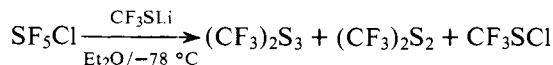
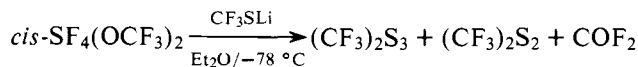
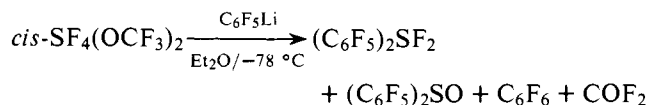


Regardless of the molar ratio of the reactants, these are the only products obtained.

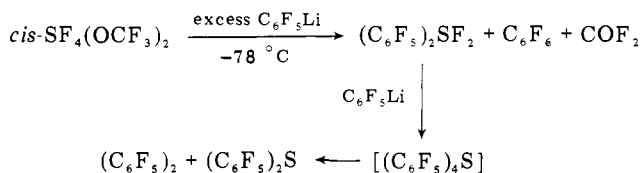
A similar type of behavior is also observed in the nucleophilic reactions of trifluorothiomethylithium.



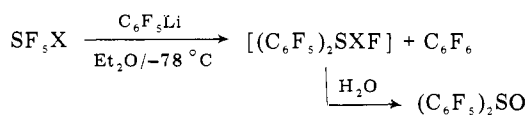
In contrast, the reaction of equimolar amounts of pentafluorophenyllithium with *cis*-SF<sub>4</sub>(OCF<sub>3</sub>)<sub>2</sub> produces bis(pentafluorophenyl)sulfur difluoride, bis(pentafluorophenyl)sulfoxide, hexafluorobenzene, and carbonyl fluoride. It is likely that bis(pentafluorophenyl)sulfoxide is formed by hydrolysis of bis(pentafluorophenyl)sulfur difluoride in the presence of traces of moisture.



In an attempt to establish the reaction path, the reaction was carried out with an excess of pentafluorophenyllithium. Under these conditions the products isolated were (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, C<sub>6</sub>F<sub>6</sub>, and COF<sub>2</sub>. The fluorine atoms of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>SF<sub>2</sub> were replaced rapidly as the latter undergoes further attack by the nucleophile. Subsequent reduction of sulfur(IV) to sulfur(II) gives rise to bis(pentafluorophenyl)sulfide and decafluorobiphenyl.<sup>20,21</sup>

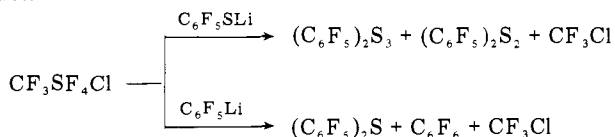


A likely intermediate in the reaction of SF<sub>5</sub>X (X = Cl, Br) with C<sub>6</sub>F<sub>5</sub>Li is the highly unstable (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>SXF. Although it was not possible to isolate the latter compound, its hydrolysis product, bis(pentafluorophenyl)sulfoxide, was found.

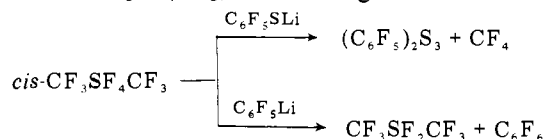


Based on our earlier studies which indicate that the sulfur-fluorine bonds in SF<sub>5</sub>X are severed readily when the molecule is attacked by nucleophiles,<sup>1</sup> we postulate the tetracoordinate intermediate, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>SXF. This is also supported by the isolation of hexafluorobenzene only and none of either chloropentafluorobenzene or bromopentafluorobenzene.

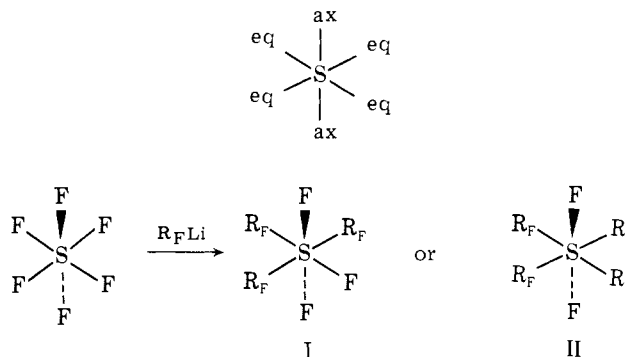
Reactions of CF<sub>3</sub>SF<sub>4</sub>Cl with pentafluorothiophenyllithium and pentafluorophenyllithium as nucleophiles were carried out and again reduction of sulfur(VI) to sulfur(II) occurred. In addition, chlorotrifluoromethane was an unexpected product.



With *cis*-CF<sub>3</sub>SF<sub>4</sub>CF<sub>3</sub>, the following reactions occur.



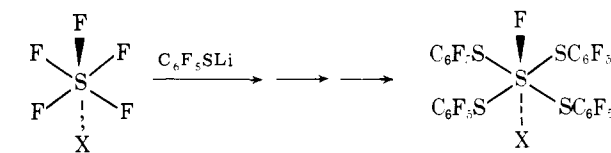
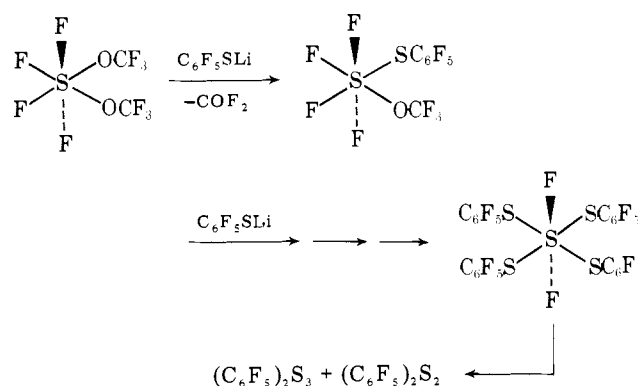
In the case with each of these sulfur hexafluoride derivatives which undergoes nucleophilic attack by these reactive lithium salts, the initial attack is most likely at the equatorial position on sulfur where the fluorine atoms exhibit a large negative <sup>19</sup>F NMR chemical shift or at the S-O bond.<sup>1</sup> A rapid ligand exchange proceeds stepwise to the tri- (I) or tetra- (II) equato-



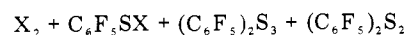
rially substituted derivatives. The next step is the collapse of the hexacoordinated species via equatorial-equatorial or axial-equatorial coupling.

Reactions of pentafluorothiophenyllithium with *cis*-SF<sub>4</sub>(OCF<sub>3</sub>)<sub>2</sub> and SF<sub>5</sub>Br lead to bis(pentafluorophenyl)trisulfane and bis(pentafluorophenyl)disulfane exclusively, whereas reaction with SF<sub>5</sub>Cl also gives pentafluorophenylsulfenyl chloride. The pentafluorophenylsulfenyl bromide decomposes to bis(pentafluorophenyl)disulfane. There is no evidence for the formation of (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub>SF<sub>2</sub> which might result from reaction intermediate type II, but also which would be expected to be unstable toward further decomposition. Scheme I accounts for the above results.

Scheme I



[X = Cl, Br]

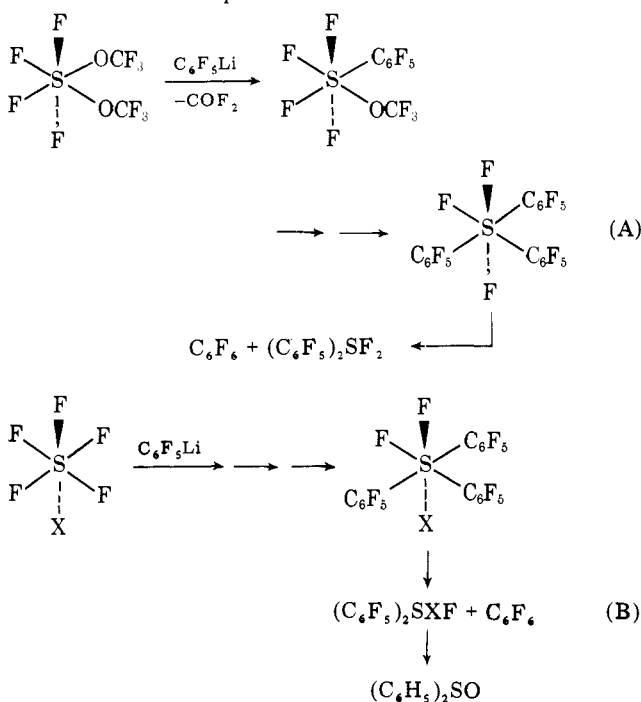


(X = Br) (X = Cl)

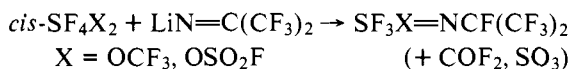
Thus for the type II intermediate, axial-equatorial coupling occurs to leave bis(pentafluorophenyl)trisulfane and produce C<sub>6</sub>F<sub>5</sub>SX (C<sub>6</sub>F<sub>5</sub>SX (X = Br) → (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub> + Br<sub>2</sub>) and C<sub>6</sub>F<sub>5</sub>SF which reacts with ether to form (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub> and unsoluble fluoro ether degradation products. The absence of (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub>SFX (X = F, Cl, Br) or (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub>SO precludes equatorial-equatorial coupling as a viable decomposition route to (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub>.

However, with pentafluorophenyllithium, the formation of bis(pentafluorophenyl)sulfur difluoride, in which the sulfur atoms are axial, requires reaction intermediate type I rather

than type II as in reaction A. In the case of type I, equatorial-equatorial coupling would occur exclusively to produce the observed products and not either chloro- or bromopentafluorobenzene where possible as in reaction B. This is so.

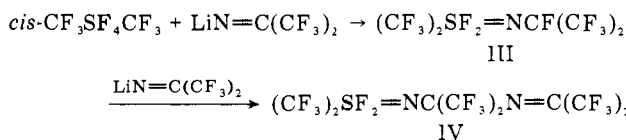


Nucleophilic attack on the sulfur at the equatorial position can be used to advantage to produce sulfur(VI) imides when several sulfur hexafluoride derivatives are allowed to react with lithium hexafluoroisopropylideneimine. In each case, fluoride ion migration from sulfur to a more electropositive center at carbon is observed.<sup>22-24</sup> The reaction of  $\text{LiN}=\text{C}(\text{CF}_3)_2$  with  $\text{cis-SF}_4\text{X}_2$  ( $\text{X} = \text{OCF}_3, \text{OSO}_2\text{F}$ ) involves preferential breaking of the sulfur-oxygen bond with subsequent fluoride ion migration.



With an excess of nucleophile,  $\text{SF}_2(=\text{NCF}(\text{CF}_3)_2)_2$ <sup>25</sup> was obtained in low yield.

In contrast, the compounds  $\text{cis-CF}_3\text{SF}_4\text{CF}_3$  and  $(\text{CF}_2\text{SF}_4)_2$ , in which the equatorial sulfur fluorine atoms exhibit large negative <sup>19</sup>F NMR chemical shifts, can be reacted with  $\text{LiN}=\text{C}(\text{CF}_3)_2$  without breaking the equatorial sulfur-carbon bonds.



Interestingly, when this reaction is carried out with an excess of nucleophile the remaining two sulfur-fluorine atoms in III are unsatylated with attack occurring only at the electropositive isopropyl carbon center to produce IV. The geometry at the sulfur atom(s) in compounds III, IV, and V approaches tri-

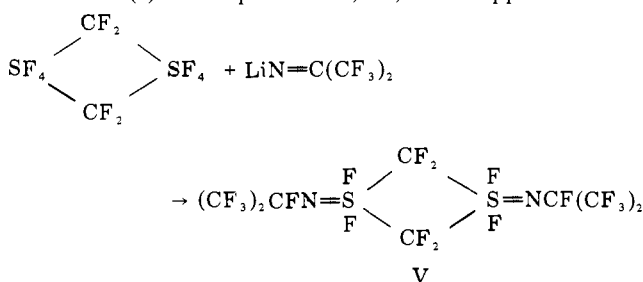
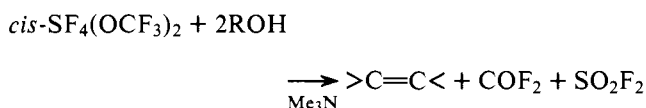


Table I

ROH	Olefin	Yield, %
$(\text{CF}_3)_2(\text{CH}_3)\text{COH}$	$(\text{CF}_3)_2\text{C}=\text{CH}_2$	75
$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}_2$	68
$(\text{CH}_3)_3\text{COH}$	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	64
$\text{PhCH}_2\text{CH}_2\text{OH}$	$\text{PhCH}=\text{CH}_2$	72

gonal bipyramidal with the fluorine atoms bonded to sulfur occupying axial positions. The  $\nu_{\text{S-Fasym}}$  and  $\nu_{\text{S-Fsym}}$  vibrational modes are at 828 m, 576 w; 828 m, 582 w; and 848 m, 583  $\text{cm}^{-1}$  w, respectively. These assignments agree well with the analogous axial vibrational modes in  $\text{OSF}_4$  at 819 vs and 588  $\text{mw}$ .<sup>26</sup>

An interesting synthetic application of  $\text{cis-SF}_4(\text{OCF}_3)_2$  is in the smooth conversion of alcohols to olefins. In addition to the olefin, carbonyl fluoride and sulfuranyl fluoride are formed, also. Yields are given in Table I.



## Experimental Section

**Materials.** Literature methods were used to prepare  $\text{SF}_5\text{Cl}$ ,<sup>27</sup>  $\text{SF}_5\text{Br}$ ,<sup>28</sup>  $\text{CF}_3\text{SF}_4\text{Cl}$ ,<sup>29</sup>  $\text{CF}_3\text{SF}_4\text{CF}_3$ ,<sup>30</sup>  $\text{cis-SF}_4(\text{OSO}_2\text{F})_2$ ,<sup>31</sup>  $(\text{CF}_2\text{SF}_4)_2$ ,<sup>32</sup>  $\text{CF}_3\text{SH}$ ,<sup>33</sup>  $\text{LiN}=\text{C}(\text{CF}_3)_2$ ,<sup>34</sup> and  $\text{CF}_3\text{OCl}$ .<sup>35</sup> Pentafluorobenzene and pentafluorothiophenol, which are available from PCR, Inc., were used without further purification.

**General Procedures.** Gases and volatile liquids were handled in a conventional Pyrex vacuum line equipped with a Heise-Bourdon tube gauge. Volatile starting materials and purified products were measured quantitatively by PVT techniques. Vapor-pressure studies were carried out by using an isoteniscope method.

Infrared spectra were obtained by using a Perkin-Elmer 457 spectrometer with a 10-cm gas cell fitted with KBr windows. The <sup>19</sup>F spectrum was recorded using a Varian HA-100 spectrometer with  $\text{CCl}_3\text{F}$  as an internal standard. Mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV.

**Preparation of  $\text{cis-SF}_4(\text{OCF}_3)_2$ .**<sup>36</sup> Sulfur tetrafluoride (5 mmol) was condensed into a 150-mL quartz vessel followed by 10 mmol of trifluoromethyl hypochlorite. The mixture was allowed to warm to 25 °C and was photolyzed for 24 h with a Hanovia utility ultraviolet quartz lamp. After this period, the remaining material was vacuum distilled and  $\text{cis-SF}_4(\text{OCF}_3)_2$  was retained in a trap at -78 °C. The yield ranged from 90 to 95%.

**Reaction of  $\text{C}_6\text{F}_5\text{SLi}$  with  $\text{cis-SF}_4(\text{OCF}_3)_2$ .** A hexane solution of *n*-butyllithium (8 mmol) was added via syringe through the side arm to a solution of pentafluorothiophenol (8 mmol) in dry ethyl ether (3 mL) under argon atmosphere in a 50-mL vessel with the temperature held at -78 °C. The reaction mixture was stirred for 1 h at -78 °C.  $\text{cis-SF}_4(\text{OCF}_3)_2$  (2 mmol) was condensed into the vessel at -196 °C and the reaction mixture was held at -78 °C. After stirring for 5 h,  $\text{CF}_2\text{O}$  (2.68 mmol) was collected at -116 °C by trap-to-trap distillation. The involatile product was separated by filtration to give bis(pentafluorophenyl)trisulfane in a yield of 62%, mp 57-58 °C (lit.<sup>37</sup> mp 57.5 °C). The filtrate solidified slowly in a refrigerator to give the bis(pentafluorophenyl)disulfane, mp 50-51 °C (lit.<sup>38</sup> mp 50-51 °C), in a yield of 57%.

**With  $\text{SF}_5\text{Cl}$ .** Pentafluorosulfur chloride (2 mmol) and pentafluorothiophenyllithium (8 mmol) in  $\text{Et}_2\text{O}$  (3 mL) were condensed as above and after stirring for 5 h at -78 °C distillation gave  $\text{C}_6\text{F}_5\text{SCLi}$ <sup>39</sup> (1.18 mmol) and  $(\text{C}_6\text{F}_5\text{S})_2$  (0.53 mmol). The involatile compound was recrystallized from petroleum ether to give bis(pentafluorophenyl)trisulfane in a yield of 73%.

**With  $\text{SF}_5\text{Br}$ .** Pentafluorosulfur bromide (2 mmol) and  $\text{C}_6\text{F}_5\text{SLi}$  (8 mmol) in dry  $\text{Et}_2\text{O}$  (3 mmol) were used as in the above reaction and worked up similarly. The products were  $(\text{C}_6\text{F}_5\text{S})_2$  (1.12 mmol) and  $(\text{C}_6\text{F}_5)_2\text{S}_3$  (1.16 mmol, 58%). Bromine in ethyl ether was isolated as *N*-bromosuccinimide.

**Reaction of  $\text{CF}_3\text{SLi}$ .** With *cis*- $\text{SF}_4(\text{OCF}_3)_2$ . Into a hexane solution of *n*-butyllithium (8 mmol) and dry ethyl ether (3 mL),  $\text{CF}_3\text{SH}$  (8 mmol) was condensed at  $-196^\circ\text{C}$  and after stirring for 2 h at  $-78^\circ\text{C}$ , *cis*- $\text{SF}_4(\text{OCF}_3)_2$  (2 mmol) was condensed into the vessel at  $-196^\circ\text{C}$ . The reaction mixture was allowed to warm to  $-78^\circ\text{C}$ , and was stirred for 5 h. The resulting mixture was fractionally distilled through a trap at  $-116^\circ\text{C}$  which retained  $\text{CF}_2\text{O}$  (2.27 mmol). A trap at  $-50^\circ\text{C}$  contained a mixture of  $(\text{CF}_3)_2\text{S}_3$ ,  $(\text{CF}_3)_2\text{S}_2$ , and  $\text{Et}_2\text{O}$ . Final purification (via gas chromatography using a column of 20% Kel-F on Chromosorb P) gave  $(\text{CF}_3)_2\text{S}_3$ <sup>40</sup> (1.02 mmol) and  $(\text{CF}_3)_2\text{S}_2$  (1.31 mmol).

With  $\text{SF}_5\text{Cl}$ ,  $\text{SF}_5\text{Cl}$  (2 mmol) and  $\text{CF}_3\text{SLi}$  (8 mmol) in dry ethyl ether (3 mL) were condensed at  $-196^\circ\text{C}$  as above and worked up similarly. The products were separated by gas chromatography using a column of 20% Kel-F on Chromosorb P to give  $\text{CF}_3\text{SCl}$  (0.89 mmol),  $\text{CF}_3\text{SSCF}_3$  (0.41 mmol), and  $(\text{CF}_3)_2\text{S}_3$  (1.09 mmol).

**Reaction of  $\text{C}_6\text{F}_5\text{Li}$ .** With *cis*- $\text{SF}_4(\text{OCF}_3)_2$ . A. Into a solution of pentafluorobenzene (6 mmol) and dry ethyl ether (3 mL) cooled to  $-78^\circ\text{C}$  under an argon atmosphere, a hexane solution of *n*-butyllithium (6 mmol) was added dropwise over 15 min. via a syringe through a side arm. After 1.5 h of stirring at  $-78^\circ\text{C}$ , *cis*- $\text{SF}_4(\text{OCF}_3)_2$  (2 mmol) was condensed into the vessel at  $-196^\circ\text{C}$ . The reaction mixture was allowed to warm to  $-78^\circ\text{C}$  and stirred for 5 h. After the trap-to-trap distillation,  $\text{CF}_2\text{O}$  (2.41 mmol) was collected at  $-116^\circ\text{C}$  and  $\text{C}_6\text{F}_6$  (0.98 mmol) was also collected at  $-78^\circ\text{C}$ . Chromatography of the residual solid on silica separated the bis(pentafluorophenyl)sulfur difluoride (0.24 mmol), mp  $74\text{--}76^\circ\text{C}$  (lit.<sup>41,42</sup> mp  $73\text{--}77^\circ\text{C}$ ), and the bis(pentafluorophenyl) sulfoxide (0.97 mmol), mp  $77\text{--}78^\circ\text{C}$  (lit.<sup>21</sup> mp  $77\text{--}78^\circ\text{C}$ ).

B.  $\text{C}_6\text{F}_5\text{Li}$  (10 mmol) and *cis*- $\text{SF}_4(\text{OCF}_3)_2$  (2 mmol) in dry  $\text{Et}_2\text{O}$  (5 mL) were used as above and worked up similarly.  $\text{CF}_2\text{O}$  (2.56 mmol) and  $\text{C}_6\text{F}_6$  (0.96 mmol) were collected by trap-to-trap distillation at  $-116$  and  $-78^\circ\text{C}$ . The residual precipitate was dissolved in *n*-hexane, and the precipitate was filtered and recrystallized from tetrahydrofuran to give the decafluorobiphenyl (1.77 mmol), mp  $206^\circ\text{C}$  (lit.<sup>43</sup> mp  $206^\circ\text{C}$ ). The filtrate was bis(pentafluorophenyl) sulfide (1.02 mmol), mp  $84\text{--}85^\circ\text{C}$  (lit.<sup>40</sup> mp  $84\text{--}85^\circ\text{C}$ ).

With  $\text{SF}_5\text{Cl}$ . Pentafluorosulfur chloride (2 mmol) and pentafluorophenyllithium (6 mmol) in dry ethyl ether (3 mL) were used as in the above reaction and worked up in a similar manner. The distillation gave a mixture of  $\text{C}_6\text{F}_6$  (0.88 mmol) and ethyl ether, and final purification by gas chromatography through use of a column which contained 20% Kel-F no. 3 oil on Chromosorb P. The involatile product was very unstable and hydrolyzed easily when exposed to air to give bis(pentafluorophenyl) sulfoxide in a yield of 60%.

With  $\text{SF}_5\text{Br}$ . Pentafluorosulfur bromide (2 mmol) and  $\text{C}_6\text{F}_5\text{Li}$  (6 mmol) in dry ethyl ether (3 mL) were condensed as above and worked up similarly. The mixture of  $\text{C}_6\text{F}_6$  (0.78 mmol) and ethyl ether was separated from the majority of the involatile product by distillation and purified finally by gas chromatography using a column of 20% Kel-F no. 3 oil on Chromosorb P. The involatile material hydrolyzed to give bis(pentafluorophenyl) sulfoxide in a yield of 56%.

**Reaction of  $\text{CF}_3\text{SF}_4\text{Cl}$ .** With  $\text{C}_6\text{F}_5\text{SLi}$ . Into the solution of  $\text{C}_6\text{F}_5\text{SLi}$  (6 mmol) and ethyl ether (3 mL),  $\text{CF}_3\text{SF}_4\text{Cl}$  (2 mmol) was condensed at  $-196^\circ\text{C}$  and was allowed to warm slowly to  $-78^\circ\text{C}$ . After stirring for 5 h at  $-78^\circ\text{C}$  chlorotrifluoromethane (1.16 mmol) was collected at  $-196^\circ\text{C}$  by trap-to-trap distillation. The residual precipitate was filtered and recrystallized to give the bis(pentafluorophenyl)trisulfane (1.26 mmol). The oily material was solidified slowly in a refrigerator to give the bis(pentafluorophenyl)disulfane (0.69 mmol).

With  $\text{C}_6\text{F}_5\text{Li}$ .  $\text{CF}_3\text{SF}_4\text{Cl}$  (2 mmol) and  $\text{C}_6\text{F}_5\text{Li}$  (6 mmol) in ethyl ether (3 mL) were condensed as in the above reaction and worked up similarly. The resulting mixture was fractionally distilled to collect the chlorotrifluoromethane (1.06 mmol) and hexafluorobenzene (1.31 mmol). The residual solid was recrystallized from hexane to give the bis(pentafluorophenyl) sulfide.

**Reaction of *cis*- and *trans*- $\text{CF}_3\text{SF}_4\text{CF}_3$ .** Into a solution of  $\text{C}_6\text{F}_5\text{SLi}$  (4 mmol) and ethyl ether (5 mL), *cis*- and *trans*- $\text{CF}_3\text{SF}_4\text{CF}_3$  (6.2 mmol, isomer ratio 1:2.1) was condensed and warmed slowly to  $-78^\circ\text{C}$ . After 5 h of stirring at  $-78^\circ\text{C}$ , the products were separated by low-temperature distillation. The tetrafluoromethane (3.21 mmol) was retained in a trap at  $-98^\circ\text{C}$  while a trap at  $-98^\circ\text{C}$  was used to remove unreacted *cis*- and *trans*- $\text{CF}_3\text{SF}_4\text{CF}_3$  (4.3 mmol, isomer ratio 1:14). The residual precipitate was recrystallized to give the bis(pentafluorophenyl)trisulfane (1.56 mmol).

With  $\text{C}_6\text{F}_5\text{Li}$ . Pentafluorophenyllithium (2 mmol) and *cis*- and

*trans*- $\text{CF}_3\text{SF}_4\text{CF}_3$  (6.2 mmol, isomer ratio 1:2.1) in ethyl ether (3 mL) were used as in the above reaction and worked up in a similar manner. The trap-to-trap distillation gave the bis(trifluoromethyl)sulfur difluoride (1.21 mmol)<sup>11</sup> in a trap at  $-98^\circ\text{C}$ . The product which was retained in a trap at  $-78^\circ\text{C}$  was purified finally by distillation. Hexafluorobenzene (1.16 mmol) was collected.

**Preparation of  $\text{SF}_3(\text{OSO}_2\text{F})=\text{NCF}(\text{CF}_3)_2$ .** The literature method was used to prepare  $\text{LiN}=\text{C}(\text{CF}_3)_2$  (2 mmol) in a rigorously flame-dried 50-mL reaction vessel. The solvent was removed under dynamic vacuum leaving a brown, amorphous solid. Onto the solid was condensed  $\text{SF}_4(\text{OSO}_2\text{F})_2$ <sup>31</sup> (2.1 mmol) at  $-196^\circ\text{C}$  and the vessel was warmed slowly to ambient temperature. After 5 h the volatile product was separated by trap-to-trap distillation and  $\text{SF}_3(\text{OSO}_2\text{F})=\text{NCF}(\text{CF}_3)_2$  (1.27 mmol) was obtained. This compound is a colorless liquid with boiling point of  $124^\circ\text{C}$  from the equation  $\log P_{\text{Torr}} = 7.15 - 1695/T$ . The molar heat of vaporization is 7.8 kcal and the Trouton constant is 19.5 eu.

The  $^{19}\text{F}$  NMR spectrum contains resonances at  $\phi$  144.1, 67.6,  $-36.9$ ,  $-67.5$ , and  $-69.1$  in the ratio 1:6:1:1:2, respectively. The resonance at  $\phi$  144.1 assigned to the isopropyl fluorine is split by two  $\text{CF}_3$  groups on carbon ( $J_{\text{F-CF}_3\text{C}} = 4.0$  Hz), the two axial fluorines on sulfur ( $J_{\text{F-SF}_{\text{ax}}} = 13.6$  Hz), and the equatorial fluorine on sulfur ( $J_{\text{F-SF}_{\text{eq}}} = 7.6$  Hz). The resonance at  $\phi$  67.6 is assigned to the  $\text{CF}_3$  groups on carbon. At  $\phi$   $-36.9$  the resonance of the fluorine on the  $\text{OSO}_2\text{F}$  group is split by the axial fluorines on sulfur ( $J_{\text{OSO}_2\text{F-SF}_{\text{ax}}} = 9.6$  Hz) and the equatorial fluorine on sulfur ( $J_{\text{OSO}_2\text{F-SF}_{\text{eq}}} = 2.1$  Hz). The resonance at  $\phi$   $-67.5$  is assigned to the equatorial fluorine on sulfur which is split by the axial fluorines on sulfur ( $J_{\text{SF}_{\text{eq-SF}_{\text{ax}}} = 146$  Hz), the fluorine on  $\text{OSO}_2\text{F}$  group, and the isopropyl fluorine. The axial fluorine atoms on sulfur resonate at  $\phi$   $-69.1$ . The infrared spectrum is as follows: 1478 s, 1370 s, 1296 s, 1245 s, 1211 m, 1119 m, 1058 w, 1034 w, 985 ms, 933 w, 913 ms, 837 m, 758 w, 726 w, 706 w, 578 w, 434  $\text{cm}^{-1}$  w.

Anal. Calcd for  $\text{C}_3\text{NS}_2\text{O}_3\text{F}_{11}$ : C, 9.70; N, 3.77. Found: C, 9.52; N, 3.76.

**Preparation of  $\text{SF}_3(\text{OCF}_3)=\text{NCF}(\text{CF}_3)_2$ .** *cis*- $\text{SF}_4(\text{OCF}_3)_2$  (2.3 mmol) was condensed onto  $\text{LiN}=\text{C}(\text{CF}_3)_2$  (2 mmol) at  $-196^\circ\text{C}$  and then warmed slowly to ambient temperature. After 24 h, the product was separated by trap-to-trap distillation through a trap at  $-50^\circ\text{C}$  which retained the  $\text{SF}_3(\text{OCF}_3)=\text{NCF}(\text{CF}_3)_2$  (1.68 mmol) and a trap at  $-116^\circ\text{C}$  which retained the  $\text{CF}_2\text{O}$  (1.41 mmol). A trap at  $-98^\circ\text{C}$  contained the *cis*- $\text{SF}_4(\text{OCF}_3)_2$  (0.16 mmol).  $\text{SF}_3(\text{OCF}_3)=\text{NCF}(\text{CF}_3)_2$  is a colorless liquid with a boiling point of  $116^\circ\text{C}$  from the equation  $\log P_{\text{Torr}} = 7.43 - 1770/T$ . The molar heat of vaporization is 8.1 kcal and the Trouton constant is 20.8 eu.

The  $^{19}\text{F}$  NMR spectrum show resonances at  $\phi$  144.6, 83.3, 69.2,  $-51.2$ , and  $-58.1$  in the ratio 1:3:6:1:2, respectively. The resonance at  $\phi$  144.6 assigned to the isopropyl fluorine atom is split by both axial and equatorial fluorine atoms on sulfur ( $J_{\text{F-SF}_{\text{ax}}} = 12.9$ ,  $J_{\text{F-SF}_{\text{eq}}} = 7.1$  Hz) and two  $\text{CF}_3$  groups on carbon ( $J_{\text{F-CF}_3\text{C}} = 4.2$  Hz). That at  $\phi$  83.3 is assigned to the  $\text{OCF}_3$  group on sulfur and is an overlapping triplet of doublets split by the axial fluorine atoms on sulfur ( $J_{\text{OCF}_3\text{-SF}_{\text{ax}}} = 10.1$  Hz) and the equatorial fluorine atom on sulfur ( $J_{\text{OCF}_3\text{-SF}_{\text{eq}}} = 7.2$  Hz). The resonance at  $\phi$  69.2 is assigned to the  $\text{CF}_3$  groups on carbon. The resonance at  $\phi$   $-51.2$  is assigned to the S-F equatorial fluorine atom, and that at  $\phi$   $-58.1$  to the S-F axial fluorine atoms ( $J_{\text{SF}_{\text{ax-SF}_{\text{eq}}} = 148$  Hz). The infrared spectrum is as follows: 1426 m, 1375 m, 1291 ms, 1261 s, 1239 s, 1146 ms, 989 ms, 926 m, 841 m, 708 w, 698 ms, 586  $\text{cm}^{-1}$  w.

Anal. Calcd for  $\text{C}_4\text{NSOF}_{13}$ : C, 13.45; N, 3.92. Found: C, 13.41; N, 3.88.

**Preparation of  $(\text{CF}_3)_2\text{SF}_2=\text{NCF}(\text{CF}_3)_2$ .** *cis*- and *trans*- $\text{CF}_3\text{SF}_4\text{CF}_3$  (5 mmol, isomer ratio 1:2.1) was condensed onto  $\text{LiN}=\text{C}(\text{CF}_3)_2$  (1.5 mmol) and warmed slowly to ambient temperature. After 24 h, the products were separated by low-temperature distillation. Unreacted  $\text{CF}_3\text{SF}_4\text{CF}_3$  (3.51 mmol) was recovered from the bath at  $-98^\circ\text{C}$  and  $(\text{CF}_3)_2\text{SF}_2=\text{NCF}(\text{CF}_3)_2$  (1.06 mmol) was also obtained at  $-78^\circ\text{C}$ . This compound is a colorless liquid with a boiling point of  $102^\circ\text{C}$  obtained from the equation  $\log P_{\text{Torr}} = 7.45 - 1718/T$ . The molar heat of vaporization is 7.7 kcal and the Trouton constant is 20.9 eu.

The  $^{19}\text{F}$  NMR spectrum contains resonances at  $\phi$  144.1, 78.3, 65.1, and  $-57.6$  in the ratio 1:6:6:2, respectively. The resonances at  $\phi$  144.1, assigned to the isopropyl fluorine atom, is split by all other fluorines in the molecule ( $J_{\text{F-CF}_3\text{C}} = 4.5$ ,  $J_{\text{F-SF}_{\text{ax}}} = 13.9$ ,  $J_{\text{F-CF}_3\text{S}} = 0.4$  Hz). The  $\text{CF}_3$  groups on carbon at  $\phi$  78.3 are a doublet. At  $\phi$  65.1 the two

CF<sub>3</sub> groups on sulfur give an overlapping triplet of doublets from splitting by two axial fluorine atoms on sulfur ( $J_{\text{CF}_3\text{S-SF}_{\text{ax}}} = 12.8$  Hz) and the isopropyl fluorine atom. The S-F axial resonance at  $\phi -57.6$  is a doublet of heptets split by the isopropyl fluorine atom and the two CF<sub>3</sub> groups on sulfur. The infrared spectrum is as follows: 1333 m, 1298 w, 1260 s, 1205 s, 1158 s, 1121 w, 994 m, 921 w, 828 m, 740 m, 735 m, 706 w, 685 s, 576 w, 541 cm<sup>-1</sup> w.

Anal. Calcd for C<sub>5</sub>NSF<sub>15</sub>: C, 15.36; N, 3.58. Found: C, 15.28; N, 3.51.

**Preparation of (CF<sub>3</sub>)<sub>2</sub>SF<sub>2</sub>=NC(CF<sub>3</sub>)<sub>2</sub>N=C(CF<sub>3</sub>)<sub>2</sub>.** *cis*- and *trans*-CF<sub>3</sub>SF<sub>4</sub>CF<sub>3</sub> (2 mmol, isomer ratio 1:2.1) was condensed onto LiN=C(CF<sub>3</sub>)<sub>2</sub> (3 mmol) and warmed to ambient temperature. After 24 h the volatile products were fractionally distilled through a trap at -50 °C which retained the (CF<sub>3</sub>)<sub>2</sub>SF<sub>2</sub>=NC(CF<sub>3</sub>)N=C(CF<sub>3</sub>)<sub>2</sub> (0.47 mmol) and a trap at -98 °C which retained unreacted CF<sub>3</sub>SF<sub>4</sub>CF<sub>3</sub> (1.42 mmol). (CF<sub>3</sub>)<sub>2</sub>SF<sub>2</sub>=NC(CF<sub>3</sub>)<sub>2</sub>N=C(CF<sub>3</sub>)<sub>2</sub> is a colorless liquid with a boiling point of 117 °C obtained from the equation  $\log P_{\text{Torr}} = 8.16 - 2059/T$ . The molar heat of vaporization is 9.4 kcal and the Trouton constant is 24.2 eu.

The <sup>19</sup>F NMR spectrum shows resonances at  $\phi$  68.6, 66.9, 64.6, and -46.6 in the ratio 6:6:6:2, respectively. The resonance at  $\phi$  68.6 is assigned to the internal CF<sub>3</sub> groups (S=NC<), and the broadened resonance at  $\phi$  66.9 is assigned to the CF<sub>3</sub> groups adjacent to the imine moiety. At  $\phi$  64.6 the resonance of the CF<sub>3</sub> groups on sulfur is a triplet from splitting by two axial fluorine atoms on sulfur. The S-F axial fluorine atoms resonance at  $\phi -46.6$  is split by the CF<sub>3</sub> groups on sulfur ( $J_{\text{SF}_{\text{ax}}-\text{CF}_3\text{S}} = 13.6$  Hz) and the internal CF<sub>3</sub> groups on carbon ( $J_{\text{SF}_{\text{ax}}-\text{CF}_3\text{C}} = 1.3$  Hz).

The infrared spectrum is as follows: 1730 w, 1331 m, 1271 s, 1259 s, 1209 s, 1156 ms, 1125 m, 996 ms, 828 m, 746 w, 736 m, 687 m, 582 cm<sup>-1</sup> w.

Anal. Calcd for C<sub>8</sub>N<sub>2</sub>SF<sub>20</sub>: C, 17.92; N, 5.23. Found: C, 17.86; N, 5.16.

**Preparation of {CF<sub>2</sub>SF<sub>2</sub>=(NCF(CF<sub>3</sub>)<sub>2</sub>)}<sub>2</sub>.** {CF<sub>2</sub>SF<sub>4</sub>}<sub>2</sub> (2 mmol) was condensed onto LiN=C(CF<sub>3</sub>)<sub>2</sub> (4.5 mmol) at -196 °C and warmed to ambient temperature. After 24 h the precipitate was recrystallized from *n*-hexane to give {CF<sub>2</sub>SF<sub>2</sub>=(NCF(CF<sub>3</sub>)<sub>2</sub>)}<sub>2</sub> in a yield of 61%, mp 76-77.5 °C.

The <sup>19</sup>F NMR spectrum shows resonances at  $\phi$  144.5, 96.1, 69.1, and -41.0 in the ratio 2:4:12:4, respectively. The isopropyl fluorine resonance at  $\phi$  144.5 is a triplet of heptets split by the axial fluorine atoms on sulfur ( $J_{\text{F-SF}_{\text{ax}}} = 14.8$  Hz) and the CF<sub>3</sub> groups on carbon ( $J_{\text{F-CF}_3\text{C}} = 3.1$  Hz). The resonance at  $\phi$  96.1 is assigned to the CF<sub>2</sub> group, and the resonance at  $\phi$  69.1 is assigned to the CF<sub>3</sub> groups on carbon. At  $\phi -41.0$ , the resonance of the axial fluorine atoms on sulfur is a multiplet from splitting by the isopropyl fluorine atom and the CF<sub>2</sub> groups ( $J_{\text{SF}_{\text{ax}}-\text{CF}_3\text{S}} = 11.8$  Hz). The infrared spectrum is as follows: 1369 m, 1276 ms, 1254 s, 1226 s, 1198 m, 1121 s, 1056 s, 988 ms, 842 m, 728 w, 691 ms, 583 cm<sup>-1</sup> w.

Anal. Calcd for C<sub>8</sub>N<sub>2</sub>S<sub>2</sub>F<sub>22</sub>: C, 15.85; N, 4.62. Found: C, 15.77; N, 4.53.

**Preparation of Olefin.** In a typical reaction, *cis*-SF<sub>4</sub>(OCF<sub>3</sub>)<sub>2</sub> (2 mmol) was condensed into a glass vessel which contained 2-methylhexafluoro-2-propanol (4 mmol) followed by 8 mmol of trimethylamine. The mixture was allowed to warm slowly to 25 °C and to remain for 3 h. After separation by trap-to-trap distillation, 2,2-di(trifluoromethyl)ethene (2.98 mmol) was retained in a trap at -116 °C while traps at -196 and -137 °C were used to remove the SO<sub>2</sub>F<sub>2</sub>

(1.08 mmol) and CF<sub>2</sub>O (2.74 mmol). Other alcohols were run in a similar manner and the results are given in the Table I.

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