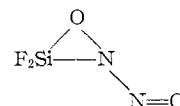


been taken to indicate the possible presence of some triplet SiF_2 (see above). Second, the initial complex formed between SiF_2 and nitric oxide rapidly converts to a more stable species at 35°K , as all of the sharp new bands initially present are replaced by a different set of bands which persist until the matrix collapses above 55°K . Since very little SiF_2 dimer is formed, the species produced is assumed to be the reaction product of monomeric SiF_2 with the *cis*-dimeric form of nitric oxide which is predominant in the matrix. Mass spectrometric investigations indicate that this reaction product decomposes explosively at -150° to yield silicon oxyfluoride polymer and nitrous oxide. A structure for the reaction product that correlates

well with this energetic release of N_2O and the observed frequencies is the heterocycle



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CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
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The Preparation and Chemistry of N-Chlorimidodisulfuryl Fluoride

By JOHN K. RUFF

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The preparation of $\text{ClN}(\text{SO}_2\text{F})_2$ is described. It was found to undergo addition with CO , ClCN , and BrCN to produce $\text{ClC}(\text{=O})\text{N}(\text{SO}_2\text{F})_2$, $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$, and $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$, respectively. Photodecomposition of $\text{ClN}(\text{SO}_2\text{F})_2$ produced $\text{N}_2(\text{SO}_2\text{F})_4$ in high yield. The salt $\text{NON}(\text{SO}_2\text{F})_2$ was formed by the interaction of NO and $\text{ClN}(\text{SO}_2\text{F})_2$. Substitution of chlorine by the $\text{N}(\text{SO}_2\text{F})_2^-$ ion was also found to occur in several metallic and organometallic chlorides. Some of the physical properties of these derivatives are discussed.

Although the preparation of N-fluorimidodisulfuryl fluoride was readily achieved by the action of fluorine on imidodisulfuryl fluoride,¹ the conversion of imidodisulfuryl fluoride to the N-chloro compound could not be accomplished in an analogous manner. However, chlorination of silver imidodisulfuryl fluoride produced N-chlorimidodisulfuryl fluoride in moderate yield. Furthermore the N-chloro compound proved to be a useful intermediate in the preparation of other derivatives containing the $\text{N}(\text{SO}_2\text{F})_2$ group. For example, it was found to undergo addition reactions with various unsaturated systems as well as to substitute the $\text{N}(\text{SO}_2\text{F})_2$ group for chlorine in several metallic and organometallic chlorides.

Experimental Section

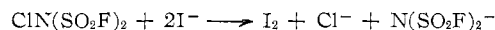
Preparation of $\text{ClN}(\text{SO}_2\text{F})_2$.—Chlorine gas, 31.1 mmoles, was condensed into a pressure reactor containing 6.0 g (20.8 mmoles) of $\text{AgN}(\text{SO}_2\text{F})_2$.² The mixture was allowed to stand at ambient temperature for 48 hr before fractionation on the vacuum line through -8 , -78 , and -196° traps. The product from four runs, which was found in the -78° trap, was distilled through a Holzman³ column, bp 36° (36 mm) (mp -52.5 to -52.0°). A yield of 62% (2.78 g) was obtained. *Anal.* Calcd for $\text{ClN}(\text{SO}_2\text{F})_2$: F, 17.6; Cl, 16.5; N, 6.50. Found: F, 17.6; Cl, 16.1; N, 6.66.

(1) M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

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Reaction of $\text{ClN}(\text{SO}_2\text{F})_2$ with Aqueous KI.—A 0.3171-g sample of $\text{ClN}(\text{SO}_2\text{F})_2$ was added to 1.521 g of KI in 10 ml of 0.1 *N* H_2SO_4 solution which was frozen at -78° . The mixture was allowed to warm to 25° and was then stirred for 0.5 hr. The iodine formed required 12.17 ml of a 0.2428 *M* $\text{Na}_2\text{S}_2\text{O}_3$ solution to reach the end point, suggesting that the reaction followed the equation



Preparation of $\text{NON}(\text{SO}_2\text{F})_2$.—Nitrogen oxide, 27.9 mmoles, was condensed into a pressure reactor containing 0.917 g (4.25 mmoles) of $\text{ClN}(\text{SO}_2\text{F})_2$. The reaction mixture was stirred 3 hr at 35 – 40° before static fractionation through -64 , -126 , and -196° cold baths. Unreacted nitrogen oxide, 23.6 mmoles, was found in the -196° cold trap. Nitrosyl chloride, 4.11 mmoles, was obtained in the -126° cold bath. It was identified by infrared spectroscopy and by reaction with excess SbCl_5 to produce 1.361 g of NOSbCl_5 . *Anal.* Calcd for NOSbCl_5 : N, 3.84; Cl, 58.3. Found: N, 3.69; Cl, 58.0. The product, 0.876 g (4.17 mmoles), remained in the reactor as a nonvolatile white solid; mp 43° . *Anal.* Calcd for $\text{NON}(\text{SO}_2\text{F})_2$: N, 13.35; F, 18.1. Found: N, 13.50; F, 17.7.

Reaction of $\text{NON}(\text{SO}_2\text{F})_2$ with HCl.—Anhydrous HCl gas, 25.8 mmoles, was condensed into a pressure reactor containing 1.296 g (6.17 mmoles) of $\text{NON}(\text{SO}_2\text{F})_2$. The mixture was allowed to stand 3 hr at 25° before fractionation through -64 , -126 , and -196° cold traps. Nitrosyl chloride, 6.05 mmoles, and $\text{HN}(\text{SO}_2\text{F})_2$, 1.026 g (5.67 mmoles) were formed, and 18.9 mmoles of HCl was recovered.

Preparation of $(\text{FSO}_2)_2\text{NCOCl}$.—Carbon monoxide, 36.5 mmoles, was added to 3.637 g (16.9 mmoles) of $\text{ClN}(\text{SO}_2\text{F})_2$ contained in a 1-l. bulb. The reactor was heated to 50° for 3 hr before fractionation. The product was found in a -78° trap. The product from two runs was distilled through a Holzman column; bp 42° (31.5 mm). A yield of 84% was realized.

Reaction of $(\text{FSO}_2)_2\text{NCOCl}$ with H_2O .—The addition of 2 g of water to 1.978 g of $(\text{FSO}_2)_2\text{NCOCl}$ frozen in a glass bulb at -78° resulted in gas evolution upon warming. The mixture was stirred 1 hr at 25° , before the solution was made slightly basic by the addition of $(\text{CH}_3)_3\text{NOH}$ solution. A 1.75-g sample of $(\text{CH}_3)_3\text{N}(\text{SO}_2\text{F})_2$ was obtained after recrystallization from hot water.

Preparation of $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$.—Cyanogen chloride, 1.573 g, was condensed into a pressure reactor containing 3.392 g of $\text{ClN}(\text{SO}_2\text{F})_2$, and the mixture was heated at $85\text{--}90^\circ$ for 2 hr. The reaction mixture was then fractionated through -10 , -78 , and -196° traps on the vacuum line. The crude product, which was trapped in the -78° trap, was dissolved in 10 ml of CH_2Cl_2 and extracted with water. The solvent was removed from the CH_2Cl_2 layer, and the product was distilled; bp 46° (10 mm). The yield was 86%. *Anal.* Calcd for $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$: N, 10.11; C, 4.33; F, 13.7. Found: N, 10.28; C, 4.23; F, 12.9.

Preparation of $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$.—The above procedure was repeated with a 3.612-g sample of BrCN and a 4.106-g sample of $\text{ClN}(\text{SO}_2\text{F})_2$. A reaction temperature of 80° was employed. The yield of product was 82%; bp 45° (4.5 mm). *Anal.* Calcd for $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$: C, 3.73; N, 8.71; F, 11.8. Found: C, 3.59; N, 8.84; F, 11.5.

Preparation of $\text{N}_2(\text{SO}_2\text{F})_4$.—An 8.20-g sample of $\text{ClN}(\text{SO}_2\text{F})_2$ was condensed into a 600-ml Pyrex bulb equipped with a vertical internal quartz finger which was shielded on the bottom. The vapor above the liquid in the bottom of the reactor (directly under the shielded end of the quartz finger) was irradiated with a Hanovia low-pressure mercury lamp (Model No. 88A45) at 25° . Periodically, the reaction bulb was cooled to -78° , and the material, which was volatile at this temperature, was removed. After 26 hr a total of 16.75 mmoles of chlorine gas was obtained. Less than 0.5 mmole of sulfur-containing materials was obtained by this process. The product was condensed out of the reactor and purified by vapor phase chromatography using an 8-ft column containing 30% Kel-F grease on Chromosorb P at 112° . The yield obtained was 87%; mp $63\text{--}64^\circ$. The molecular weight of $\text{N}_2(\text{SO}_2\text{F})_4$ was determined cryoscopically in benzene,² and an average value for three runs of 353 ± 17 was obtained. For example, the dissolution of 1.927 g of $\text{N}_2(\text{SO}_2\text{F})_4$ in 25.713 g of benzene resulted in a depression of the freezing point of 1.04° . *Anal.* Calcd for $\text{N}_2(\text{SO}_2\text{F})_4$: N, 7.77; F, 21.2. Found: N, 7.58; F, 20.9.

Reaction of $\text{ClN}(\text{SO}_2\text{F})_2$ with $(\text{CH}_3)_3\text{SnCl}$.—To 1.551 g of $(\text{CH}_3)_3\text{SnCl}$ in 10 ml of CCl_4 , 2.323 g of $\text{ClN}(\text{SO}_2\text{F})_2$ was added. The mixture was stirred for 1 hr at 25° and then fractionated on the vacuum line. Chlorine, 8.86 mmoles, was obtained along with a nonvolatile oil. Attempted distillation of the oil was not successful. However, analysis indicated that it had an empirical composition in agreement with its formulation as $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$. *Anal.* Calcd for $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$: C, 10.47; H, 2.62; N, 4.07; F, 11.1. Found: C, 10.39; H, 2.78; N, 4.12; F, 10.5.

Analysis.—The analysis of the gaseous materials formed during reaction was performed by mass spectrometry. Carbon, hydrogen, and nitrogen analyses were carried out by the usual microcombustion techniques. The fluorine content of the samples was determined by titration of the fluoride ion formed by hydrolysis of the sample with 30% aqueous KOH at 100° for 12 to 15 hr.

Nmr Spectra.—The F^{19} nmr spectra of the new materials prepared in this investigation were obtained with a Varian Model V4310A spectrometer operating at 40 Mc. Trichlorofluoromethane was used as an internal standard. All of the materials were run in CH_2Cl_2 at about 10% concentration except for $\text{NON}(\text{SO}_2\text{F})_2$ which was run in CH_3NO_2 . The values (ϕ) of the chemical shift for the single observed band in each compound are: $\text{ClN}(\text{SO}_2\text{F})_2$, -57.9 ; $\text{NON}(\text{SO}_2\text{F})_2$, -52.8 ; $\text{ClCN}(\text{SO}_2\text{F})_2$, -61.0 ; $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$, -59.6 ; $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$, -60.2 ; $\text{N}_2(\text{SO}_2\text{F})_4$, -60.6 ; and $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$, -55.5 . The H^1 nmr spectrum of the last compound consisted of a single band at -0.98 ppm from tetramethylsilane.

Ultraviolet Spectra.—The ultraviolet spectra of the compounds

were taken on solutions in cyclohexane using a Beckman DKU spectrophotometer. Methylene chloride was used as a solvent for $\text{ClN}(\text{SO}_2\text{F})_2$ since it was not soluble in cyclohexane. Only end absorption was observed for $\text{N}_2(\text{SO}_2\text{F})_4$ beginning at $225 \text{ m}\mu$ for a $3.81 \times 10^{-2} M$ solution, for $\text{ClN}(\text{SO}_2\text{F})_2$ beginning at $260 \text{ m}\mu$ for a $2.73 \times 10^{-3} M$ solution, for $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ beginning at $232 \text{ m}\mu$ for a $1.13 \times 10^{-4} M$ solution, and for $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ beginning at $245 \text{ m}\mu$ for a $4.91 \times 10^{-5} M$ solution. In addition, inflection points were observed in the spectra of the latter two compounds at 221 and $228 \text{ m}\mu$, respectively.

Infrared Spectra.—The infrared spectra of all the compounds were taken with a Perkin-Elmer Model 521 spectrophotometer. The observed bands are tabulated in Table I.

TABLE I

INFRARED SPECTRA OF SOME DERIVATIVES CONTAINING THE $\text{N}(\text{SO}_2\text{F})_2$ GROUP (IN CM^{-1})

$\text{ClN}(\text{SO}_2\text{F})_2(\text{g})$	
1495 (s), 1231 (s), 904 (w), 849 (s), 800 (s)	
$\text{NON}(\text{SO}_2\text{F})_2(\text{cap. melt})^a$	
2267 (m), 1953 (vw), 1852 (vw), 1370 (s), 1214 (w, sh), 1178 (s), 1107 (m), 847 (s, sh), 763 (vs)	
$(\text{FSO}_2)_2\text{NCOCl}(\text{l})$	
1795 (m), 1493 (s), 1471 (w, sh), 1232 (s), 1041 (m), 988 (m), 885 (w, sh), 839 (s, br), 808 (w, sh)	
$\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2(\text{l})$	
1589 (m), 1495 (s), 1236 (s), 1159 (s), 968 (s), 907 (m), 839 (vs), 738 (w)	
$\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2(\text{l})$	
1577 (m), 1499 (ms), 1235 (s), 1149 (d), 964 (s), 887 (s), 835 (vs), 735 (mw)	
$\text{N}_2(\text{SO}_2\text{F})_4(\text{cap. melt})^a$	
1499 (ms), 1242 (d), 917 (s), 851 (vs, br), 796 (w)	
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2(\text{l})$	
2985 (w), 1481 (m), 1383 (vs), 1225 (w, sh), 1190 (vs), 1123 (m), 930 (w), 862 (s), 792 (vs, br), 758 (w, sh)	
$\text{S}_2\text{O}_5\text{F}_2$	
1513 (s), 1248 (s), 872 (vw), 824 (vs), 735 (m)	

^a A capillary layer of liquid, obtained by melting the solid directly on the infrared sample plates.

Mass Spectra.—The mass spectra of $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ and $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ were taken by injecting a $9\text{-}\mu\text{l}$. sample into the inlet system of a Consolidated Engineering Corp. Model 21-620 spectrometer operating with an ionization voltage of 100 v. The mass number, molecular ion assignment, and relative abundance, respectively, for $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ are: 28, $\text{CO}^+(\text{N}_2^+)$, 3.5%; 30, NO^+ , 4.2%; 32, S^+ , O_2^+ , 2.8%; 35, Cl^{35+} , 5.6%; 37, Cl^{37+} , 1.7%; 40, CN_2^+ , 2.0%; 46, SN^+ , 2.2%; 47, ClC^+ , 6.5%; 48, SO^+ , 11.5%; 49, NCl^{36} , 9.8%; 51, NCl^{37} , 3.2%; 61, $\text{Cl}^{35}\text{NC}^+$, 13.5%; 63, $\text{Cl}^{37}\text{NC}^+$, 4.5%; 64, SO_2^+ , 6.2%; 67, SOF^+ , 24.7%; 75, Cl^{35}NCN , 12.1%; 77, Cl^{37}NCN , 4.0%; 83, SO_2F , 100%; 85, $\text{S}^{34}\text{O}_2\text{F}$, 4.1%; 96, $\text{Cl}^{35}\text{NCCl}^{36}$, 10.4%; 98, $\text{Cl}^{35}\text{NCCl}^{37}$, 6.5%; 100, $\text{Cl}^{37}\text{NCCl}^{37}$, 1.1%; 139, $\text{Cl}^{35}\text{NCNSO}_2$, 10.6%; 141, $\text{Cl}^{37}\text{NCNSO}_2$, 3.3%; 144, $\text{Cl}^{36}\text{CNSO}_2\text{F}$, 68.6%; 146, $\text{Cl}^{37}\text{CNSO}_2\text{F}$, 24.7%; 158, $\text{Cl}^{35}\text{NCNSO}_2\text{F}$, 7.5%; 160, $\text{Cl}^{37}\text{NCNSO}_2\text{F}$, 3.2%; 241, $\text{Cl}^{35}\text{NCN}(\text{SO}_2\text{F})_2$, 11.0%; 243, $\text{Cl}^{37}\text{NCN}(\text{SO}_2\text{F})_2$, 3.9%; 278, $\text{Cl}^{35}\text{CNCl}^{35}\text{N}(\text{SO}_2\text{F})_2$, 4.2%; 280, $\text{Cl}^{35}\text{CNCl}^{37}\text{N}(\text{SO}_2\text{F})_2$, 1.8%; and 282, $\text{Cl}^{37}\text{CNCl}^{37}\text{N}(\text{SO}_2\text{F})_2$, 0.7%. For $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$: 28, CO^+ , N_2^+ , 4.7%; 30, NO^+ , 3.7%; 32, S^+ , O_2^+ , 2.3%; 35, Cl^{35+} , 2.3%; 37, Cl^{37} , 0.7%; 40, CN_2^+ , 1.7%; 46, SN^+ , 1.5%; 47, Cl^{35}C^+ , 1.9%; 48, SO^+ , 9.2%; 49, NCl^{35+} , 3.2%; 51, SF , 2.0%; 64, SO_2^+ , 5.3%; 67, SOF^+ , 21.1%; 69, S^{34}OF^+ , 1.2%; 75, $\text{Cl}^{35}\text{NCN}^+$, 11.6%; 77, $\text{Cl}^{37}\text{NCN}^+$, 3.7%; 79, Br^{79+} , 5.4%; 81, Br^{81+} , 5.2%; 83, SO_2F^+ , 100%; 85, $\text{S}^{34}\text{O}_2\text{F}^+$, 4.3%; 105, $\text{Br}^{79}\text{CN}^+$, 5.4%; 107, $\text{Br}^{81}\text{CN}^+$, 5.3%; 139, Cl^{35}NC

NSO_2^+ , 19.4%; 141, $\text{Cl}^{37}\text{NCNSO}_2^+$, 6.6%; 158, $\text{Cl}^{36}\text{NCNSO}_2\text{F}^+$, 11.1%; 160, $\text{Cl}^{37}\text{NCNSO}_2\text{F}^+$, 4.0%; 188, $\text{Br}^{79}\text{CNSO}_2\text{F}^+$, 1.4%; 190, $\text{Br}^{81}\text{CNSO}_2\text{F}^+$, 1.4%; 241, $\text{Cl}^{36}\text{NCN}(\text{SO}_2\text{F})_2^+$, 27.4%; and 243, $\text{Cl}^{37}\text{NCN}(\text{SO}_2\text{F})_2^+$, 10.1%.

Conductance Measurements.—The conductance measurements were performed at $25 \pm 0.2^\circ$ using the equipment previously described.⁴ Spectral grade nitromethane which had been dried over Linde 5A Molecular Sieve and had a specific conductivity of 1.2×10^{-7} ohm⁻¹ was used as a solvent. The cell employed had a cell constant of 0.1674 cm⁻¹. The concentration (M) and the observed equivalent conductance (cm²/ohm equiv), respectively, for $\text{NON}(\text{SO}_2\text{F})_2$ are: 1.570×10^{-2} , 83.3; 7.850×10^{-3} , 90.7; 3.925×10^{-3} , 91.3; 1.963×10^{-3} , 100.2; and 9.815×10^{-4} , 102.6. This gives a value of the equivalent conductance at infinite dilution of 109.4 cm²/ohm equiv.

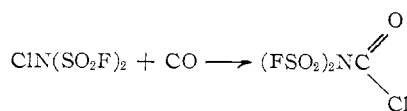
Results and Discussion

Although attempts to chlorinate imidodisulfuryl fluoride were not successful, chlorine was found to react with silver imidodisulfuryl fluoride, $\text{AgN}(\text{SO}_2\text{F})_2$, to produce N-chlorimidodisulfuryl fluoride in moderate yield. The product, a colorless, reactive liquid, was easily purified by distillation. The similarity in the infrared spectrum of $\text{ClN}(\text{SO}_2\text{F})_2$ with that of pyrosulfuryl fluoride suggests that there are two equivalent sulfuryl fluoride groups in the molecule connected by a central atom (see Table I). The F^{19} nmr spectrum shows only one kind of fluorine which further supports the formulation of the product as an N-chloro derivative. One equivalent of N-chlorimidodisulfuryl fluoride was found to react with two equivalents of iodide in acidic solution. This would be expected if the chlorine was formally in the +1 oxidation state.

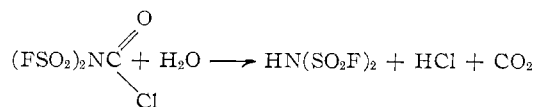
The ultraviolet spectrum of N-chlorimidodisulfuryl fluoride does not show a distinct band which can be attributed to the presence of an N-Cl bond as was found at 246 m μ in the spectrum of $(\text{CF}_3)_2\text{NCl}$.⁵ However, end absorption begins at 260 m μ so that the photolytic decomposition of the sulfuryl fluoride derivative is readily accessible. It was suggested that $(\text{CF}_3)_2\text{N}\cdot$ and chlorine radicals were the primary photolysis products derived from bis(trifluoromethyl)chloramine,⁵ and this type of cleavage is also apparent with $\text{ClN}(\text{SO}_2\text{F})_2$. Irradiation of the latter compound produces chlorine and the hydrazine, $\text{N}_2(\text{SO}_2\text{F})_4$, in high yield along with traces of other products. Tetraakis(fluorosulfuryl)hydrazine is a volatile white solid which may be handled in air and is soluble in a variety of organic solvents but insoluble in water. The infrared spectrum of $\text{N}_2(\text{SO}_2\text{F})_4$, like that of $\text{ClN}(\text{SO}_2\text{F})_2$, greatly resembles the spectrum of pyrosulfuryl fluoride. Only small changes are observed in the frequency of the bands attributable to the asymmetric and symmetric S=O stretching modes. These bands are found in the range of 1500–1490 cm⁻¹ for the asymmetric stretching mode and 1250–1230 cm⁻¹ for the symmetric stretching mode for these compounds as well as for $\text{HN}(\text{SO}_2\text{F})_2$ and $\text{FN}(\text{SO}_2\text{F})_2$.¹ The difference in the frequency of the bands in the S-F, S-O, or S-N stretching region is larger than that for the S=O bands although

the over-all appearance of the spectra in this region is similar. The F^{19} nmr spectrum of $\text{N}_2(\text{SO}_2\text{F})_4$ consists of a single line as expected since all four of the fluorines in the hydrazine would be equivalent. No evidence was found for the dissociation of $\text{N}_2(\text{SO}_2\text{F})_4$ into $\text{N}(\text{SO}_2\text{F})_2$ radicals when sealed, evacuated tubes containing the hydrazine, either neat or in solution in Kel-F oil, were heated to 150° in the cavity of an electron spin resonance spectrometer. It appears that $\text{N}_2(\text{SO}_2\text{F})_4$ more closely resembles hydrazine than tetrafluorohydrazine with respect to N-N bond cleavage.⁶

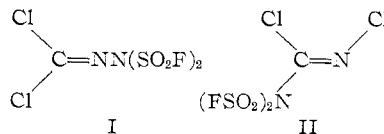
N-Chlorimidodisulfuryl fluoride was found to add to several unsaturated substrates to produce materials containing the $\text{N}(\text{SO}_2\text{F})_2$ group. For example, when carbon monoxide was employed, a single product, N-chlorocarbonylimidodisulfuryl fluoride, was isolated in high yield.



The presence of a chlorocarbonyl group is indicated by a strong band in the infrared spectrum of the adduct at 1795 cm⁻¹ which is close to the position found for many acid chlorides.⁷ The positions of the two S=O stretching modes suggest that a normal covalent $\text{N}(\text{SO}_2\text{F})_2$ group is present. Hydrolysis of $(\text{FSO}_2)_2\text{NCOCI}$ in water produces imidodisulfuryl fluoride, which was isolated as the tetramethylammonium salt,² thus demonstrating the presence of the $\text{N}(\text{SO}_2\text{F})_2$ group in the adduct. The reaction of the N-chloro derivative with carbon monoxide is similar to that observed between $(\text{CF}_3)_2\text{NCl}$ or $(\text{CF}_3)_2\text{NBr}$ and carbon monoxide.⁵



A similar addition reaction was observed when $\text{ClN}(\text{SO}_2\text{F})_2$ was allowed to react with either cyanogen chloride or cyanogen bromide, and 1:1 adducts were obtained in high yield. Unfortunately, the infrared spectrum of the adducts $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ and $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ does not distinguish between the two possible addition isomers, e.g.



The bands at 1589 and 1577 cm⁻¹ are assigned to the C=N stretching mode in the infrared spectrum of $\text{ClCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$ and $\text{BrCN}\cdot\text{ClN}(\text{SO}_2\text{F})_2$, respectively. The asymmetric and symmetric S=O modes appear normal in the adducts. The F^{19} nmr spectrum of both adducts consists of a single line suggesting that an isomeric mixture was not formed. The mass spec-

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(7) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 125.

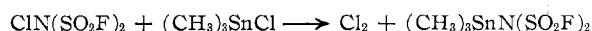
trum of the two compounds contains two peaks which arise from the molecular ions NCl^{35+} and NCl^{37+} . Furthermore peaks which correspond to the molecular ions $\text{Cl}^{35}\text{CNSO}_2\text{F}^+$, $\text{Cl}^{36}\text{CNSO}_2\text{F}^+$, $\text{Br}^{79}\text{CNSO}_2\text{F}^+$, and $\text{Br}^{81}\text{CNSO}_2\text{F}^+$ are observed in the expected isotopic ratios. These fragments (neglecting rearrangements) can only arise from structure II. The presence of a peak due to an NCl fragment also supports this structure. However, since rearrangements are known to occur in mass cracking patterns,⁸ this evidence cannot be taken as conclusive proof of structure II.

N-Chlorimidodisulfuryl fluoride was found to react slowly with nitric oxide at ambient temperature. Nitrosyl chloride and a solid having the composition $\text{NON}(\text{SO}_2\text{F})_2$ were formed in almost quantitative yield. The product is a low-melting, nonvolatile solid which is soluble in polar organic solvents such as nitromethane or acetonitrile. The solid is apparently not the nitrosamine $\text{O}=\text{NN}(\text{SO}_2\text{F})_2$ since no band which can be attributed to the $-\text{NN}=\text{O}$ group is observed in its infrared spectrum [e.g., the electronegatively substituted nitrosamine $(\text{CF}_3)_2\text{NNO}$ has a band at 1631 cm^{-1}].⁹ Instead, a band is found at 2267 cm^{-1} which suggests the presence of the nitrosonium cation.¹⁰ Furthermore, no bands are present in the region where the $\text{S}=\text{O}$ asymmetric and symmetric stretching modes are observed in the spectra of the other covalent derivatives containing the $\text{N}(\text{SO}_2\text{F})_2$ group. A comparison of the spectrum of $\text{NON}(\text{SO}_2\text{F})_2$ with that of other salts containing the $\text{N}(\text{SO}_2\text{F})_2$ anion² strongly suggests that the product is nitrosonium imidodisulfuryl fluoride.

Conductance studies on $\text{NON}(\text{SO}_2\text{F})_2$ in nitromethane solution confirm the presence of a 1:1 electrolyte in this media. A plot of $\Lambda_\infty - \Lambda$ vs. \sqrt{C} resulted in a straight line having a slope of 204, a value which is indicative of a 1:1 electrolyte.¹¹ A value of 224 was found in a conductance study on $\text{CsN}(\text{SO}_2\text{F})_2$ in nitromethane.² The chemical shift of the single line ($\phi - 52.8$) observed

in the F^{19} nmr spectrum of $\text{NON}(\text{SO}_2\text{F})_2$ in nitromethane solution is also in agreement with the presence of the $\text{N}(\text{SO}_2\text{F})_2$ anion. The chemical shift of the fluorine signal in the F^{19} nmr spectra of the covalent derivatives is at lower field by several ϕ units (see the Experimental Section). The chemical reactivity of $\text{NON}(\text{SO}_2\text{F})_2$ is more in accordance with its formulation as a nitrosonium salt than as a nitrosamine. For example, reaction of $\text{NON}(\text{SO}_2\text{F})_2$ with anhydrous hydrogen chloride resulted in the formation of nitrosyl chloride and imidodisulfuryl fluoride. Similarly nitrosation of methanol to methyl nitrite occurred when an excess of the alcohol was added to the sulfuryl fluoride derivative.

N-Chlorimidodisulfuryl fluoride was found to undergo another type of reaction with compounds containing chlorine. Thus, when $\text{ClN}(\text{SO}_2\text{F})_2$ was allowed to react with anhydrous hydrogen chloride, chlorine gas was liberated. Similarly, chlorine and $\text{CsN}(\text{SO}_2\text{F})_2$ were formed when cesium chloride was treated with the N-chloro compound.¹² Trimethyltin chloride and N-chlorimidodisulfuryl fluoride were found to react in carbon tetrachloride according to the equation



The product could not be distilled or crystallized. However, the elemental analysis and infrared, H^1 , and F^{19} nmr spectroscopy suggested that the isolated material was substantially trimethyltin imidodisulfuryl fluoride. The formation of chlorine in the above reactions suggests that the chlorine in $\text{ClN}(\text{SO}_2\text{F})_2$ possesses a partial positive charge. This is not unexpected since the group electronegativity of the $\text{N}(\text{SO}_2\text{F})_2$ is greater than that of chlorine.² This reaction should be capable of being extended to the preparation of numerous other metallic and organometallic imidodisulfuryl fluoride derivatives.

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(12) It is necessary to use silver chloride plates in obtaining the infrared spectrum of $\text{ClN}(\text{SO}_2\text{F})_2$ since this reaction also occurs with sodium chloride