n\text{-}C_3F_7$) gives $R_fN{=}SCl_2$ which, in turn, when R_f = C_2F_5, with AgNCO, $(CF_3)_3COH{\cdot}N(C_2H_5)_3$, $(CF_3)_3COCl$, $AgOC(O)CF_3$, or $(CH_3)_2NSi(CH_3)_3$ forms $C_2F_5N{=}S(NCO)_2$, $C_2F_5N{=}S(OC(CF_3)_3)_2$, $C_2F_5N{=}S(Cl)OC(CF_3)_3$, C_2F_5NSO, or $C_2F_5N{=}S(Cl)N(CH_3)_2$. When R_f = C_2F_5 or $n\text{-}C_3F_7$, with yellow HgO, the respective sulfinylimine, $R_fN{=}S{=}O$, is obtained which, when reacted with chlorine in the presence of CsF, gives $R_fN{=}S(O)ClF$ and $R_fN{=}S(O)F_2$ as well as $CF_3CF{=}NCl$ or $CF_3CF_2CF{=}NCl$. Higher temperature favors the formation of the sulfur difluoride.

Introduction

Studies based on the reaction chemistry of *F*-alkylsulfur imide dihalides ($R_fN{=}SX_2$) have been extensive and have led to a very large number of interesting new compounds.[2] The reaction modes of most recent interest have involved (1) the nucleophilic displacement of halogen, e.g., eq 1–3, (2) the oxidation of sulfur(IV) to sulfur(VI) with or without retention of the N=S bond, viz., eq 4–6, and (3) breaking the N=S bond to form R_fNCl_2, eq 7.

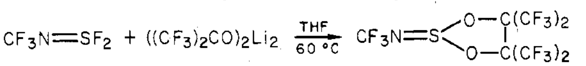
$$R_fN{=}SF_2 + (CH_3)_2NSi(CH_3)_3 \rightarrow R_fN{=}S(F)N(CH_3)_2 \qquad (1)^{3-6}$$

R_f = CF_3, CF_2ClCF_2, $CFCl_2CF_2$, SF_5



(2)[7,8]

R_f = $i\text{-}C_3F_7$, C_2F_5; E = NCH_3, O



(3)[9]

$$R_fN{=}SF_2 + OF_2 \rightarrow R_fN{=}S(O)F_2 + R_fNSF_2NR_f$$

$$R_f = CF_3,\ C_2F_5,\ i\text{-}C_3F_7,\ CF_2ClCF_2,\ CF_2BrCF_2 \qquad (4)^{10}$$

$$R_fN{=}SF_2 + F_2 \xrightarrow{UV} R_fN{=}SF_4 \text{ etc.}$$

$$R_f = C_2F_5,\ SF_5 \text{ (no UV)} \qquad (5)^{11}$$

$$R_fN{=}SF_2 + F_2 \xrightarrow{CsF} R_fN(F)SF_5$$

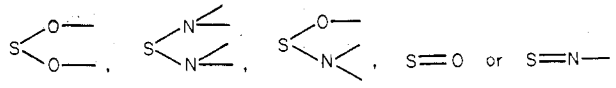
$$R_f = CF_3,\ C_5F_5,^{12}\ SF_5{}^{13} \qquad (6)$$

$$R_fN{=}SF_2 + ClF \rightarrow R_fNCl_2 + SF_4 \quad (50\text{–}90\%)$$

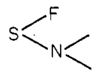
$$R_f = FC(O),\ CF_3C(O),\ CF_3,\ i\text{-}C_3F_7,\ F_2SNCF_2CF_2{}^{-14} \qquad (7)$$

Additionally the sulfur(VI) analogues, *F*-alkylsulfoxyimide dihalides ($R_fN{=}S(O)X_2$), have been synthesized from OSF_4 with primary amines and silylated amines, from fluorination of sulfinylimides with fluorine under photolytic conditions, or by reaction of OF_2 with $R_fN{=}SF_2$.[2,5] Their reaction modes are similar to those of $R_fN{=}SF_2$.

In this paper, we report a variety of new compounds arising primarily from reactions of type 1 with $R_fN{=}SX_2$ where in general both S–X bonds are broken and replaced by



or sometimes



or from chlorofluorination or fluorination of *n*-R_fNSO to form *n*-$R_fN{=}S(O)ClF$ or *n*-$R_fN{=}S(O)F_2$ (R_f = C_2F_5, *n*-C_3F_7).

Results and Discussion

F-Ethylsulfur imide difluoride, $C_2F_5N{=}SF_2$, is readily susceptible to nucleophilic attack by metalated alkoxides and silylated amines as is demonstrated by reactions 8 and 9. The

$$C_2F_5N{=}SF_2 + 2LiOCH_2CF_3 \rightarrow C_2F_5N{=}S(OCH_2CF_3)_2 \quad 76\% \qquad (8)$$

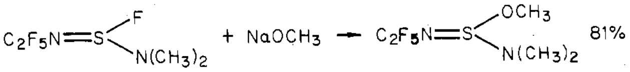
$$C_2F_5N{=}SF_2 + 2NaOCH_3 \rightarrow C_2F_5N{=}S(OCH_3)_2 \quad 91\% \qquad (9)$$

products are transparent, light yellow liquids which decompose gradually at 25 °C. Depending on the amount of silylated amine used, either a monosubstituted or a disubstituted S(IV) compound is formed, viz., eq 10 and 11.

$$C_2F_5N{=}SF_2 + 2(CH_3)_2NSi(CH_3)_3 \rightarrow C_2F_5N{=}S(N(CH_3)_2)_2 \quad 79\% \qquad (10)$$

$$C_2F_5N{=}SF_2 + (CH_3)_2NSi(CH_3)_3 \rightarrow C_2F_5N{=}S(F)N(CH_3)_2 \quad 67\% \qquad (11)$$

The latter compound can be treated further with $NaOCH_3$ to displace the remaining fluorine bonded to sulfur (eq 12).



$$C_2F_5N{=}S(F)N(CH_3)_2 + NaOCH_3 \rightarrow C_2F_5N{=}S(OCH_3)N(CH_3)_2 \quad 81\% \qquad (12)$$

However, in the reaction of $C_2F_5N{=}SF_2$ with $NaOCH_3$, even when a 2:1 molar ratio was used, it was impossible to isolate the monosubstituted derivative. The disubstituted compound

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(1) On leave from the Government Industrial Research Institute, Nagoya, Japan, 1979–1980.
(2) Glemser, O.; Mews, R. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 333 and references therein. Shreeve, J. M. *Sulfur Org. Inorg. Chem.*, in press.
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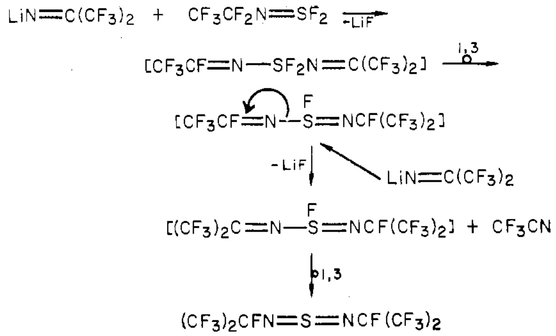
Scheme I



was always the sole product with unreacted $C_2F_5N{=}SF_2$ being recovered.

However, rather surprising products, di-*F*-isopropylsulfur diimide[15] and *F*-acetonitrile, were formed when $C_2F_5N{=}SF_2$ was reacted with $LiN{=}C(CF_3)_2$ (Scheme I).

Chlorination of $C_2F_5N{=}SF_2$ occurs readily with PCl_5 or $AlCl_3$ to form $C_2F_5N{=}SCl_2$[16] which is a useful precursor to new S(IV) derivatives (eq 13 and 14). Similarly, *n*-$C_3F_7N{=}SF_2$ was treated with $AlCl_3$ to give the new dichloro imide *n*-$C_3F_7N{=}SCl_2$. However, $AlCl_3$ is not as effective in chlorinating the propyl derivative with most of the *n*-$C_3F_7N{=}SF_2$ being recovered and only a 38% yield of *n*-$C_3F_7N{=}SCl_2$ realized after 23 h at 25 °C.

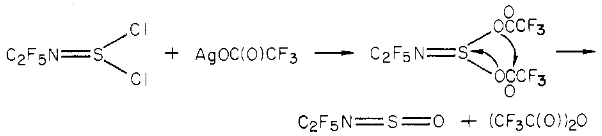
$$C_2F_5N{=}SF_2 + PCl_5 \xrightarrow[24\ h]{50\ °C} C_2F_5N{=}SCl_2\ (99\%) + P(ClF) \quad (13)$$

$$C_2F_5N{=}SF_2 + AlCl_3 \xrightarrow[3\ h]{25\ °C} C_2F_5N{=}SCl_2\ (58\%) + Al(ClF) \quad (14)$$

When $C_2F_5N{=}SCl_2$ was treated with $(CH_3)_3SiN(CH_3)_2$ (1:1), a transparent, light yellow liquid and a deep yellow liquid were obtained (eq 15). The latter was determined to be the monosubstituted compound, $C_2F_5N{=}S(Cl)N(CH_3)_2$. The former, based on ^1H and ^{19}F NMR spectra and the volatile decomposition products (CH_3Cl), is thought to be $C_2F_5N{=}S{=}NCH_3$.

$$C_2F_5N{=}SCl_2 + (CH_3)_2NSi(CH_3)_3 \rightarrow C_2F_5N{=}S(Cl)N(CH_3)_2 + (CH_3)_3SiCl \quad (15)$$

In metathetical reactions with silver pseudohalides, $C_2F_5N{=}SCl_2$ forms $C_2F_5N{=}S(NCO)_2$ with AgNCO. However, it did not form either $C_2F_5N{=}S(SCN)_2$ or $C_2F_5N{=}S(CN)_2$ with AgNCS or AgCN under the conditions used. The diisocyanate $C_2F_5N{=}S(NCO)_2$ is a wine-colored, unstable compound at 25 °C which has only been characterized by infrared and ^{19}F NMR spectroscopy. A strong peak appears at 2260 cm^{-1} in the infrared spectrum which is in the region characteristic for $\nu_{asym}(NCO)$. With $AgOC(O)CF_3$, oxygenation occurs, and a 1:1 mixture of C_2F_5NSO and $(CF_3C(O))_2O$ is found (eq 16).


(16)

$$C_2F_5N{=}SCl_2 + AgOC(O)CF_3 \rightarrow C_2F_5N{=}S(OC(O)CF_3)_2 \rightarrow C_2F_5N{=}S{=}O + (CF_3C(O))_2O \quad (16)$$

When the $(CF_3)_3COH{\cdot}(C_2H_5)_3N$ complex[17] is employed, two *F*-butoxy groups are introduced successfully (eq 17).

$$C_2F_5N{=}SCl_2 + (CF_3)_3COH{\cdot}(C_2H_5)_3N \rightarrow C_2F_5N{=}S(OC(CF_3)_3)_2 \quad 71\% \quad (17)$$

Previously, a di-*F*-alkoxysulfimide was synthesized with dilithio-*F*-pinacolate as the nucleophile.[9] This new di-*F*-butoxy compound is a slightly volatile, colorless liquid which melts at ~20 °C. In the infrared spectrum, a band at 1398 cm^{-1} is assigned to $\nu(N{=}S)$. The ^{19}F NMR spectrum consists of two broad multiplets centered at ϕ −87.2 and −70.5 in a peak area ratio of 1:3.4. This discrepancy from the expected 3:2:18 ratio arises due to the nearly perfect superimposition of the CF_3 and CF_2 peaks of the *F*-ethyl group to produce the band at ϕ −87.2.

With yellow HgO, oxygenation occurred (eq 18). Although

$$C_2F_5N{=}SCl_2 + HgO \rightarrow C_2F_5N{=}S{=}O\ (75\%) + HgCl_2 \quad (18)$$

this sulfinylimide decomposed quantitatively into CF_3CN and OSF_2 in the presence of CsF, it showed considerable resistance to thermolysis when CsF was absent (eq 19). $C_2F_5N{=}SCl_2$

$$C_2F_5N{=}S{=}O \xrightarrow[a\ or\ b]{} CF_3CN + SOF_2 \quad (19)$$

(a) CsF, 23 h, 140 °C, 100% decompn

(b) 10 h, 164 °C, 14% decompn

also decomposes around 160 °C (eq 20).

$$C_2F_5N{=}SCl_2 \xrightarrow[160\ °C]{3\ h} CF_3CN + SCl_2 + Cl_2 + C_2F_5N{=}SF_2\ (35\%\ decompn) \quad (20)$$

When $C_2F_5N{=}S{=}O$ was heated with $CF_3C(O)R$ (R = CF_3, CH_3) at 144 °C or with $CF_3C(O)OH$ at 84 °C, no reaction occurred. With $CH_3C(O)CH_3$ at 25 °C, only tarry materials were obtained. However, the reactivity of $R_fN{=}S{=}O$ with ClF and $ClOSO_2F$ has been demonstrated in this laboratory and elsewhere (eq 21–23). Similarly, the reaction

$$CF_3N{=}S{=}O + 2ClF \rightarrow CF_3NCl_2 + SOF_2 \quad (21)^{14}$$

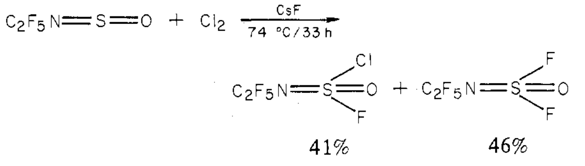
$$FSO_2N{=}S{=}O + 2ClF \rightarrow FSO_2NCl_2 + SOF_2 \quad (22)^{18}$$

$$2ClN{=}S{=}O + 4ClOSO_2F \rightarrow 2SO(OSO_2F)_2 + 3Cl_2 + N_2 \quad (23)^{19}$$

of $C_2F_5N{=}S{=}O$ with $ClOSO_2F$ gave only degraded products, viz., eq 24. However, the reaction of $C_2F_5N{=}S{=}O$ with Cl_2

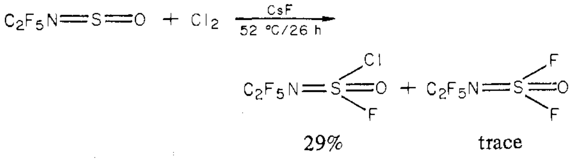
$$C_2F_5N{=}S{=}O + 2ClOSO_2F \rightarrow C_2F_5NCl_2 + SO(OSO_2F)_2 \quad (24)$$

in the presence of CsF resulted in oxidative chlorofluorination or fluorination[5] (eq 25 and 26). After trap-to-trap separation, the $C_5F_5N{=}S(O)F_2$ was contaminated with a considerable amount of $CF_3CF{=}NCl$ which must result from reaction with CF_3CN formed when $C_2F_5N{=}S{=}O$ decomposes in the presence of CsF (eq 27). Also, new *n*-$C_3F_7N{=}S(O)ClF$ was


(25)

$$C_2F_5N{=}S{=}O + Cl_2 \xrightarrow[74\ °C/33\ h]{CsF} C_2F_5N{=}S(O)(Cl)F + C_2F_5N{=}S(O)F_2 \quad (25)$$

41% 46%


(26)

$$C_2F_5N{=}S{=}O + Cl_2 \xrightarrow[52\ °C/26\ h]{CsF} C_2F_5N{=}S(O)(Cl)F + C_2F_5N{=}S(O)F_2 \quad (26)$$

29% trace

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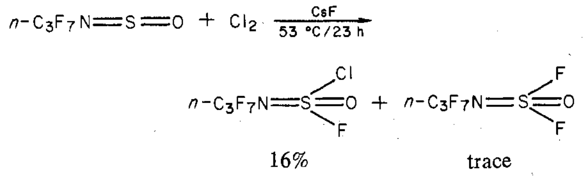
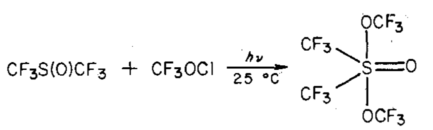
$$CF_3CN + Cl_2 + CsF \rightarrow CF_3CF{=}NCl \quad (27)^{20,21}$$

prepared in a similar manner, and small amounts of $CF_3CF_2CF{=}NCl$ were found (eq 28).



(28)

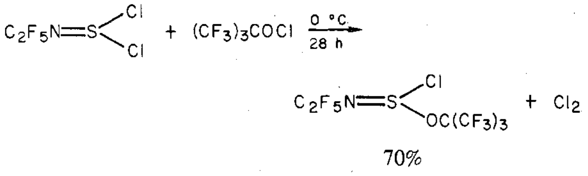
The oxidative addition reactions of $R_fN{=}SF_2$ with OF_2[10,22] or F_2[11,22] have been reported. Also, several new sulfuranes and sulfurane oxides have been synthesized via oxidative addition of hypochlorites to sulfur(II) and sulfur(IV) compounds,[23] e.g., eq 29 and 30, although sometimes an oxidative displacement reaction takes place (eq 31). Since $R_fN{=}SX_2$ is isoelectronic with $O{=}SX_2$, it seemed likely that similar reaction modes might be observed when hypochlorites were photolyzed with the sulfur imides. However, only degradation products of the CF_3OCl were obtained. With $(CF_3)_3COCl$ oxidative displacement does occur at 0 °C to form the monosubstituted compound which had not been observed when the $(CF_3)_3COH{\cdot}(C_2H_5)_3N$ complex was reacted with $C_2F_5N{=}SCl_2$ (eq 32).



(29)

$$CF_3S(O)CF_3 + (CF_3)_3COCl \overset{0\ ^{\circ}C}{\not\longrightarrow} \quad (30)$$

$$CF_3S(O)Cl + (CF_3)_3COCl \xrightarrow{0\ ^{\circ}C} (CF_3)_3COS(O)CF_3 + Cl_2 \quad (31)$$



(32)

Although a molecular ion is not observed in the mass spectrum of $C_2F_5N{=}S(Cl)OC(CF_3)_3$, peaks assigned to $[M - Cl]^+$ and $[M - OC(CF_3)_3]^+$ support the structure of this compound.

It is well-known that the ^{19}F NMR spectra of compounds which contain the methylene or *F*-methylene group[22,24] very often are second order due to the asymmetric center at the sulfur atom. In this work, the ^{19}F NMR spectra of the *F*-methylene group of $C_2F_5N{=}SXX'$ ($X = F$, $X' = N(CF_3)_2$; $X = OCH_3$, $X' = N(CF_3)_2$; $X = Cl$, $X' = OC(CF_3)_3$) exhibit AB patterns (J = 186–202 Hz). However, the *F*-methylene spectrum of $C_2F_5N{=}S(Cl)N(CH_3)_2$ is first order. In the ^1H NMR spectrum of $C_2F_5N{=}S(OCH_2CF_3)_2$, the methylene protons are observed as two quartets (J_{H-F} = 8.0 Hz) centered at δ 4.48 and 4.51, and in $C_2F_5N{=}S(F)N(CH_3)_2$, the methyl groups are found as doublets centered at δ 2.98 and 3.06.

Experimental Section

Apparatus. All gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus with use of *PVT* techniques. Purification of products was conducted by low-temperature, vacuum-distillation methods and/or gas chromatography. Infrared spectra were recorded with a Perkin-Elmer Model 599B infrared spectrometer. Varian HA-100 and EM-360 nuclear magnetic resonance spectrometers were used for ^{19}F and ^1H spectra with CCl_3F and $(CH_3)_4Si$ (Me_4Si), respectively, as internal standards. The mass spectra were determined on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Vapor pressure studies were made by an isoteniscopic method. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany, or at the University of Idaho.

Materials. Literature methods were used to prepare $C_2F_5N{=}SF_2$,[25] $C_3F_7N{=}SF_2$,[25] CF_3OCl,[26] $LiN{=}C(CF_3)_2$,[27] $(CF_3)_3COCl$,[28] and $ClOSO_2F$.[29] CF_3CH_2OH, CH_3OH, and $(CH_3)_2NSi(CH_3)_3$, were used as obtained without further purification.

Preparation of $C_2F_5N{=}S(OCH_2CF_3)_2$. Into a hexane solution of *n*-butyllithium (22 mmol) and 5 mL of ether was condensed CF_3CH_2OH (20 mmol) at −196 °C, and after standing for 2 h at 25 °C, the contents were evaporated to dryness to give 20 mmol of CF_3CH_2OLi. Onto this was condensed 10.55 mmol of $C_2F_5N{=}SF_2$ at −196 °C, and the vessel was warmed slowly to ambient temperature. After 13 h, the volatile product was separated by trap-to-trap distillation, and $C_2F_5N{=}S(OCH_2CF_3)_2$ was obtained (75.8% yield). This compound is a slightly volatile, light yellow liquid. IR (capillary film): 2980 (m), 1451 (w), 1395–1400 (m), 1170–1290 (vs), 1090 (s), 1005–1020 (s), 962 (s), 920 (w), 855 (m) cm^{-1}. Mass spectrum (*m*/*e*): 363 $[M]^+$; 294 $[M - CF_3]^+$, 264 $[M - OCH_2CF_3]^+$. ^{19}F NMR: $\phi(CF_3{-}CF_2)$ −87.3 (s); $\phi(CF_2)$ −80.7 (s); $\phi(CF_3CH_2)$ −74.3 (t). ^1H NMR: $\delta(CH_2)$ 4.51 (q), 4.48 (q) ($J_{CF_3-CH_2}$ = 8.0 Hz).

Anal. Calcd for $C_6H_4NSO_2F_{11}$: C, 19.84; H, 1.10; N, 3.86. Found: C, 21.74; H, 1.30; N, 3.59.

Preparation of $C_2F_5N{=}S(N(CH_3)_2)_2$. $C_2F_5N{=}SF_2$ (3.15 mmol) was condensed onto $(CH_3)_3SiN(CH_3)_2$ (7.10 mmol) at −196 °C, and then the solution was maintained at 0 °C during 17 h. Purification was conducted by using trap-to-trap distillation during which $C_2F_5N{=}S(N(CH_3)_2)_2$ (78.6%) was retained at 0°C. The compound is a slightly volatile, colorless liquid. IR (capillary film): 1980–2960 (m), 1456 (m), 1401 (m), 1170–1260 (vs), 1045–1060 (s), 990 (s), 915–940 (s), 786 (m), 745 (m), 645–680 (ms), 540 (w) cm^{-1}. Mass spectrum (*m*/*e*): 253 $[M]^+$, 209 $[M - N(CF_3)_2]^+$, 146 $[C_2F_4NS]^+$. ^{19}F NMR: $\phi(CF_3)$ −86.0 (s); $\phi(CF_2)$ −70.7 (s). ^1H NMR: $\delta(CH_3)$ 2.70 (s).

Anal. Calcd for $C_6H_{12}N_3SF_5$: C, 28.46; H, 4.76; N, 16.60. Found: C, 28.94; H, 4.79; N, 16.79.

Preparation of $C_2F_5N{=}S(OCH_3)_2$. $C_2F_5N{=}SF_2$ (7.03 mmol) was condensed onto CH_3ONa (13.3 mmol) at −196 °C, and the solution was then warmed slowly to ambient temperature. After 4 h, the product was separated by trap-to-trap distillation through a trap at −78 °C which retained $C_2F_5N{=}S(OCH_3)_2$ (6.39 mmol, 90.9% yield). The compound is a slightly volatile, light yellow liquid which has a vapor pressure of 0.5 torr at room temperature. IR (capillary film): 2960 (m), 1455 (m), 1398 (m) ($\nu(S{=}N)$), 1255–1270 (vs), 1205–1220 (vs), 1073 (s), 965–970 (s), 761 (m), 710 (ms) cm^{-1}. Mass spectrum (*m*/*e*): 227 $[M]^+$, 196 $[M - OCH_3]^+$, 158 $[C_2F_3NSOCH_3]^+$. ^{19}F NMR: $\phi(CF_3)$ −87.1 (s); $\phi(CF_2)$ −77.7 (s). ^1H NMR: $\delta((CH_3)_3)$ 3.94 (s).

Anal. Calcd for $C_4H_6NSO_2F_5$: C, 21.15; H, 2.64; N, 6.17. Found: C, 20.80; H, 2.54; N, 6.25.

Preparation of $C_2F_5N{=}S(F)N(CH_3)_2$. $C_2F_5N{=}SF_2$ (3.26 mmol) was condensed onto $(CH_3)_3SiN(CH_3)_2$ (2.88 mmol) at −196 °C, and the solution was then maintained at 0 °C. After 18 h, the product was separated by trap-to-trap distillation through a trap at −40 °C which retained the $C_2F_5N{=}S(F)N(CH_3)_2$ (66.6%) and a trap at −196 °C which contained a mixture of $(CH_3)_3SiF$ and $C_2F_5N{=}SF_2$ (3.44 mmol). The compound is a slightly volatile, light yellow liquid which has a vapor pressure of 2 torr at room temperature. IR (capillary film): 2940–2990 (m), 1460–1480 (m), 1397 (m) ($\nu(S{=}N)$), 1195–1285 (vs), 1070–1100 (s), 1018 (m), 467 (s), 802 (w), 751 (w), 708 (s), 600–605 (s), 543 (w) cm^{-1}. Mass spectrum (*m*/*e*): no molecular ion, 190 $[C_4H_6N_2SF_4]^+$, 146 $[C_2F_4NS]^+$, 112 $[C_3F_4]^+$, 69

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$[CF_3]^+$, 63 $[SCF]^+$. ^{19}F NMR: $\phi(CF_3)$ −87.2 (m); $\phi(CF_A)$ −79.1 (d); $\phi(CF_B)$ −81.8 (d); $\phi(SF)$ 32.7 (br). ^1H NMR: $\delta((CH_3)_A)$ 3.06; $\delta((CH_3)_B)$ 2.98 ($J_{F_A-F_B}$ = 190.4 Hz; $J_{F_A-SF} = J_{F_B-SF}$ = 12.9 Hz).

Anal. Calcd for $C_4H_6N_2SF_6$: C, 21.05; H, 2.63; N, 12.28. Found: C, 21.06; H, 2.66; N, 11.98.

Preparation of $C_2F_5N{=}S(OCH_3)N(CH_3)_2$. $C_2F_5N{=}S(F)N(CH_3)_2$ (9.18 mmol) was condensed onto CH_3ONa (8.0 mmol), and then the solution was warmed slowly from −40 °C to ambient temperature. After 6 h, the volatile products were pumped out at 25 °C, and the high-boiling compound which was found to be pure $C_2F_5N{=}S(OCH_3)N(CH_3)_2$ was obtained (80.7%). The compound is a slightly volatile, colorless liquid which has a vapor pressure of ~0.5 torr at room temperature. IR (capillary film): 2955 (m), 1460 (m), 1180–1275 (vs), 970–1080 (vs), 945 (s), 797 (m), 748 (m), 650–690 (m–s), 545 (w), 485 (w), 435 (w) cm^{-1}. Mass spectrum (*m/e*): 240 $[M]^+$, 209 $[M - OCH_3]^+$, 196 $[M - N(CH_3)_2]^+$. ^{19}F NMR: $\phi(CF_3)$ −86.6 (s); $\phi(CF_A)$ −73.2 (d); $\phi(CF_B)$ −75.5 (d). ^1H NMR: $\delta(OCH_3)$ 3.63 (s); $\delta(N(CH_3)_2)$ 2.93 (s) ($J_{F_A-F_B}$ = 186 Hz).

Anal. Calcd for $C_5H_9N_2SOF_5$: C, 25.00; H, 3.75; N, 11.67. Found: C, 25.10; H, 3.71; N, 11.60.

Preparation of $C_2F_5N{=}SCl_2$. Method A. Into a 150-mL Hoke bomb which contained 2 g of PCl_5 was condensed $C_2F_5N{=}SF_2$ (12.73 mmol), and then the solution was held at 75 °C for 24 h. Purification was carried out by trap-to-trap distillation using traps at −196 and −64 °C. The compound which was retained in the trap of −196 °C was PF_5, and the compound at −64 °C was found to be crude $C_2F_5N{=}SCl_2$ (3.23 g) which was contaminated with chlorofluorophosphoranes. However, on standing several days at room temperature, a white solid precipitated, and pure $C_2F_5N{=}SCl_2$ was obtained in almost quantitative yield.

Method B. $C_2F_5N{=}SF_2$ (4.50 mmol) was condensed onto anhydrous $AlCl_3$ (0.7 g), and the solution was warmed gradually to 25 °C. After 3 h, the product was separated by trap-to-trap distillation through a trap at −64 °C which retained the pure $C_2F_5N{=}SCl_2$ (57.8%). No starting material was recovered.

Reaction of $C_2F_5N{=}SF_2$ with $LiN{=}C(CF_3)_2$. The literature method was used to prepare $LiN{=}C(CF_3)_2$[27] (4.4 mmol) in a rigorously flame-dried 100-mL reaction vessel. The solvent was removed under dynamic vacuum, leaving a brown amorphous solid. Onto the solid was condensed $C_2F_5N{=}SF_2$ (5.44 mol) at −196 °C, and the vessel was warmed slowly to ambient temperature. After 23 h, volatile products were separated by trap-to-trap distillation, and $i\text{-}C_3F_7N{=}S{=}NC_3F_7\text{-}i$ (1.07 mmol) was obtained together with CF_3CN (0.67 mmol) and starting $C_2F_5N{=}SF_2$ (3.98 mmol). The products were identified from infrared and ^{19}F NMR spectra.

Preparation of $C_2F_5N{=}S(Cl)N(CH_3)_2$. In a 100-mL flask, $C_2F_5N{=}SCl_2$ (8.91 mmol) and $(CH_3)_2NSi(CH_3)_3$ (7.23 mmol) were condensed, and the solution was kept at −78 °C for 1 h and at 0 °C for 12 h. Purification was conducted through traps at −98 °C which retained primarily $(CH_3)_3SiCl$ and a small amount of CH_3Cl (1.0 g), −40 °C which retained unreacted $C_2F_5N{=}SCl_2$ (0.07 g), and −24 °C which retained a yellow liquid. Purification of the latter was further accomplished by allowing the more volatile components of the reaction mixture to vaporize from the less volatile portion. A clear light yellow liquid (0.49 g) and an orange-yellow liquid, $C_2F_5N{=}S(Cl)N(CH_3)_2$ (49.6%), were obtained. For the former ^{19}F NMR and ^1H NMR spectra were consistent with that expected for $C_2F_5N{=}S{=}NCH_3$. However, mass spectra and elemental analysis did not afford satisfactory results due to its thermal instability.

$C_2F_5N{=}S{=}NCH_3$ (?) IR (gas): 2960 (w), 1452 (w), 1380 (w), 1275 (s), 1225 (vs), 1122 (s), 1023 (s), 1000 (w), 855 (w), 748 (w), 714 (ms), 600 (w), 545 (w) cm^{-1}. ^{19}F NMR: $\phi(CF_3)$ −86.8 (s); $\phi(CF_2)$ −96.8 (s). ^1H NMR: $\delta(CH_3)$ 3.13 (s).

$C_2F_5N{=}S(Cl)N(CH_3)_2$ is a slightly volatile liquid. IR (capillary film): 1990–2940 (m), 1712 (w), 1609 (w), 1447–1470 (m), 1412 (w), 1388 (m), 1185–1265 (vs), 1140 (m, sh), 1045–1090 (s–vs), 1010 (m), 960 (s), 853 (m), 799 (m), 747 (ms), 705 (ms), 605 (w), 568 (w), 543 (w), 515 (w), 455 (w), 410 (m) cm^{-1}. Mass spectrum (*m/e*): 190 $[C_4H_6N_2SF_4]^+$, 112 $[C_3F_4]^+$, 76 $[C_2F_2N]^+$, 69 $[CF_3]^+$, 63 $[SCF]^+$. ^{19}F NMR: $\phi(CF_3)$ −86.5 (s); $\phi(CF_2)$ −84.1 (s). ^1H NMR: $\delta(CH_3)$ 3.10 (s).

Anal. Calcd for $C_4H_6N_2SF_5Cl$: C, 19.63; H, 2.45; N, 11.45. Found: C, 19.43; H, 2.33; N, 11.35.

Preparation of $C_2F_5N{=}S(OC(CF_3)_3)_2$. Into a reaction vessel were condensed $(CF_3)_3COH$ (6.03 mmol) and $(C_2H_5)_3N$ (6.62 mmol) at −196 °C, and the solution was warmed gradually to 25 °C. After it was held at 25 °C for 10 min, the excess $(C_2H_5)_3N$ was removed under dynamic vacuum to leave a white solid, $(CF_3)_3COH{\cdot}(C_2H_5)_3N$.[17] Then, $C_2F_5N{=}SCl_2$ (2.96 mol) was condensed onto this solid at −196 °C and kept at 0 °C for 8 h. Purification was conducted by trap-to-trap distillation through a trap at −98 °C which retained the unreacted $C_2F_5N{=}SCl_2$ (trace) and a trap at −24 °C which retained $C_2F_5N{=}S(OC(CF_3)_3)_2$ (71.3%). The compound is a colorless liquid which solidifies at around 20 °C. IR (capillary film): 1398 (m) ($\nu(N{=}S)$), 1220–1335 (vs), 1193 (m, sh), 1135–1150 (s), 1115 (s), 1085 (vs), 1038 (s), 1000 (vs), 985 (s), 780 (m), 747 (s), 737 (s), 717 (m), 655 (w), 625 (w), 592 (w), 562 (m), 550 (m) cm^{-1}. Mass spectrum (*m/e*): 635 $[M]^+$, 616 $[M - F]^+$ 566 $[M - CF_3]^+$, 400 $[M - OC(CF_3)_3]^+$. ^{19}F NMR: $\phi(CF_3{-}CF_2)$ −87.2 (s); $\phi(CF_2)$ −87.2 (s); $\phi((CF_3)_3C)$ −170.4 (s).

Anal. Calcd for $C_{10}F_{23}NSO_2$: C, 18.90; F, 68.82; N, 2.20; S, 5.04. Found: C, 19.16; F, 68.4; N, 2.21; S, 5.23.

Reaction of $C_2F_5N{=}SCl_2$ with $AgOC({=}O)CF_3$. Into a 1-L bulb which contained $AgOC({=}O)CH_3$ (6.33 mmol) was condensed $C_2F_5N{=}SCl_2$ (2.47 mmol) at −196 °C, and the solution was warmed slowly to 25 °C. After 2 h, the product was separated by trap-to-trap distillation by using traps at −116 and at −64 °C. In the trap at −116 °C, a clear liquid (0.81 g) was obtained which was found to be a 1:1 mixture of $C_5F_5N{=}S{=}O$ and $(CF_3C({=}O))_2O$ by IR and ^{19}F NMR spectroscopy. In the trap cooled at −64 °C, small quantities of $C_2F_5N{=}SCl_2$ (0.08 g) were recovered.

Preparation of $C_2F_5N{=}S(NCO)_2$. $C_2F_5N{=}SCl_2$ (2.21 mol) was condensed onto freshly prepared AgNCO (4.60 mmol) at −196 °C, and the solution was warmed gradually to 25 °C. Purification was conducted by trap-to-trap distillation through a trap at −64 °C which retained $C_2F_5N{=}S(NCO)_2$ (44.6%). The compound is a slightly volatile, red wine colored liquid which has a vapor pressure of 3 torr at 25 °C. The color of this compound changes gradually into brown at 25 °C. Mass spectra and elemental analysis did not afford satisfactory results. IR (capillary film): 2260 (vs) ($\nu_{as}(NCO)$), 1415 (w), 1380 (m) ($\nu(N{=}S)$), 1280–1305 (vs), 1215–1235 (vs), 1150 (s), 1127 (vs), 1100 (m, sh), 1030 (vs), 720 (ms), 602 (w) cm^{-1}. ^{19}F NMR: $\phi(CF_3)$ −86.8 (s); $\phi(CF_2)$ −96.8 (s).

Preparation of $C_2F_5N{=}S{=}O$.[16] $C_2F_5N{=}SCl_2$ (2.59 mmol) was condensed onto an excess of yellow HgO (0.7 g) at −196 °C, and the solution was warmed gradually to 25 °C during 5 h. Purification was conducted by trap-to-trap distillation through traps at −98 °C which retained $C_2F_5N{=}S{=}O$ (70.0%) and at −64 °C which retained small amounts of unreacted $C_2F_5N{=}SCl_2$.

Thermolysis of $C_2F_5N{=}S{=}O$. (A) Without CsF. In a 30-mL Hoke cylinder, $C_2F_5N{=}S{=}O$ (1.25 mmol) was condensed, and the solution was kept at 164 °C for 10 h. The product was separated by trap-to-trap distillation by using traps at −196 and −78 °C. In the trap at −196 °C, small quantities of CF_3CN, SOF_2, and SO_2F_2 were found (<0.19 mmol). At −78 °C, unreacted $C_2F_5N{=}S{=}O$ (0.94 mmol) was recovered.

(B) In the Presence of CsF. In a 30-mL Hoke cylinder which contained 1.5 g of CsF was condensed $C_2F_5N{=}S{=}O$ (3.83 mmol), and the solution was kept at 140 °C during 11 h. The analysis was conducted by IR spectroscopy, and the products (7.5 mmol) were found to be almost in equal amounts of CF_3CN and SOF_2.

Preparation of $C_2F_5N{=}S(O)ClF$. Run 1. In a 30-mL Hoke cylinder which contained 1.7 g of CsF were condensed $C_2F_5N{=}S{=}O$ (2.49 mmol) and Cl_2 (3.0 mmol), and the solution was kept at 74 °C. After 33 h, the product was purified by trap-to-trap distillation through traps at −78 °C which retained $C_2F_5N{=}S(O)ClF$ (46.3%), at −98 °C which retained $C_2F_5N{=}S(O)F_2$[5] (40.6%), and at −196 °C which retained SOF_2, SO_2F_2, and CF_3CN (0.82 mmol). The mass spectrum of $C_2F_5N{=}S(O)F_2$, in addition to the expected fragmentation pattern, showed peaks at *m/e* 149 and 151 $[CF_3CF{=}NCl]^+$ due to the presence of $CF_3CF{=}NCl$. Its ^{19}F NMR spectrum also suggests the presence of considerable quantities of $CF_3CF{=}NCl$.[20,21] ^{19}F NMR: $\phi(CF_3)$ −72.1 (d); $\phi(CF)$ −42.2 (q) (J_{CF_3-CF} = 5.2 Hz). For $CF_3CF_2N{=}S(O)F_2$, ^{19}F NMR: $\phi(CF_3)$ −87.7 (t); $\phi(CF_2)$ −78.0 (t); $\phi(SF)$ −50.5 (t of q) (J_{CF_3-SF} = 1.3 Hz; J_{CF_2-SF} = 9.4 Hz).

Run 2. Similarly, $C_2F_5N{=}S{=}O$ (8.13 mmol) and Cl_2 (8.2 mmol) were heated at 52 °C for 10 h in a Hoke cylinder which contained 1.7 g of CsF. The purification was conducted by trap-to-trap distillation and gas chromatography. Thus, $C_2F_5N{=}S(O)ClF$ (34.4%) and $C_2F_5N{=}S(O)F_2$ (0.04 g) were obtained together with small quantities of starting $C_2F_5N{=}S{=}O$ (1.22 mmol). $C_2F_5N{=}S(O)ClF$ is a colorless liquid having a boiling point of 52.9 °C calculated from the equation $\log P_{\text{torr}} = 8.55 - (1849/T)$. The molar heat of vaporization is 8.5 kcal/mol and the Trouton constant is 25.9 eu. IR (gas): 1430 (vs) (ν_{as}(S=O)), 1377 (m) (ν(N=S)), 1290 (vs), 1235 (vs), 1140 (vs), 1045 (s), 851 (w), 815 (s), 775 (m), 724 (ms), 632 (ms), 572 (m), 518 (w), 487 (w) cm^{-1}. Mass spectrum (*m*/*e*): 216 $[M - F]^+$, 200 $[M - {}^{35}Cl]^+$, 166 $[CF_3NSO^{35}Cl]^+$, 150 $[CF_3NS^{35}Cl]^+$. ^{19}F NMR: $\phi(CF_3)$ −87.3; $\phi(CF_A)$ −88.4 (d); $\phi(CF_B)$ −91.8 (d); ϕ(SF) −116.2 (d of d) ($J_{CF_A-SF} = 10.7$ Hz; $J_{CF_B-SF} = 12.3$ Hz).

Anal. Calcd for C_2F_6NSOCl: C, 10.19; N, 5.95. Found: C, 10.39; N, 5.85.

Reaction of $C_2F_5N{=}S{=}O$ with $ClSO_3F$. In a 100-mL flask were condensed $C_2F_5N{=}S{=}O$ (2.17 mmol) and $ClSO_3F$ (2.10 mmol) at −196 °C, and the solution was kept a −78 °C for 30 min and at −40 °C for 2 h. The volatile products were separated by trap-to-trap distillation using traps at −40, −98, and −196 °C. In the traps at −196 and −98 °C, Cl_2 (1.09 mmol) and a mixture of $C_2F_5N{=}S{=}O$ and $C_2F_5NCl_2$ (1:0.6; 1.50 mmol) were found, respectively. In the trap at −40 °C, a clear, colorless liquid was retained which fumes in air. This compound reacted with NaCl and KBr IR plates. From ^{19}F NMR spectral measurements, it was identified as $O{=}S(OSO_2F)$.[19]

Preparation of $C_2F_5N{=}S(Cl)OC(CF_3)_3$. In a 100-mL flask were condensed $C_2F_5N{=}SCl_2$ (0.97 mmol) and $(CF_3)_3COCl$ (2.6 mmol), and the solution was kept at 0 °C for 16 h. Purification was conducted by trap-to-trap distillation through a trap at −40 °C which retained $C_2F_5N{=}S(Cl)OC(CF_3)_3$ (70.1%). The compound is a slightly volatile, colorless liquid. The mass spectrum of this compound, however, showed a small peak at *m*/*e* 556 $[C_2F_5N{=}S(OC(CF_3)_3)_2 - CF_3]^+$ which indicated the contamination of $C_2F_5N{=}S(OC(CF_3)_3)_2$ in very small quantities. IR (capillary film): 1388 (m) (ν(N=S)), 1220–1315 (vs), 1195 (s, sh), 1125–1160 (s), 1090–1105 (s), 1035 (s), 980–1005 (s), 783 (m), 746 (s), 737 (s), 710 (ms), 635 (w), 608 (m), 572 (w), 550 (m), 510 (w), 456 (s), 412 (m) cm^{-1}. Mass spectrum (*m*/*e*): 400 $[M - {}^{35}Cl]^+$, 284 $[C_4F_{10}NS]^+$, 200 $[M - OC(CF_3)_3]^+$. ^{19}F NMR: $\phi(CF_3)$ −87.1; $\phi(CF_A)$ −89.7; $\phi(CF_B)$ −93.8; $\phi((CF_3)_3C)$ −70.7 ($J_{F_A-F_B}$ = 201.8 Hz).

Anal. Calcd for $C_6F_{14}NSOCl$: C, 16.53; F, 61.1; N, 3.22; S, 7.35; Cl, 8.15. Found: C, 16.61; F, 61.7; N, 3.10; S, 7.00; Cl, 7.90.

Preparation of *n*-$C_3F_7N{=}SCl_2$. *n*-$C_3F_7N{=}SF_2$ (2.79 mmol) was condensed onto $AlCl_3$ (0.7 g) in a 100-mL flask at −196 °C, and the solution was kept at room temperature for 23 h. Purification was conducted through traps at −40 °C which retained *n*-$C_3F_7N{=}SCl_2$ (38.0%) and −78 °C which retained unreacted *n*-$C_3F_7N{=}SF_2$ (0.35 g). *n*-$C_3F_7N{=}SCl_2$ obtained in this manner still showed contamination of small quantities of *n*-$C_3F_7N{=}SF_2$ in its IR spectrum. However, traces of *n*-$C_3F_7N{=}SF_2$ could not be removed from *n*-$C_3F_7N{=}SCl_2$ by trap-to-trap distillation and/or gas chromatography. This compound is a transparent yellow liquid having a boiling point of 88.4 °C from the equation $\log P_{\text{torr}} = 7.11 - (1528/T)$. The molar heat of vaporization is 7.0 kcal/mol, and the Trouton constant is 19.4 eu. IR (gas): 1345 (s), 1330 (s), 1278 (s), 1250 (s), 1235 (vs), 1210 (m), 1145 (m), 1080 (m), 982 (ms), 928 (m), 730 (ms), 455 (m), 433 (ms) cm^{-1}. Mass spectrum (*m*/*e*): 250 $[M - {}^{35}Cl]^+$, 231 $[M - {}^{35}Cl - F]^+$. ^{19}F NMR: $\phi(CF_3)$ −81.3 (t), $\phi(\alpha\text{-}CF_2)$ −93.1 (mult), $\phi(\beta\text{-}CF_2)$ 129.3 (mult) ($J_{CF_3-\alpha\text{-}CF_2}$ = 8.3 Hz).

Anal. Calcd for $C_3F_7NSCl_2$: C, 12.59; F, 46.5. Found: C, 12.79; F, 46.6.

Preparation of *n*-$C_3F_7N{=}S{=}O$. *n*-$C_3F_7N{=}SCl_2$ (2.93 mmol) was condensed onto yellow HgO (1 g) at −196 °C, and the solution was warmed gradually to 25 °C over 4 h. Purification was conducted by trap-to-trap distillation through a trap at −64 °C which retained $C_3F_7N{=}S{=}O$ (88.1%). The compound is a transparent, colorless liquid having a boiling point of 51.8 °C from the equation $\log P_{\text{torr}} = 7.65 - (1550/T)$. The molar heat of vaporization is 7.1 kcal/mol, and the Trouton constant is 21.8 eu. IR (gas): 1330 (s), 1280 (ms), 1245 (vs), 1208 (m), 1170 (m, sh), 1142 (ms), 1095 (w), 1056 (m), 963 (ms), 918 (m) cm^{-1}. Mass spectrum (*m*/*e*): 212 $[M - F]^+$, 169 $[C_3F_7]^+$, 112 $[C_3F_4]^+$. ^{19}F NMR: $\phi(CF_3)$ −81.3 (t); $\phi(\alpha\text{-}CF_2)$ −86.4 (q); $\phi(\beta\text{-}CF_2)$ −128.5 (q) ($J_{CF_3-\alpha\text{-}CF_2}$ = 8.6 Hz).

Anal. Calcd for C_3F_7NSO: C, 15.58; F, 57.6. Found: C, 15.65; F, 57.7.

Preparation of *n*-$C_3F_7N{=}S(O)ClF$. *n*-$C_3F_7N{=}S{=}O$ (7.21 mmol) and Cl_2 (7.7 mmol) were condensed in a 30-mL Hoke cylinder which contained 1.7 g of CsF, and the solution was kept at 53 °C for 23 h. Purification was conducted by trap-to-trap distillation and gas chromatography. The product which was retained in the −98 °C trap was further separated by gas chromatography. Thus *n*-$C_3F_7N{=}S(O)ClF$ (15.7%) was obtained. Other compounds separated were *n*-$C_3F_7N{=}S(O)F_2$ (trace), $CF_3CF_2CF{=}NCl$ (trace), and recovered *n*-$C_3F_7N{=}S{=}O$ (0.73 mmol). *n*-$C_3F_7N{=}S(O)ClF$ is a colorless liquid having a boiling point of 73.2 °C from the equation of $\log P_{\text{torr}} = 7.4 - (1565/T)$. The molar heat of vaporization is 7.2 kcal/mol, and the Trouton constant is 20.7 eu. *n*-$C_3F_7N{=}S(O)ClF$ IR (gas): 1422 (vs)(ν_{as}(S=O)), 1350 (m), 1330 (ms), 1275 (ms), 1240 (vs), 1208 (m, sh), 1138 (m), 1090 (m), 975 (m), 945 (w), 810 (m), 767 (w) cm^{-1}. Mass spectrum (*m*/*e*): 266 $[M - F]^+$, 250 $[M - Cl]^+$, 166 $[CF_3NSO^{35}Cl]^+$, 114 $[C_2F_4N]^+$. ^{19}F NMR: $\phi(CF_3)$ −81.3 (t); $\phi(\alpha\text{-}CF_A)$ −84.4; $\phi(\alpha\text{-}CF_B)$ −87.7; $\phi(\beta\text{-}CF_2)$ −129.2 (mult); ϕ(SF) 116.2 (t) ($J_{CF_3-\alpha\text{-}CF_2}$ = 8.5 Hz; $J_{\alpha\text{-}CF_A-SF} = J_{\alpha\text{-}CF_B-SF}$ = 11.5 Hz).

Anal. Calcd for C_3F_8NSOCl: C, 12.61; N, 4.90. Found: C, 12.66; N, 4.86.

n-$C_3F_7N{=}S(O)F_2$ IR (gas): 1460 (vs)(ν_{as}(S=O)), 1345 (s), 1283 (m), 1235 (vs), 1208 (m), 1140 (m), 1108 (m), 981 (m), 862 (ms), 835 (s), 760 (w), 740 (m), 570 (m), 540 (w) cm^{-1}. Mass spectrum (*m*/*e*): 250 $[M - F]^+$, 150 $[C_3F_6]^+$. ^{19}F NMR: $\phi(CF_3)$ −81.4 (t); $\phi(\alpha\text{-}CF_2)$ −82.7 (q of t); $\phi(\beta\text{-}CF_2)$ −128.4 (mult); ϕ(SF) 50.6 (t of t) ($J_{CF_3-\alpha\text{-}CF_2}$ = 8.4 Hz; $J_{\beta\text{-}CF_2-SF}$ = 1.9 Hz; $J_{\alpha\text{-}CF_2-SF}$ = 9.3 Hz).

Anal. Calcd for C_3F_9NSO: C, 13.38; N, 5.21. Found: C, 13.57; N, 5.02.

$CF_3CF_2CF{=}NCl$ IR (gas): 1690 (m) (ν(C=N)), 1338 (m), 1315 (m), 1235 (vs), 1210 (m), 1145 (ms), 1020 (s), 812 (w), 738 (ms), 695 (w), 590 (w), 545 (w) cm^{-1}. Mass spectrum (*m*/*e*): 199 $[M]^+$ very intense. ^{19}F NMR: $\phi(CF_3)$ −83.6 (d); $\phi(CF_2)$ −119.0 (d); ϕ(CF) −37.1 (q of t) (J_{CF_3-CF} = 4.4 Hz; J_{CF_2-CF} = 14.9 Hz).

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Registry No. $C_2F_5N{=}S(OCH_2CF_3)_2$, 74366-03-3; $C_2F_5N{=}S(N(CH_3)_2)_2$, 74366-04-4; $C_2F_5N{=}S(OCH_3)_2$, 74366-05-5; $C_2F_5N{=}S(F)N(CH_3)_2$, 74366-06-6; $C_2F_5N{=}S(OCH_3)N(CH_3)_2$, 74366-07-7; $C_2F_5N{=}SCl_2$, 10564-48-4; $C_2F_5N{=}S(Cl)N(CH_3)_2$, 74366-08-8; $C_2F_5N{=}S(OC(CF_3)_3)_2$, 74366-09-9; $C_2F_5N{=}S(NCO)_2$, 74366-10-2; $C_2F_5N{=}S{=}O$, 10564-50-8; $C_2F_5N{=}S(O)ClF$, 74366-11-3; $C_2F_5N{=}S(Cl)OC(CF_3)_3$, 74366-12-4; *n*-$C_3F_7N{=}SF_2$, 5131-89-5; *n*-$C_3F_7N{=}S{=}O$, 74366-13-5; *n*-$C_3F_7N{=}S(O)ClF$, 74366-14-6; CF_3CH_2OLi, 69163-14-0; $C_2F_5N{=}SF_2$, 4101-37-5; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; CH_3ONa, 124-41-4; PCl_5, 10026-13-8; $AlCl_3$, 7446-70-0; $LiN{=}C(CF_3)_2$, 31340-36-0; *i*-$C_3F_7N{=}S{=}NC_3F_7$-*i*, 34451-12-2; $C_2F_5N{=}S{=}NCH_3$, 74366-15-7; $(CF_3)_3COH\cdot(C_2H_5)_3N$, 56285-73-5; $AgOC({=}O)CH_3$, 563-63-3; $(CF_3C({=}O))_2O$, 407-25-0; AgNCO, 3315-16-0; HgO, 21908-53-2; CsF, 13400-13-0; SOF_2, 7783-42-8; $C_2F_5N{=}S(O)F_2$, 59617-28-6; $ClSO_3F$, 13997-90-5; $C_2F_5NCl_2$, 677-66-7; $(CF_3)_3COCl$, 13027-23-1; Cl_2, 7782-50-5; *n*-$C_3F_7N{=}S(O)F_2$, 74366-16-8; $CF_3CF_2CF{=}NCl$, 664-07-3.