REACTIONS OF PENTAFLUOROSULFANYLIMINODIHALOSULFANES, $SF_5N=SX_2$, WITH NUCLEO-PHILES. PREPARATION AND CHARACTERIZATION OF PENTAFLUOROSULFANYLSULFINYLAMINE, $SF_5N=S=O$.

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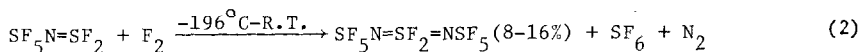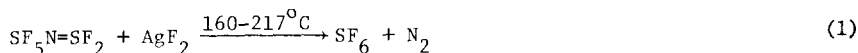
SUMMARY

Reactions of $SF_5N=SF_2$ with sodium alkoxides and aryloxides have produced both the mono- and disubstituted derivatives $SF_5N=S(F)OR$ and $SF_5N=S(OR)_2$, where R=CH_3, $CH_2CH=CH_2$, C_6H_5, $p-C_6H_4NO_2$, $p-C_6H_4Br$, $p-C_6H_4CN$. The reaction of $SF_5N=SCl_2$ with AgNCO produced $SF_5N=S(NCO)_2$. This diisocyanate can also be prepared from the reaction of $SF_5N=SCl_2$ with KOCN in liquid SO_2. The proposed intermediate, $SF_5N=S=O$, in the hydrolysis of $SF_5N=SF_2$ was prepared from the low temperature reaction of $SF_5N=SCl_2$ and Ag_2O in $C_6H_5NO_2$. The new pentafluorosulfanyl derivatives were characterized by IR, ^{1}H and ^{19}F NMR, mass spectrometry and where possible ^{13}C NMR and elemental analysis.
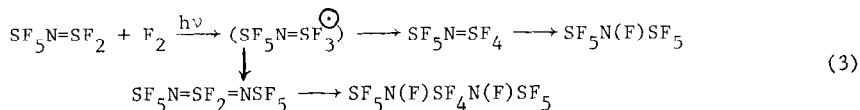
INTRODUCTION

Pentafluorosulfanyliminodifluorosulfane, $SF_5N=SF_2$, was synthesized independently by Cohen et al. [1] from the fluorination of S_4N_4 and by Clifford [2,3] from the reaction of NSF_3 and SF_4 in the presence of HF. Since then, most of the reaction chemistry of $SF_5N=SF_2$ has involved its chlorination to $SF_5N=SCl_2$ or its further fluorination. Chlorinating agents which have been used successfully include $SiCl_4$ [4], PCl_5 [4,5], $SbCl_5$, $SnCl_4$, and $TiCl_4$ [6], where $TiCl_4$ produces $SF_5N=SCl_2$ in highest yield. Even the mixed halide $SF_5N=SClF$ [6,7] has been isolated and found to be stable with respect to disproportionation at room temperature.

Clifford and Zeilenga [3] studied the fluorination of $SF_5N=SF_2$ with both silver difluoride and fluorine. Recently, Mews and co-workers [7] have studied

$$SF_5N=SF_2 + AgF_2 \xrightarrow{160-217^{\circ}C} SF_6 + N_2 \tag{1}$$

$$SF_5N=SF_2 + F_2 \xrightarrow{-196^{\circ}C-R.T.} SF_5N=SF_2=NSF_5 (8-16\%) + SF_6 + N_2 \tag{2}$$

the photolytic fluorination of $SF_5N=SF_2$ and have postulated a radical mechanism as shown in equation 3.

$$SF_5N=SF_2 + F_2 \xrightarrow{h\nu} (SF_5N=S\overset{\odot}{F_3}) \longrightarrow SF_5N=SF_4 \longrightarrow SF_5N(F)SF_5$$
$$\downarrow$$
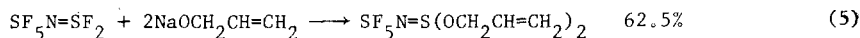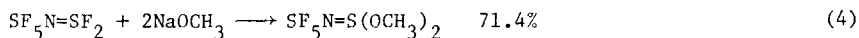$$SF_5N=SF_2=NSF_5 \longrightarrow SF_5N(F)SF_4N(F)SF_5 \tag{3}$$

Very few other derivatives of $SF_5N=SF_2$ have been reported. Höfer and Glemser [5] have shown that $SF_5N=SF_2$ will cleave the Si-N bond in silylamines to produce both the $SF_5N=S(F)NR_2$ and $SF_5N=S(NR_2)_2$ derivatives. Clifford and Shanzer [4] produced the sulfodiimide $SF_5N=S=NSF_5$ from the reaction of $SF_5N=SCl_2$ with SF_5NH_2. Most recently Mews et al. [8] reported the synthesis of $SF_5N=S(F)NSF_2$ from the reaction of $SF_5N=SCl_2$ with $Hg(NSF_2)_2$. This penta-fluorosulfanyliminosulfane derivative loses NSF presumably through an intra-molecular fluoride ion transfer to give $SF_5N=SF_2$.

We wish to report here the results of our study of the reactions of $SF_5N=SF_2$ and $SF_5N=SCl_2$ with various nucleophilic reagents including sodium alkoxides and aryloxides. Also included is a synthesis for $SF_5N=S=O$, a presumed but previously unisolated intermediate in several reactions [1,2,6].
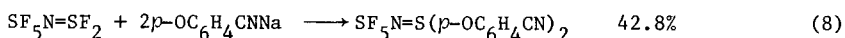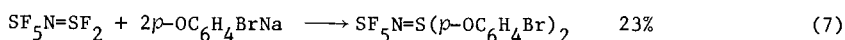

RESULTS AND DISCUSSION

Both sulfur(IV)-fluorine bonds in $SF_5N=SF_2$ are readily cleaved when allowed to react with excess sodium alkoxides as shown in equations 4 and 5.

$$SF_5N=SF_2 + 2NaOCH_3 \longrightarrow SF_5N=S(OCH_3)_2 \quad 71.4\% \tag{4}$$

$$SF_5N=SF_2 + 2NaOCH_2CH=CH_2 \longrightarrow SF_5N=S(OCH_2CH=CH_2)_2 \quad 62.5\% \tag{5}$$

When $SF_5N=SF_2$ and $NaOCH_3$ react in a 1:1 molar ratio, a mixture of $SF_5N=S(F)OCH_3$ and $SF_5N=S(OCH_3)_2$ is obtained. These two compounds could not be separated by vacuum distillation, and liquid chromatography gave only the disubstituted compound, as the $SF_5N=S(F)OCH_3$ did not elute off the column. However, gas

chromatography mass-spectrometry gave an excellent separation. In their recent study of the reactions of perfluoroalkyliminodihalosulfanes with nucleophiles, Abe and Shreeve [9] were unable to isolate the monosubstituted derivative in the reaction of $C_2F_5N=SF_2$ with $NaOCH_3$. Even when using a 2:1 molar ratio, they were still able to recover only the disubstituted derivative, $C_2F_5N=S(OCH_3)_2$, and unreacted $C_2F_5N=SF_2$.

The reaction of $SF_5N=SF_2$ with $NaOC_6H_5$ was carried out in a 1:2 molar ratio and was allowed to proceed for 3-4 hours in an attempt to obtain both the mono- and disubstituted products. Purification by liquid chromatography and trap-to-trap distillation afforded $SF_5N=S(F)OC_6H_5$ in 46.2% yield and $SF_5N=S(OC_6H_5)_2$ in 13.3% yield. Subsequent reactions to increase the yield of the disubstituted compound were not attempted. However, $SF_5N=SF_2$ was reacted with several other sodium aryloxides under conditions appropriate for disubstitution. In each reaction the sodium aryloxide was used in excess and the reaction was allowed to proceed for 24 hours or longer. In only one instance,

$$SF_5N=SF_2 + 2p-OC_6H_4NO_2Na \longrightarrow SF_5N=S(p-OC_6H_4NO_2)_2 \quad 28\% \qquad (6)$$

$$SF_5N=SF_2 + 2p-OC_6H_4BrNa \longrightarrow SF_5N=S(p-OC_6H_4Br)_2 \quad 23\% \qquad (7)$$

$$SF_5N=SF_2 + 2p-OC_6H_4CNNa \longrightarrow SF_5N=S(p-OC_6H_4CN)_2 \quad 42.8\% \qquad (8)$$
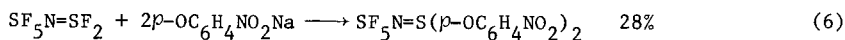
the reaction of $SF_5N=SF_2$ with $p-OC_6H_4CNNa$, was any evidence for monosubstitution seen in the ^{19}F NMR spectrum of the crude product mixture, and this was removed during the purification process.

The parasubstituted aryloxy derivatives of $SF_5N=SF_2$ were synthesized in order to obtain materials with further sites of reactivity. We were also interested in the synthesis of a diisocyanate containing the pentafluorosulfanyl moiety, and thus the reaction of $SF_5N=SCl_2$ with AgNCO was attempted. The product isolated in 28% yield was analyzed by infrared, ^{19}F NMR and mass spectroscopy and was found to be the disubstituted derivative $SF_5N=S(NCO)_2$. Even though no parent ion was obtained in the mass spectrum, the fragment $[NS(NCO)_2]^+$ (m/e 130) and the lack of chlorine isotope ratios indicate disubstitution of the product.

For the last few years, we have been synthesizing the $Si(NCO)_4$ used in our laboratory by the reaction of KOCN and $SiCl_4$ in liquid SO_2 [10]. Therefore, we attempted the reaction of $SF_5N=SCl_2$ with KOCN in liquid SO_2 and obtained a 10% conversion to a material with properties identical to those of the product

obtained in the reaction described above with AgNCO. The product $SF_5N=S(NCO)_2$ is a yellow colored, nonvolatile liquid (v.p. < 1 torr @ 25°C) which slowly deepens in color upon standing at room temperature. The $SF_5N=S(NCO)_2$ was also found to become increasingly more viscous and less volatile when held at 25°C. These observations along with the progressive appearance of a carbonyl stretch in the infrared spectrum led us to believe that this material may be polymerizing. The diisocyanate $C_2F_5N=S(NCO)_2$ recently synthesized by Abe and Shreeve [9] was also reported to be unstable at 25°C and was characterized only by infrared and ^{19}F NMR spectroscopy.

The following explanation is given in answer to a referee's question on the identity of $SF_5N=S(NCO)_2$ as an isocyanate and not a cyanate. An isocyanate can usually be distinguished from a cyanate by infrared spectroscopy even though both exhibit stretching frequencies in the region of 2250 cm^{-1}. The absorption of weak intensity at 1405 cm^{-1} in the infrared spectrum of $SF_5N=S(NCO)_2$ can be assigned to the NCO deformation; whereas, cyanates have no vibrational mode in this region [11]. Also organic cyanates have been shown to exhibit a strong absorption at ~ 1100 cm^{-1} attributable to the alkyl C-O vibration [11]. No absorption which can readily be assigned to an analogous S-O stretch, if $SF_5N=S(NCO)_2$ was to be a cyanate, could be found in the infrared spectrum. As referenced above, the reaction of $C_2F_5N=SCl_2$ with AgNCO led to a product identified as an isocyanate by infrared spectroscopy alone [9]. The product $C_2F_5N=S(NCO)_2$ exhibits an absorption of weak intensity at 1415 cm^{-1} which can also be assigned to the NCO bending mode. It has been shown that alkyl cyanates isomerize to isocyanates prior to polymerization, while pure aryl cyanates are quite stable toward isomerization and polymerization [12]. In view of these facts, the physical observations described above for $SF_5N=S(NCO)_2$ are consistent with this compound's being an isocyanate.

The isolation of $\sim 3\%$ yield of SF_5NCO in the reaction of $SF_5N=SCl_2$ and AgNCO led us to examine another route of decomposition of $SF_5N=S(NCO)_2$. When it was subjected to a 70 eV discharge or even upon standing, $SF_5N=S(NCO)_2$ was found to eliminate SF_5NCO. This mode of decomposition should also lead to $N\equiv SNCO$. The latter product might be expected to trimerize at room temperature

$$\underset{SF_5}{\overset{N=S}{\bigwedge}}\overset{NCO}{\underset{NCO}{}} \qquad \longrightarrow \qquad SF_5NCO + N\equiv SNCO \qquad (9)$$

like all other known $N\equiv SX$ derivatives [13]; however, we have no proof for its existence at this time.

The isocyanate SF_5NCO, known to be N-bonded from its preparation from SF_5NH_2 and COF_2 [14], is spectroscopically identical to the material isolated from the above decomposition. We have also prepared various ureas, urethanes, thiolurethanes, amides, and imines from this isocyanate, and know of no case where the nitrogen is not bonded directly to sulfur [4,14,15].

The compound $SF_5N=S=O$ has previously been proposed as an intermediate in both the reaction of $SF_5N=SF_2$ with water, leading to SF_5NH_2 and SO_2 [1,2], and the reaction of SF_5NH_2 with $SOCl_2$, leading to $SF_5N=SCl_2$ and $SF_5N=SClF$ [6]. However, this compound was not isolated in either reaction. In an attempt to produce $SF_5N=S=O$, the reaction of $SF_5N=SCl_2$ with Ag_2O was carried out under conditions similar to those used by Lustig [16] in the preparation of several perfluoroalkylsulfinylamines. By maintaining the reaction temperature between 0 and 5°C and utilizing nitrobenzene as the solvent $SF_5N=S=O$ was produced in ∿15% yield. This reaction had been previously attempted in our laboratory with heat (50°C) and no solvent and had led to equimolar amounts of NSF_3 and SOF_2 [17]. However once isolated, $SF_5N=S=O$ was found to be stable without decomposition into NSF_3 and SOF_2 at temperatures even up to 150°C. Mews and co-workers have independently synthesized $SF_5N=S=O$ under similar reaction conditions [18].

All of the compounds described in this paper exhibit a characteristic AB_4 splitting pattern in the ^{19}F NMR spectrum, indicating the presence of the pentafluorosulfanyl moiety. As shown in Table 1, the resonance of the axial fluorine is downfield from that of the equatorial fluorines in the disubstituted alkoxy derivatives while quite the opposite trend is seen in the disubstituted aryloxy derivatives. The resonance of the sulfur(IV) fluorine in both mono-substituted derivatives $SF_5N=S(F)OCH_3$ and $SF_5N=S(F)OC_6H_5$ appears as a quintet with only the J_{BX} coupling readily resolvable. This is consistent with the fact that in SF_5X compounds, where X contains fluorine, $|J_{BX}|$ is always much larger than $|J_{AX}|$ [19]. The pentafluorosulfanyliminosulfane derivatives all show characteristic S-F stretching and wagging frequencies, and the S=N stretch of each appears in the 1300 to 1200 cm^{-1} region. The compound $SF_5N=S=O$ displays stretches at 1277 and 1131 cm^{-1} attributable to the N=S=O group [20].

The assignment of resonances in the ^{13}C NMR spectra of the $SF_5N=S(OC_6H_4R)_2$ derivatives was aided by the use of an empirical additivity rule [21] shown in equation 10. Ai(R) represents the chemical shift increment for a substituent R

$$\delta_C(k) = 128.5 + \sum_i Ai(R) \qquad (10)$$

in the ith position (C-1, ortho, meta or para). By using known empirical parameters [21] for R=OH, H, NO_2, Br and CN we were able to calculate additivity parameters for R=-O(X)S=NSF$_5$. A comparison of the experimental ^{13}C NMR values

R	Ai			
	C-1	ortho	meta	para
-O(X)S=NSF$_5$	+21.8	-7.1	+2.3	-2.0

and those calculated using the empirical additivity rule is given in Table 2. It can be seen from the ^{13}C NMR chemical shift values given for $SF_5N=S(F)OC_6H_5$ that changes in X should have little influence on the ^{13}C NMR resonances of the aryl substitution.

TABLE 1

^{19}F NMR Data of the Pentafluorosulfanyliminosulfane Derivatives

Compound	δ_A/ppm	δ_B/ppm	δ_X/ppm	J_{AB}/Hz	J_{BX}/Hz
$SF_5N=SF_2$ [6]	-70.7	-84.2	-52.3	155.9	13.6
$SF_5N=SClF$ [6]	-71.0	-79.0	-63.9	156.3	13.7
$SF_5N=SCl_2$ [6]	-71.5	-75.1	——	156.7	——
$SF_5N=S(F)N(CH_3)_2$ [5]	-90.69	-85.47	-24.01	156.5	9.1
$SF_5N=S(F)N(C_2H_5)_2$ [5]	-90.76	-85.16	-42.76	156.7	9.1
$SF_5N=S(F)NSF_2$ [8]	-76.3	-81.5	-39.5	155.5	12.0
$SF_5N=S(F)OCH_3$	-80.0	-83.9	-32.7	157.1	11.3
$SF_5N=S(F)OC_6H_5$	-77.3	-84.0	-39.6	157.3	12.4
$SF_5N=S[N(CH_3)_2]_2$ [5]	-102.99	-87.94	——	156.7	——
$SF_5N=S[N(C_2H_5)_2]_2$ [5]	-103.86	-87.85	——	157.0	——
$SF_5N=S(OCH_3)_2$	-93.3	-87.3	——	157.4	——
$SF_5N=S(OCH_2CH=CH_2)_2$	-92.8	-88.1	——	158.9	——
$SF_5N=S(OC_6H_5)_2$	-84.3	-86.3	——	156.4	——
$SF_5N=S(p-OC_6H_4NO_2)_2$	-82.1	-85.6	——	156.5	——
$SF_5N=S(p-OC_6H_4Br)_2$	-82.9	-86.7	——	157.4	——
$SF_5N=S(p-OC_6H_4CN)_2$	-82.6	-86.1	——	156.5	——
$SF_5N=S(NCO)_2$	-72.2	-76.4	——	155.1	——
$SF_5N=S=O$	-68.1	-76.6	——	155.9	——

TABLE 2

^{13}C NMR Data of the $SF_5N=S(OC_6H_4R)_2$ Derivatives

(values in parentheses were obtained using the empirical additivity rule)

Compound	R	1	2	3	4
$SF_5N=S(OC_6H_5)_2$	H	150.0	120.7	129.5	126.3
		(150.3)	(121.4)	(130.8)	(126.5)
$SF_5N=S(F)OC_6H_5$	H	148.9	119.9	129.6	126.9
$SF_5N=S(p-OC_6H_4NO_2)_2$	NO_2	155.9	122.6	127.0	147.1
		(156.1)	(122.3)	(126.0)	(146.5)
$SF_5N=S(p-OC_6H_4Br)_2$	Br	149.9	123.7	134.0	120.8
		(148.7)	(123.1)	(134.2)	(121.0)
$SF_5N=S(p-OC_6H_4CN)_2$	CN	153.5	121.8	134.7	111.0
		(154.2)	(122.0)	(134.4)	(111.1)

EXPERIMENTAL

An all pyrex-glass high-vacuum system was employed for handling the reactants and products except for anhydrous HF which was handled on a metal vacuum system. Infrared spectra were obtained with a Beckman 20A-X infrared spectrophotometer on either gases, pressure 1 to 100 torr, or as mulls in either halocarbon or mineral oil. Mass spectra were obtained with either a Hitachi Perkin-Elmer RMU-7 mass spectrometer or a Varian MAT 112 high re-solution mass spectrometer using either a solid inlet probe or a controlled gas flow inlet. The ^{19}F and ^{1}H NMR spectra were taken on either a Jeol PS-100 or a Varian EM-390 nuclear magnetic resonance spectrometer using CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The ^{13}C NMR spectra were taken on a Jeol FX 60 Q nuclear magnetic resonance spectrometer. Elemental analyses were obtained from the Chemistry Department's Perkin-Elmer 240 elemental analyzer or from Galbraith Laboratories, Knoxville, TN. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

The liquid chromatographic purification of some of the products was per-formed on a 2 ft glass column packed with 60-200 mesh Type H silica gel and column effluents were monitored by means of a refractive index detector.

Known literature methods [2,3] were used to prepare and purify $SF_5N=SF_2$. The compound $SF_5N=SCl_2$ was prepared by the reaction of $SF_5N=SF_2$ and $TiCl_4$ [6]. All solvents and reagents were distilled or sublimed prior to use.

Preparation of $SF_5N=S(F)OCH_3$

The compound $SF_5N=SF_2$ (10.0 mmol) was condensed at $-196°C$ into a 250 ml glass reaction flask containing $NaOCH_3$ (10.0 mmol, freshly prepared from the reaction of NaH and CH_3OH) and 50 ml dry $(C_2H_5)_2O$. The reaction mixture was then allowed to warm slowly to room temperature by which time a gelatinous precipitate had formed. After 2-3 h at room temperature the reaction mixture was filtered through a vacuum frit and the ether was stripped off. The re- maining liquid residue (v.p. < 1 torr @ 25°C) was then distilled slowly into a detachable U-trap held at $-196°C$. The product collected (0.87g) was analyzed by ^1H and ^{19}F NMR and was found to be an approximately 50:50 mixture of $SF_5N=S(F)OCH_3$ and $SF_5N=S(OCH_3)_2$. Repeated trap-to-trap distillations did not produce a separation of the product mixture and liquid chromatography proved to be unsuccessful as only $SF_5N=S(OCH_3)_2$ was recovered from the column. However, gas chromatography mass-spectrometry utilizing a 10% SP-2100 column gave an excellent separation. The properties of $SF_5N=S(F)OCH_3$ (nc) observed were: mass spectrum (70 eV) m/e (rel intensity): 223 M^+ (0.2), 204 $[M-F]^+$ (2.4), 192 $[M-OCH_3]^+$ (27.4), 127 $[SF_5]^+$ (100.0), 118 (1.0), 110 (4.6), 108 (1.2), 103 (1.8), 101 (13.7), 96 (1.0), 89 $[SF_3]^+$ (23.5), 82 (3.7), 81 (3.7), 80 (2.9), 79 (34.2), 76 (1.5), 70 (4.6), 69 (1.0), 68 (2.0), 67 $[SOF]^+$ (20.0), 66 (33.2), 65 (5.9), 64 (2.4), 63 (1.0); ^1H NMR: $\delta(CH_3)$ 4.00 (s); ^{19}F NMR: δ_A -80.0 (n), δ_B -83.9 (d of m), δ_X -32.7 (qu) (J_{AB} = 157.1 Hz, J_{BX} = 11.3 Hz).


Preparation of $SF_5N=S(OCH_3)_2$

The $NaOCH_3$ was prepared by reacting methanol with NaH at $0°C$ utilizing the evolution of H_2 to monitor the reaction. Methanol and $SF_5N=SF_2$ (15.5 mmol) were then condensed into the 250 ml glass reaction vessel containing $NaOCH_3$ (2.76g, 52.07 mmol) held at $-196°C$. This mixture was allowed to warm to room temperature over a period of 18 h. After stirring for several hours at room temperature the solution was filtered through a glass frit and the methanol removed under vacuum. The remaining colorless viscous liquid was fractionated through a series of traps at $-15°$, $-30°$, and $-196°C$. The $-30°C$ trap contained the water clear liquid $SF_5N=S(OCH_3)_2$ (nc) (2.60g, 11.06 mmol) in 71.38% yield. The properties of $SF_5N=S(OCH_3)_2$ observed were: v.p. < 1 torr @ 25°C; IR (capillary film): 2968 (ws), 1199 (mb) ($\nu(S=N)$), 1130 (ms), 970 (ms), 869 (ss), 858 (ssh), 720 (sb), 585 (mb) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 235 M^+ (0.4), 216 $[M-F]^+$ (2.9), 206 (6.4), 204 (74.3), 139 (4.5), 127 $[SF_5]^+$ (100.0), 94 (4.1), 89 $[SF_3]^+$ (17.1), 79 (17.9), 78 (16.4), 67 $[SOF]^+$ (19.3); ^1H NMR (neat): $\delta(CH_3)$ 3.79 (s); ^{19}F NMR (neat): δ_A -93.3 (n), δ_B -87.3 (d of m) (J_{AB} = 157.4 Hz); ^{13}C NMR (neat): δC 52.6.

Anal: Calcd for $C_2H_6NS_2O_2F_5$: C, 10.21; H, 2.55; N, 5.96; S, 27.33; O, 13.62; F, 40.43. Found: C, 10.24; H, 2.60; N, 5.94; S, 27.24; O, 13.61; F, 40.22.

Preparation of $SF_5N=S(OCH_2CH=CH_2)_2$

The compound $NaOCH_2CH=CH_2$ was prepared by reacting allyl alcohol with a solution of NaH in THF. The reaction was monitored by measuring the H_2 evolved. The solution was filtered and excess allyl alcohol and the THF were removed by evaporation. The reactant $SF_5N=SF_2$ (7.17g, 34 mmol) and THF (150 ml) were then condensed into the 250 ml glass flask containing $NaOCH_2CH=CH_2$ (8.73g, 110.5 mmol) held at -196°C. The reaction mixture was allowed to warm from -78°C to room temperature over a period of 10-12 h. After stirring for 1h at room temperature the solvent was stripped off at -30°C leaving a water clear liquid that was fractionated through a series of traps at 0°C, -15°C, and -30°C. The -15°C trap contained the water-clear liquid $SF_5N=S(OCH_2CH=CH_2)_2$ (nc) (6.10g, 21.25 mmol) in 62.5% yield. The properties of $SF_5N=S(OCH_2CH=CH_2)_2$ observed were: b.p. 189°C in 1 atm. N_2, 106°C in 10^{-6} torr vacuum; IR (capillary film): 3080 (mb), 1640 (ms), 1450 (ms), 1350 (mb), 1245 (ms) (ν(S=N)), 1155 (ssh), 895 (ss), 825 (sb), 650 (ms) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 282 (0.4), 232 (3.9), 230 (1.6), 127 $[SF_5]^+$ (38.1), 104 (16.7), 89 $[SF_3]^+$ (31.8), 57 (100.0); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 290 (9.7), 289 (8.3), 288 $[M+1]^+$ (100.0), 269 (4.2), 268 (51.1); ^{1}H NMR (neat δ_d 4.50, $\delta_{b,c}$ 5.27, δ_a 5.80 (J_{ab} = 16.8 Hz,
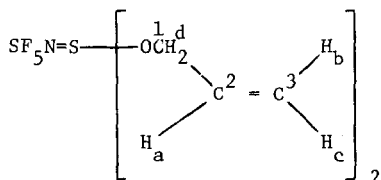
J_{ac} = 9.6 Hz, J_{ad} = 6.0 Hz, J_{bd} = 1.2 Hz, J_{cd} = 0.6 Hz); ^{19}F NMR (neat): δ_A -92.8 (n), δ_B -88.1 (d of m) (J_{AB} = 158.9 Hz); ^{13}C NMR (neat): δC_1 67.145, δC_3 120.145, δC_2 130.486.

Anal. Calcd for $C_6H_{10}NS_2O_2F_5$: C, 10.21; H, 2.55; N, 5.96; S, 27.33; O, 13.61; F, 40.43. Found: C, 10.24; H, 2.60; N, 5.94; S, 27.24; O, 13.61; F, 40.22.

Reaction of $SF_5N=SF_2$ with $NaOC_6H_5$

The $NaOC_6H_5$ (13.0 mmol) was prepared by reacting phenol with NaH in dry $(C_2H_5)_2O$. The hydrogen evolved was pumped off and $SF_5N=SF_2$ (6.5 mmol) was condensed into the reaction flask held at $-196°C$. The reaction mixture was then allowed to warm slowly to room temperature by which time a gelatinous precipitate had formed. After allowing the reaction to proceed for 3-4 h at room temperature, the contents of the flask were filtered through a vacuum frit to remove the NaF and any unreacted $NaOC_6H_5$. The ether was then stripped leaving a fairly non-volatile (v.p. < 1 mm), red liquid residue (2.84g). This liquid residue was further purified by liquid chromatography on the system described earlier. The resulting pale yellow liquid was found by mass spectrometry to be a mixture of $SF_5N=S(F)OC_6H_5$ and $SF_5N=S(OC_6H_5)_2$. The compound $SF_5N=S(F)OC_6H_5$ (nc) (0.85g; 46.2% yield) was distilled from the mixture into a detachable U-trap held at $-196°C$ by pumping under vacuum overnight. The remaining residue was further purified by repeated liquid chromatography to give $SF_5N=S(OC_6H_5)_2$ (nc) (0.31g; 13.3% yield).

The properties of $SF_5N=S(F)OC_6H_5$ observed were: IR (capillary film): 3072 (w), 3050 (wsh), 1590 (m), 1490 (s), 1458 (wsh), 1255 (sb) ($\nu(S=N)$)), 1215 (wsh), 1176 (s), 1152 (s), 1073 (w), 1026 (w), 875 (vsb), 837 (ssh), 810 (vsb), 775 (s), 732 (m), 688 (s), 646 (w), 603 (msh), 589 (s) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 285 M^+ (17.5), 266 $[M-F]^+$ (1.6), 218 (6.2), 192 $[M-OC_6H_5]^+$ (1.9), 158 $[NS(F)OC_6H_5]^+$ (2.6), 139 (1.4), 127 $[SF_5]^+$ (23.0), 93 $[OC_6H_5]^+$ (100.0), 89 (9.9), 70 (2.0), 65 (84.0), 51 (1.7), 48 (0.5), 46 (9.3), 39 (20.0); ^1H NMR: $\delta(C_6H_5)$ 6.90 (bm); ^{19}F NMR: δ_A -77.3 (n), δ_B -84.0 (d of m), δ_X -39.6 (qu) (J_{AB} = 157.3 Hz, J_{BX} = 12.4 Hz); ^{13}C NMR: δC_1 148.9, δC_2 119.9, δC_3 129.6, δC_4 126.9.

Anal: Calcd for $C_6H_5NS_2OF_6$: C, 25.26; H, 1.75; N, 4.91. Found: C, 25.06; H, 1.65; N, 4.90.

The properties of $SF_5N=S(OC_6H_5)_2$ observed were: IR (capillary film): 3070 (w), 3048 (wsh), 1590 (m), 1490 (s), 1458 (w), 1285 (wsh), 1212 (m) ($\nu(S=N)$)), 1175 (s), 1153 (s), 1073 (w), 1025 (w), 970 (w), 912 (msh), 860 (vsb), 828 (ssh), 807 (vsb), 769 (s), 723 (m), 687 (s), 647 (w), 600 (msh), 578 (s) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 359 M^+ (14.8), 340 $[M-F]^+$ (2.2), 266 $[M-OC_6H_5]^+$ (100.0), 238 (20.0), 234 (8.5), 170 (14.4), 154 (7.0), 141 (11.9), 139 (40.7), 119 (11.7), 111 (19.3), 94 (29.6), 93 (55.5), 89 $[SF_3]^+$ (6.3), 85 (33.3), 77 (51.9), 66 (12.0), 65 (72.2), 46 (6.1), 39 (20.4); ^1H NMR: $\delta(C_6H_5)$ 6.46 (bm); ^{19}F NMR: δ_A -84.3 (n), δ_B -86.3 (d of m) (J_{AB} = 156.4 Hz); ^{13}C NMR: δC_1 150.0, δC_2 120.7, δC_3 129.5, δC_4 126.3. Elemental analysis did not afford satisfactory results.

Preparation of SF$_5$N=S(p-OC$_6$H$_4$NO$_2$)$_2$

The compounds SF$_5$N=SF$_2$ (6.7 mmol) and diethyl ether (40 ml) were condensed at -196°C into a 250 ml glass flask containing p-OC$_6$H$_4$NO$_2$Na (2.16g, 13.4 mmol). The reaction mixture was warmed slowly to ambient temperature. After 24 h the ether solution was filtered through a glass frit and the solvent removed under vacuum. The white powder remaining in the bottom of the vessel was dissolved in CH$_2$Cl$_2$ and purified by preparative liquid chromatography as described above. Evaporation of the CH$_2$Cl$_2$ yielded the white solid SF$_5$N=S(p-OC$_6$H$_4$NO$_2$)$_2$ (nc) (0.86g, 1.92 mmol) in 28% yield. The properties of SF$_5$N=S(p-OC$_6$H$_4$NO$_2$)$_2$ observed were: m.p. 75°C; IR (mull): 3118 (ws), 1616 (ms), 1529 (ms), 1350 (ss), 1218 (mb) (ν(S=N)), 1150 (sb), 887 (sb), 810 (sb), 590 (mb) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 430 [M-F]$^+$ (0.09), 311 (55.2), 184 (26.1), 139 (32.8), 127 [SF$_5$]$^+$ (16.4), 89 [SF$_3$]$^+$ (40.3), 64 (46.3), 63 (55.2), 46 [NS]$^+$ (100.0); chemical ionization mass spectrum (isobutane) m/e (rel intensity): 449 M$^+$ (0.36), 279 (1.57), 141 (8.33), 140 (100.0), 108 [SF$_4$]$^+$ (6.53); ^{1}H NMR (d$_6$-Acetone): δ_a 7.65 (d), δ_b 8.40 (d) (J$_{ab}$ = 9.31 Hz);
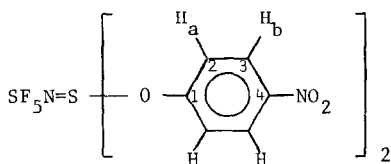
^{19}F NMR (d$_6$-Acetone): δ_A -82.1 (n), δ_B -85.6 (d of m)(J$_{AB}$ = 156.5Hz); ^{13}C NMR (d$_6$-Acetone): δC$_2$ 122.6, δC$_3$ 127.0, δC$_4$ 147.1, δC$_1$ 155.9.

Anal: Calcd for C$_{12}$H$_8$N$_3$S$_2$O$_6$F$_5$: C, 32.07; H, 1.78; N, 9.35; S, 14.25. Found: C, 31.70; H, 1.80; N, 9.05; S, 14.12.

Preparation of SF$_5$N=S(p-OC$_6$H$_4$Br)$_2$

The compound p-OC$_6$H$_4$BrNa was prepared by adding a solution of p-HOC$_6$H$_4$Br (6.90g, 39.88 mmol) in THF to a 250 ml glass vessel containing NaH (1.10g, 47.83 mmol) held at -196°C. This mixture was slowly warmed to ambient temperature and the reaction was monitored by measuring the H$_2$ evolved. Excess NaH was removed by filtration before refreezing the solution at -196°C and condensing in SF$_5$N=SF$_2$ (14.77 mmol). The reaction mixture was then allowed to warm slowly to room temperature. After 24 h the solvent was removed under

dynamic vacuum. The black residue remaining was dissolved in CH_2Cl_2 and purified by preparative LC as described above. Removal of the CH_2Cl_2 produced $SF_5N=S(p-OC_6H_4Br)_2$ (nc) (1.77g, 3.42 mmol) as a reddish brown liquid in 23% yield. The properties of $SF_5N=S(p-OC_6H_4Br)_2$ observed were: m.p. -32 to -33°C; IR (capillary film): 1482 (vss), 1220 (bsh) ($\nu(S=N)$), 1158 (ss), 868 (vsb), 809 (sb), 590 (msh), 505 (msh), 478 (wsh) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 519, 517, 515 (M)$^+$ (3.13, 5.45, 2.75), 346, 344 (51.46, 49.17), 219, 217 (20.02, 19.97), 173, 171 (65.92, 67.76), 103 (33.96), 85 (100), 70 $(SF_2)^+$ (14.54); ^1H NMR (neat): δ_a 6.95 (d), δ_b 7.34 (d) (J_{ab} = 9.90 Hz); ^{19}F NMR (neat): δ_A -82.9 (n), δ_B -86.7 (d of m) (J_{AB} = 157.4 Hz); ^{13}C NMR (d_6-Acetone): δC_2 123.7, δC_3 134.0, δC_1 149.9, δC_4 120.9.

Anal. Calcd for $C_{12}H_8NS_2O_2F_5Br_2$: C, 27.90; H, 1.55; N, 2.71; S, 12.40. Found: C, 27.74; H, 1.57; N, 2.57; S, 11.82.

Preparation of $SF_5N=S(p-OC_6H_4CN)_2$

The compound $p-OC_6H_4CNNa$ was prepared by reacting $p-HOC_6H_4CN$ (4.76g, 40 mmol), NaOH (1.2g, 30 mmol), and benzene (200 ml) in a 500 ml azeotropic reflux apparatus. When evolution of water was no longer observed the reaction mixture was filtered and the excess $p-HOC_6H_4CN$ was removed from the resulting white solid by vacuum sublimation at 120°C. The $SF_5N=SF_2$ (5 mmol) and diethyl ether (50 ml) were then condensed at -196°C into a 250 ml glass flask containing the purified $p-OC_6H_4CNNa$ (2.11g, 14.96 mmol). The reaction was slowly warmed to room temperature. After 48 h the reaction mixture was filtered through a glass frit and the solvent removed under vacuum. The white residue remaining was dissolved in CH_2Cl_2 and purified by preparative LC as described above. Evaporation of the CH_2Cl_2 afforded the light golden liquid $SF_5N=S(p-OC_6H_4CN)_2$ (nc) (0.90g, 2.14 mmol) in 42.8% yield. The properties of $SF_5N=S(p-OC_6H_4CN)_2$ observed were: v.p. < 1 torr @ 25°C; IR (capillary film): 3100 (m), 3060 (wsh), 2024 (vss), 1603 (vss), 1500 (vss), 1414 (ms), 1230 (m) ($\nu(S=N)$), 1190 (vsb), 1160 (vsb), 1024 (m), 860 (vsb), 750 (sb), 580 (ss) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 409 M$^+$ (0.2), 395 (0.2), 393 (0.2), 390 [M-F]$^+$ (0.4), 291 (32.6), 164 (27.1), 127 $[SF_5]^+$ (34.2), 119 (52.4), 118 (30.1), 91 (12.7), 90 (60.3), 89 (16.1), 64 (31.9), 46 (100.0); ^1H NMR: δ_a 7.52 (d), δ_b 7.87 (d) (J_{ab} = 8.46 Hz); ^{19}F NMR: δ_A -82.6 (n), δ_B -86.1 (d of m) (J_{AB} = 156.5 Hz); ^{13}C NMR: δC_4 110.9, δC_5 117.4, δC_2 121.8, δC_3 134.7, δC_1 153.5

Anal: Calcd for $C_{10}H_8N_3S_2O_2F_5$: C, 41.07; H, 1.97; N, 10.27. Found: C, 40.64; H, 1.71; N, 10.20.

Preparation of $SF_5N=S(NCO)_2$

(a) Method A

The compound $SF_5N=SCl_2$ (2.52g, 10.3 mmol) was condensed at -196°C into a 250 ml glass reaction cylinder containing AgNCO (4.25g, 28.3 mmol) and 10 ml of benzene. The reaction mixture was warmed quickly to 5-10°C and allowed to react at that temperature with stirring for 3 h before warming to room temperature. After 18 h the reaction mixture was filtered through a vacuum frit and the volatile reaction products distilled through a series of traps. The trap held at -25°C contained a medium yellow liquid which was identified as $SF_5N=S(NCO)_2$ (nc) (0.74g, 2.9 mmol, 28.2% yield). The contents of the -196°C trap were further fractionated through -78 and -196°C traps. The -78°C trap contained the solvent benzene and infrared spectroscopy showed no evidence for any unreacted $SF_5N=SCl_2$. The -196°C trap contained SF_5NCO (0.3 mmol) which was identified by infrared and mass spectroscopy [14].

(b) Method B

The compound KOCN (5.09g, 62.75 mmol) was placed in a 75 ml stainless steel cylinder and dried under vacuum at 100°C for 18 h. The dichloride $SF_5N=SCl_2$ (2.4g, 9.84 mmol) and SO_2 (140.0 mmol) were condensed into the vessel which had been cooled to -196°C. The mixture was allowed to come to room temperature and shaken for 24 h. The volatiles of the reaction were then fractionated by trap-to-trap distillation. The trap held at -30°C contained a medium yellow liquid $SF_5N=S(NCO)_2$ (nc) (1.01 mmol) while the trap held at -78°C contained unreacted $SF_5N=SCl_2$ (2.14g, 8.80 mmol). This represents a 97.1% yield of $SF_5N=S(NCO)_2$ based on the $SF_5N=SCl_2$ consumed.

The compound $SF_5N=S(NCO)_2$ gradually changed in color from yellow to red and became more viscous when held at room temperature. These changes were also accompanied by the loss of SF_5NCO as shown by changes in the ^{19}F NMR spectrum and infrared and mass spectroscopy of the outgases produced. The $SF_5N=S(NCO)_2$ was also observed to eliminate SF_5NCO when subjected to mass sectral analysis at 70 eV. This decomposition mode should also lead to $N\equiv SNCO$; however, we have no evidence for this compound at this time. The properties of $SF_5N=S(NCO)_2$ observed were: v.p. < 1 torr @ 25°C; IR(gas): 2270 (s), 1405 (w), 1225 (m) (ν (S=N)), 902 (s), 853 (s), 595 (m) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 238 $[M-F]^+$ (0.1), 215 $[M-NCO]^+$ (5.0), 192 (4.2), 173 (0.9), 169 $[SF_5NCO]^+$ (1.4), 168 (0.6), 150 $[SF_4NCO]^+$ (4.3), 149 (1.0), 143 (0.8), 130 $[N=S(NCO)_2]^+$ (21.7), 127 $[SF_5]^+$ (60.0), 124 (0.9), 112 (6.1), 108 (2.1), 104

(1.9), 103 (2.7), 89 (25.0), 84 (1.5), 72 (1.2), 71 (3.7), 70 (100.0), 67 (6.5), 65 (4.8), 51 (2.3), 48 (6.7), 47 (10.3), 46 (70.0), 44 (2.8), 43 (2.2), 42 (4.1); ^{19}F NMR: δ_A -72.2 (n), δ_B -76.4 (d of m) (J_{AB} = 155.1 Hz).

Preparation of $SF_5N=S=0$

The compound $SF_5N=SCl_2$ (2.24g, 9.2 mmol) was condensed at -196°C into a 250 ml glass reaction cylinder containing Ag_2O (23.17g, 100 mmol) and 60 ml of freshly distilled nitrobenzene. The reaction mixture was warmed to 0-5°C and held at that temperature for 6 h. The reaction mixture was then warmed slowly to room temperature as the volatile components were stripped to the vacuum line for distillation. Repeated trap-to-trap distillation gave unreacted $SF_5N=SCl_2$ (0.45g, 1.84 mmol) in the -65°C trap, $SF_5N=S=0$ (nc) (0.21g, 1.1 mmol, 15% yield based on consumed $SF_5N=SCl_2$) in the -90°C trap, and a mixture of SO_2, SOF_2, SiF_4, and $SF_5N=SF_2$ (0.4 mmol total) in the -196°C trap. The $SF_5N=S=0$ was contaminated by a small amount of $SF_5N=SClF$ [6] which had not initially been removed from the starting material $SF_5N=SCl_2$. The compound $SF_5N=S=0$ was found to be thermally stable with respect to decomposition to NSF_3 and SOF_2 at least up to 150°C, but after heating at 175°C for 4 days partial decomposition into the above products was observed. The properties of $SF_5N=S=0$ observed were: IR(gas): 1277 (s), 1131 (m), 905 (vs), 858 (vs), 605 (vs) cm^{-1}; mass spectrum (70 eV) m/e (rel intensity): 189 M$^+$ (3.6), 170 [M-F]$^+$ (1.1), 143 (1.2), 127 [SF_5]$^+$ (100.0), 108 (2.8), 103 (7.2), 89 [SF_3]$^+$ (30.7), 70 (4.3), 67 [SOF]$^+$ (35.7), 65 (2.8), 64 (22.5), 62 [NSO]$^+$ (0.8), 51 (1.6), 48 [SO]$^+$ (14.4), 46 [SN]$^+$ (17.1); ^{19}F NMR: δ_A -68.1 (n), δ_B -76.6 (d of m) (J_{AB} = 155.9 Hz).

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