

ories²³ involving various metal complexes and several fluoroarylphosphine ligands further substantiate these conclusions concerning the effect of fluorine substitution on the donor properties of the arylphosphine ligands.

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CONTRIBUTION FROM THE ANORGANISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT GÖTTINGEN, GÖTTINGEN, GERMANY

Some Reactions of Sulfur Difluoride Imides and Sulfur Dichloride Imides

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The fluorine atoms of the NSF₂ group in sulfur difluoride *N*-perhaloalkylimides are readily exchanged using R₂NSi(CH₃)₃, RN[Si(CH₃)₂]₂, or RONa to give compounds of the general formula R_{HAL}-N=S(NR₂)F, R_{HAL}-N=S(NR₂)₂, R_{HAL}-N=S=N-R, R_{HAL}-N=S(OR)F, and R_{HAL}-N=S(OR)₂. In the interaction of sulfur dichloride imides with *N*-silylated secondary amines, monochlorosulfur imides R_{HAL}-N=S(NR₂)Cl are formed. These compounds show physical and chemical relationships to analogs in the O=S(X)Y system.

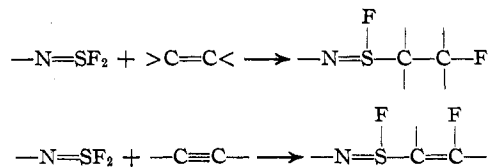
Introduction

Sulfur difluoride imides, RN=SF₂, may undergo the following reactions to give other sulfur-nitrogen compounds:¹ (a) cleavage of the R-N bond and transfer of the NSF₂ group, (b) addition to the N=S double bond, (c) oxidation of the sulfur(IV) to sulfur(VI), and (d) exchange of the fluoride atoms to give other S-substituted sulfur(IV) imides.

The first reaction type is found in the cleavage of acyl-,²⁻⁴ metal-,^{2,8,5} or *N*-halogeno sulfur difluoride imides.⁶⁻⁹ Fluorination of R-N=SF₂ gives R-NF-SF₅^{10,11} (addition and oxidation) or R-N=SF₂=N-R (oxidation and S=N bond cleavage).^{10,12} The interaction (c) is brought about by the photochemical oxidation of RNSF₂ with OF₂ to give sulfur oxydifluoride imides.¹³

Fluorine-chlorine exchange according to (d) is achieved using the Lewis chloro acids AlCl₃,¹⁴ PCl₅,¹⁵ and SiCl₄.¹⁶ In the reaction of phenylsulfur difluoride imide with nitrogen bases, alcoholates, or phenyllithium also both fluorine atoms of the N=SF₂ group were exchanged and the appropriate fluorine-free sulfur(IV) imides were generated.¹⁷ Starting from sulfur difluoride imides only their addition across the carbon-

carbon double¹⁸ and triple bond¹⁹ gave S-substituted sulfur monofluoride imides



We have investigated the value of sulfur difluoride imides as precursors for S-substituted monofluoride imides and whether the procedures given for phenylsulfur difluoride imide may be generally applied. We have also investigated the influence of substituents at the sulfur (other than fluorine) upon the stability of the compounds.

Experimental Section

General Methods.—CF₂CICF₂NSF₂,⁶ CFC₂CF₂NSF₂,⁸ (CH₃)₂-NSi(CH₃)₃,²⁰ (C₂H₅)₂NSi(CH₃)₃,²¹ and CH₃N[Si(CH₃)₃]₂.²² were prepared by the literature methods. All reactions were carried out in Pyrex-glass flasks under an atmosphere of dry nitrogen.

IR spectra were obtained in the liquid phase (KBr windows) with a Leitz infrared spectrometer. Nmr spectra were measured with a Varian A-56/60 spectrometer. Tetramethylsilane and trichlorofluoromethane were used as external standards. Mass spectra were recorded with an Atlas UFCH 4 spectrometer. Elemental analyses (Table I) were performed by Beller Microanalytical Laboratory, Göttingen, Germany.

Preparation of CF₂CICF₂N=S(F)N(CH₃)₂ (I).—The reaction was carried out in a two-necked 100-ml Pyrex-glass flask, equipped with a magnetic stirrer, dropping funnel, and reflux condenser with a nitrogen T adapter. At room temperature 7.4 g (69.1 mmol) of (CH₃)₃SiN(CH₃)₂ was slowly added to 14.8 g (67.5 mmol) of CF₂CICF₂NSF₂. Upon warming, the reaction mixture turned orange. The volatile products were removed at 12–14 Torr. Distillation of the residue gave 9.5 g of CF₂CICF₂N=S(F)N(CH₃)₂, bp 76–78° (14 Torr) with slight decomposition (yield 57%). Nmr spectrum: δ_{SF} -33.3, δ_{CF_A} +77.6, δ_{CF_B} +80.1, δ_{CF_{Cl}} +73.7, δ_{CH} -2.94 ppm; J_{SF-CF_A} = 13.4, J_{SF-CF_B}

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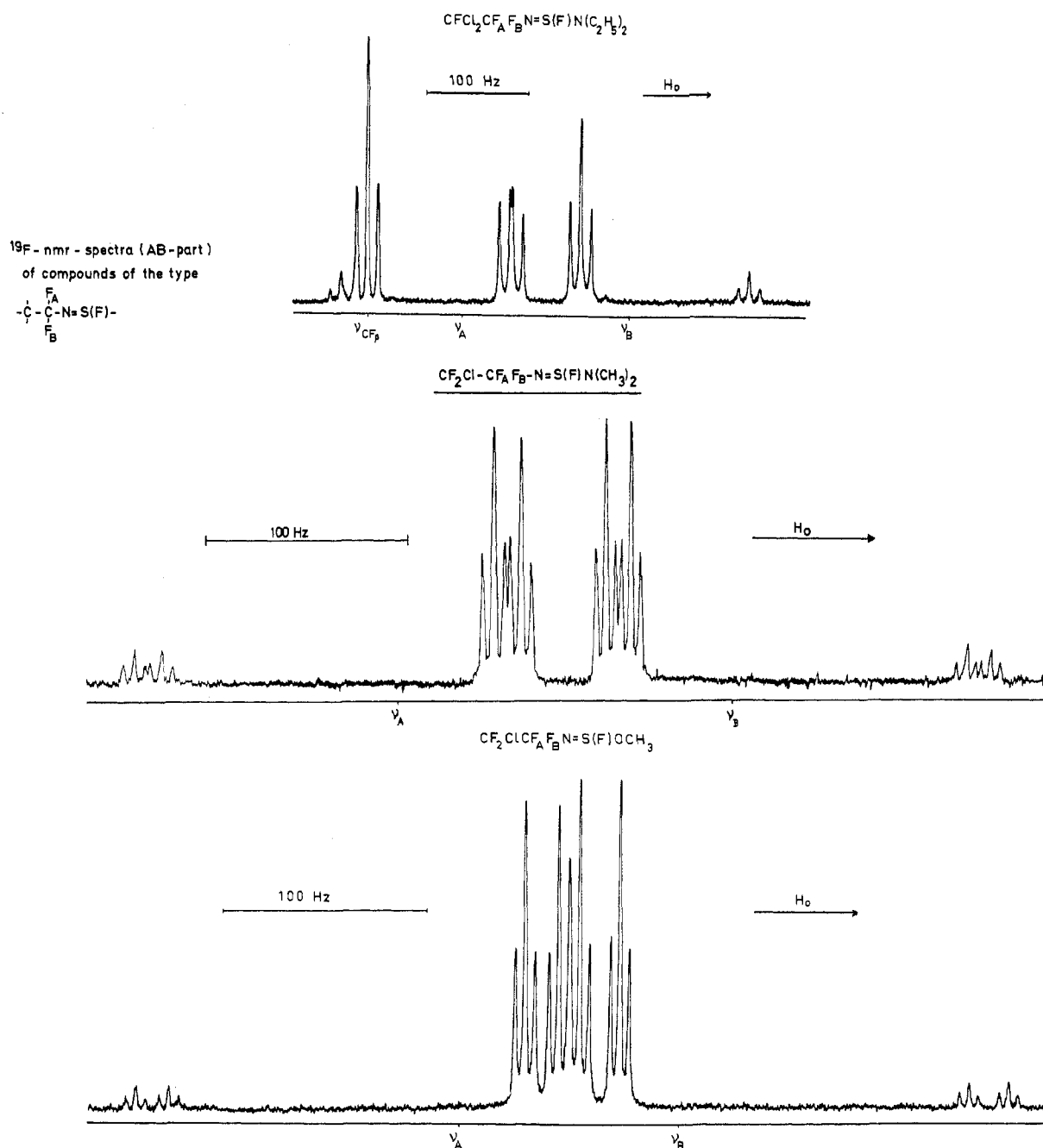
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TABLE I
ELEMENTAL ANALYSES

Compound	C, %		H, %		Cl, %		F, %		N, %		S, %		Mol wt	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
I	19.63	19.8	2.47	2.6	14.49	14.4	38.83	39.0	11.45	11.5	13.11	13.2	244.63	246/244 ^a
II	24.86	25.0	3.73	3.4	24.44	24.9	26.22	26.4	9.67	9.6	11.09	11.3	289.14	301 ^b
III	26.72	26.8	4.48	4.8	13.15	13.4	28.18	28.1	13.58	13.6	11.89	11.7	269.71	
IV	17.11	17.0	1.44	1.6	16.84	17.2	36.09	35.6	13.30	13.3	15.23	15.5	210.60	212/210 ^a
VI	19.72	19.8	2.48	2.6	14.55	14.4	31.20	31.3	5.75	5.7	13.16	13.2	243.62	
VII	9.50	9.6			42.13	41.2	30.10	29.6	5.55	5.6	12.70	12.8	252.47	251.5 ^b
VIII	18.40	18.5	2.32	2.4	27.16	27.0	29.11	28.8	10.73	10.8	12.28	12.4	261.09	

^a By mass spectrometer. ^b Cryoscopic in benzene.Figure 1.—¹⁹F nmr spectrum of some sulfur monofluoride imides, the α -CF₂ group in RCF₂N=S(F).

$J_{SF-CH} = 5.2$, $J_{SF-CH_2} = 5.2$, $J_{CF_A-CF_B} = 173.5$, $J_{CF_A-CF_2Cl} = 5.4$, $J_{CF_B-CF_2Cl} = 4.8$ cps. Ir spectrum: 2900 m, 1480 m, 1458 m, 1415 vw, 1333 vs (ν_{N-S}), 1275 w, 1230 vs, 1194 s, 1160 s, 1082 s, 1038 s, 960 s, 928 s, 900 m, 872 sh, 780 m, 708 m, 657 m, 646 m, 616 sh, 595 cm^{-1} s (ν_{S-F}). Mass spectrum (relative intensities in parentheses): 246/244 M⁺ (2/6), 227/225

(M - F)⁺ (4.5/12), 208/206 (M - 2F)⁺ (1/3), {162 CF₂CF₂NSO (12)?}, 159 CF₂NS(F)N(CH₃)₂⁺ (60), 114 CF₂CF₂N⁺ (13.5), {112 CF₂NSO⁺ (76)?}, 100 CF₂CF₂⁺ (9), 96 CF₂NS⁺ (12), 95 S(F)N(CH₃)₂⁺ (21.5), 94 S(F)N(CH₃)(CH₂)⁺ (12), 87/85 CF₂Cl⁺ (30/89), 76 SN(CH₃)₂⁺ (6), 69 CF₃⁺ (16), {67 SOF⁺ (12)}, 64 SO₂⁺, CF₂N⁺ (17), 61 SNCH₃⁺ (6), 60 NSN⁺/SNCH₂⁺ (6), 51 SF⁺ (4),

50 CF_2^+ (17), {48 SO^+ (31.5)}, 46 NS^+ (49.5), 44 $\text{N}(\text{CH}_3)_2^+$ (55), 43 $\text{N}(\text{CH}_3)(\text{CH}_2)^+$ (58), 42 $\text{N}(\text{CH}_2)(\text{CH}_2)^+$ (100), 32 S^+ (7), 31 CF^+ (21), 28 NCH_2^+ , N_2^+ (18).

Preparation of $\text{CFCl}_2\text{CF}_2\text{N}=\text{S}(\text{F})\text{N}(\text{C}_2\text{H}_5)_2$ (II).—The reaction was carried out as described for (I). At 0° 30.5 g (129 mmol) of $\text{CFCl}_2\text{CF}_2\text{NSF}_2$ and 18.5 g (128 mmol) of $(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$ gave 18 g of $\text{CFCl}_2\text{CF}_2\text{N}=\text{S}(\text{F})\text{N}(\text{C}_2\text{H}_5)_2$, bp (0.01 Torr) $53\text{--}55^\circ$ (yield 48%). Nmr spectrum: δ_{SF} -55.8 , δ_{CFA} $+75.44$, δ_{CFB} $+78.36$, δ_{CF_2} $+73.8$, δ_{CH_2} -3.63 , δ_{CH_3} -1.37 ppm; $J_{\text{SF-CFA}} = 12.8$, $J_{\text{SF-CFB}} = 10.3$, $J_{\text{SF-CH}_2} = 4.25$, $J_{\text{CFA-CFB}} = 165.5$, $J_{\text{CFA-CF}_2} = 10.6$, $J_{\text{CFB-CF}_2} = 10.3$, $J_{\text{CH}_2-\text{CH}_3} = 7.1$ cps. Ir spectrum: 3020, 2970 w, 1470 m, 1395 w, 1305 vs ($\nu_{\text{S-N}}$), 1234 w, 1190 sh, 1175 s, 1055 sh, 1017 s, 954 m, 887 s, 856 m, 792 w, 759 m, 680 m, 608 s/583 cm^{-1} s (ν_{SF}).

Preparation of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}[\text{N}(\text{CH}_3)_2]$ (III).—At 0° 18.2 g (155 mmol) of $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ was slowly added to 15.5 g (70.7 mmol) of $\text{CF}_2\text{ClCF}_2\text{NSF}_2$ in 100 ml of CCl_4 . The reaction mixture was stirred for an additional 15 hr at room temperature. The volatile products and solvent were removed at 0.001 Torr. Distillation of the residue gave 12.8 g of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}[\text{N}(\text{CH}_3)_2]$, bp (0.001 Torr) $36\text{--}39^\circ$ (yield 87%). Nmr spectrum: δ_{Cl_2} $+68.3$, $\delta_{\text{CF}_2\text{Cl}}$ $+70.3$, δ_{CH_3} -2.93 ppm; $J_{\text{CF}_2-\text{CF}_2\text{Cl}} = 7.4$ cps. Ir spectrum: 2825 m, 1580 vw, 1450 m, 1398 vw, 1332 vs ($\nu_{\text{S-N}}$), 1205 s, 1190 s, 1144 s, 1062 s, 963 s, 933 s, 910 s, 764 m, 666 m, 633 cm^{-1} m.

Preparation of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}=\text{NCH}_3$ (IV).—Under the same conditions as described for (III) 16.2 g (74 mmol) of $\text{CF}_2\text{ClCF}_2\text{NSF}_2$ and 13.3 g (76 mmol) of $[(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3$ gave 1.2 g of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}=\text{NCH}_3$, bp (59 Torr) 50° (yield 8%). Nmr spectrum: δ_{CF_2} $+84.1$, $\delta_{\text{CF}_2\text{Cl}}$ $+73.2$, δ_{CH_3} -3.56 ppm; $J_{\text{CF}_2-\text{CF}_2\text{Cl}} = 4.7$, $J_{\text{CF}_2-\text{CH}_3} = 2.2$ cps. Ir spectrum: 2900 w, 1440 w, 1298 s, 1218 vs, 1160 s, 1083 s, 1040 m, 1015 s, 927 s, 902 m, 832 m, 789 w, 757 m, 663 w, 643 w, 620 vw, 596 vw, 558 vw, 525 cm^{-1} vw. Mass spectrum: 212/210 $\text{CF}_2\text{ClCF}_2\text{NSNCH}_3^+$ (0.1/0.3), 183/181, $\text{CF}_2\text{ClCF}_2\text{NS}^+$ (0.2/0.6), 175 $\text{CF}_2\text{CF}_2\text{NSNCH}_3^+$ (6), 125 $\text{CF}_2\text{NSNCH}_3^+$ (100), 96 CF_2NS^+ (9), 87/85 CF_2Cl^+ (6/22), 76 CF_2CN^+ (22), 69 CF_3^+ (5), 66 (?) (7), 64 CF_2N^+ (SO_2^+) (26), 61 SN-CH_3^+ (36), 60 NSN^+ , SNCH_3^+ (69), 50 CF_2^+ (9), 48 SO^+ (22), 46 SN^+ (33), 32 S^+ (13), 31 CF^+ (7.5), 28 NCH_2^+ , N_2^+ (67).

Preparation of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{F})\text{OCH}_3$ (V) and $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{OCH}_3)_2$ (VI).—To a slurry of 9.4 g (174 mmol) of NaOCH_3 in 350 ml of ether was added 39 g (178 mmol) of $\text{CF}_2\text{ClCF}_2\text{NSF}_2$ in 300 ml of the same solvent. The mixture was stirred for 24 hr at room temperature. NaCl was filtered off under dry nitrogen, and ether removed at 100 Torr. Distillation of the residue at 12 Torr gave two fractions, (A) bp $31\text{--}33^\circ$ (1.3 g) and (B) bp $58\text{--}59^\circ$ (13.8 g). Fraction A consisted mainly of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{F})\text{OCH}_3$ (about 90%), contaminated by a CHNS -containing impurity. Nmr spectrum: (Figure 1) δ_{SF} -40.3 , δ_{CFA} $+80.88$, δ_{CFB} $+82.78$, δ_{CF_2} $+74.0$, δ_{CH_3} -3.97 ppm; $J_{\text{SF-CFA}} = 16.5$, $J_{\text{SF-CFB}} = 19.4$, $J_{\text{SF-CF}_2} = 2.4$, $J_{\text{SF-CH}_3} = 1.2$, $J_{\text{CFA-CFB}} = 191$, $J_{\text{CFA-CF}_2} = 4.8$, $J_{\text{CFB-CF}_2} = 4.6$ cps. Ir spectrum: 2960 w, 1455 w, 1355 s ($\nu_{\text{N-S}}$), 1263/1240 s, 1170 m, 1115 br, s, 971 s, 940 s, 905 m, 770 br, s, ~ 670 cm^{-1} s ($\nu_{\text{S-F}}$). Mass spectrum: 214/212 $\text{M} - \text{F}$ (5.9/17.0), 202/200 $\text{M} - \text{OCH}_3^+$ (1.8/5.3), 162 $\text{CF}_2\text{CF}_2\text{NSO}^+$ (1.5), 158 $\text{CF}_2\text{CF}_2\text{NSOCH}_3^+$ (2.9), 146 $\text{CF}_2\text{CF}_2\text{NS}^+$, $\text{CF}_2\text{NS}(\text{F})\text{OCH}_3^+$ (100), 137/135 $\text{CF}_2\text{ClCF}_2^+$ (2.8/8.8), 127 $\text{CF}_2\text{NSO-CH}_3^+$ (6.5), 115 CF_2NSF^+ (4.7), 112 CF_2NSO^+ (20.0), 100 CF_2CF_2^+ (5.9), 96 CF_2NS^+ , $\text{NS}(\text{F})\text{OCH}_3^+$ (5.3), 87/85 CF_2Cl^+ (10.3/34), 82 SFOCH_3^+ (11.7), 81 CF_2CF^+ (21.2), 69 CF_3^+ (12.3), 67 SOF^+ (47.3), 60 CSO^+ (?) (26.5), 51 SF^+ (5.3), 50 CF_2^+ (8.8), 48 SO^+ (15.3), 46 NS^+ (31.8), 32 S^+ (2.4), 31 OCH_3^+ , CF^+ (11.2), 30 HCHO^+ (3.8), 29 CHO^+ (25.6).

Peaks at m/e 110 and 79 were possibly due to the impurity mentioned above. Elemental analysis agreed only within 10% with the calculated values. *Anal.* Calcd for $\text{C}_2\text{H}_3\text{ClF}_2\text{NSO}$: C, 15.57; H, 1.31; F, 41.02; Cl, 15.31; N, 6.05; S, 13.80. Found: C, 16.6; H, 1.6; F, 38.1; Cl, 13.7; N, 6.2; S, 14.9.

Fraction B was $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{OCH}_3)_2$ (VI), a slightly yellow, stable liquid. Nmr spectrum: δ_{CF_2} $+76.2$, $\delta_{\text{CF}_2\text{Cl}}$ $+72.8$, δ_{CH_3} -1.26 ppm; $J_{\text{CF}_2-\text{CF}_2\text{Cl}} = 5.6$ cps. Ir spectrum: 2930 w, 1450 w, 1335 vs ($\nu_{\text{N-S}}$), 1225 vs, 1160 s, 1080 s, 1058 m, 1033 m, 975 sh, 958 sh, 927 s, 900 sh, 764 sh, 719 vs, br, 642 cm^{-1} w.

Preparation of $\text{CF}_2\text{ClCF}_2\text{NSCl}_2$ (VII).—At room temperature 35.0 g (159.5 mmol) of $\text{CF}_2\text{ClCF}_2\text{NSF}_2$ was slowly added to 14.5 g (69.7 mmol) of PCl_5 . The reaction was finished after warming to $30\text{--}40^\circ$ for a further 5 hr. Distillation gave 29 g of colorless $\text{CF}_2\text{ClCF}_2\text{NSCl}_2$, bp (12 Torr) $33\text{--}35^\circ$ (yield 68%). Nmr spectrum: δ_{CF_2} 96.3, $\delta_{\text{CF}_2\text{Cl}}$ 75.2 ppm; $J_{\text{CF}_2-\text{CF}_2\text{Cl}} = 4.95$ cps. Ir

spectrum: 1323 vs ($\nu_{\text{N-S}}$), 1258 vs, 1168 s, 1140 s, 1116 s, 1058 s, 938 s, 896 m, 877 m, 726 m, 648 m, 602 vw, 588 vw, 534 vw, 463 w, $\nu_{\text{S-Cl}}$ are below 440 cm^{-1} .

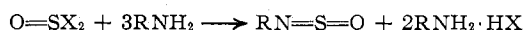
Preparation of $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{Cl})\text{N}(\text{CH}_3)_2$ (VIII).— $\text{CF}_2\text{ClCF}_2\text{NSCl}_2$, 25.5 g (101 mmol), and $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, 11.8 g (101 mmol), were stirred for 24 hr at room temperature. After removal of $(\text{CH}_3)_3\text{SiCl}$ and unreacted starting material at 0.5 mm, 21.1 g of pure $\text{CF}_2\text{ClCF}_2\text{N}=\text{S}(\text{Cl})\text{N}(\text{CH}_3)_2$ remained as residue (yield 80%). The faint yellow liquid is not distillable. Nmr spectrum: δ_{CF_2} 82.2, $\delta_{\text{CF}_2\text{Cl}}$ 72.2, δ_{CH_3} -3.11 ppm; $J_{\text{CF}_2\text{Cl}-\text{CF}_2} = 5.3$ cps. Ir spectrum: 2950 m, 2780 m, 1473/1460/1446 m, 1407 vw, 1320 vs ($\nu_{\text{N-S}}$), 1224 vs, 1184 vs, 1160 sh, 1093 vs, 1031 s, 956 s, 925 vs, 893 m, 872 sh, 768 m, 702 m, 656 w, 643 m, 440 cm^{-1} m.

Results and Discussion

The sulfur difluoride imides^{23,24} are related structurally to thionyl fluoride, $\text{O}=\text{SF}_2$,²⁵ which is similar electronically to them. The thermal stability of $\text{RN}=\text{SF}_2$ compounds depends very much upon the R radical. Perfluoroalkyl derivatives have a stability approaching that of OSF_2 , being stable up to 200° .

The similarity of $\text{R}_{\text{HAL}}\text{N}=\text{SF}_2$ and $\text{O}=\text{SF}_2$ indicated that similar synthetic routes might lead to compounds of the type $\text{X}=\text{SY}(\text{Z})$, where X is either O or $\text{R}_{\text{HAL}}\text{N}$. Variation of the substituents, Y and Z attached to the sulfur atom, was anticipated to produce similar changes in properties in each series.

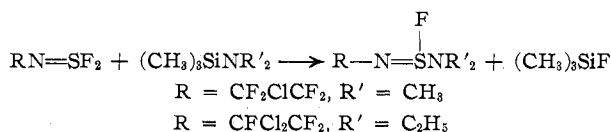
Thionyl halides interact with primary amines to give sulfonic amides²⁶



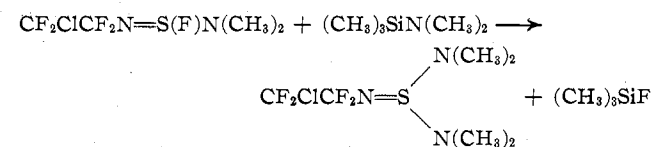
Similarly sulfur difluoride imides gave sulfur diimides, $\text{R}_{\text{HAL}}\text{N}=\text{S}=\text{NR}$.²⁷ Often better yields of the latter are obtained with N-bis-silylated primary amines



Thionyl fluoride is known to react with secondary amines²⁸ or their N-silylated derivatives^{18,29} to form fluorosulfonic amides $\text{FS}(\text{O})\text{NR}_2$. By analogy sulfur difluoride imides yield S-dialkylaminosulfur monofluoride imides.



With excess of amine, in the oxygen and the sulfur imide series, the second fluorine atom is exchanged



An alternative route to S-dialkylaminosulfur monofluoride imides is the reaction of dialkylaminosulfur trifluorides with $\text{RN}(\text{SiR}_3)_2$,³⁰ while fluorosulfonic amides are also formed in the hydrolysis of the trifluorides.³¹

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TABLE II
 $\nu_{S=O}$ AND $\nu_{S=N}$ FOR SOME THIONYL DERIVATIVES AND THEIR SULFUR(IV) *N*-PERHALOALKYL IMIDO ANALOGS

	$\nu_{S=O}$, cm^{-1}	$\nu_{S=N}$, cm^{-1}	$\nu_{S=O}$, cm^{-1}	$\nu_{S=N}$, cm^{-1}	$\nu_{S=O}$, cm^{-1}	$\nu_{S=N}$, cm^{-1}
$\text{X}=\text{O}$	1333 ^{a,b}	1250 ^b	1209 ^c	1230 ^f	1119 ^g	1230 ^d
$\text{X}=\text{CF}_2\text{CICF}_2\text{N}$	1391 ^{e,h}	1352	1337	1333	1332	1323

^a J. K. O'Loane and M. K. Wilson, *J. Chem. Phys.*, **23**, 1313 (1955). ^b F. Seel, J. Boudier, and W. Gombler, *Chem. Ber.*, **102**, 443 (1969). ^c A. Simon, H. Kriegsmann, and H. Dutz, *ibid.*, **89**, 2390 (1956). ^d D. E. Martz and R. T. Lagemann, *J. Chem. Phys.*, **22**, 1193 (1954). ^e R. Mews and O. Glemser, *Chem. Ber.*, **102**, 4188 (1969). ^f D. H. Brown, K. D. Crosbie, J. I. Darragh, D. S. Ross, and D. W. A. Sharp, *J. Chem. Soc. A*, 914 (1970). ^g R. Paetzold and E. Rönisch, *Spectrochim. Acta, Part A*, **26**, 569 (1970). ^h Gas phase.

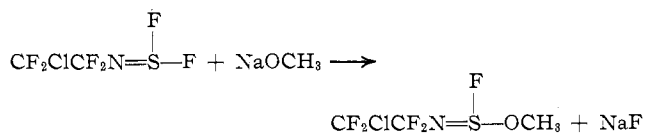
TABLE III
 ν_{SF} AND δ_{SF} FOR SOME FLUOROSULFINIC AND SULFUR(IV) MONOFLUORIDE IMIDE DERIVATIVES

R	ν_{SF} , cm^{-1}	δ_{SF} , ppm	ν_{SF} , cm^{-1}	δ_{SF} , ppm	ν_{SF} , cm^{-1}	δ_{SF} , ppm	ν_{SF} , cm^{-1}	δ_{SF} , ppm
CH_3	595	-34.1	600	-39.1	~680	-40.3	680	-54.7
C_2H_5	583	-55.8	603	-56.8			675	-58.6
<i>n</i> - C_3H_7			614	-57.7			675	-58.8
<i>i</i> - C_3H_7			605	-64.1			683	-62.4

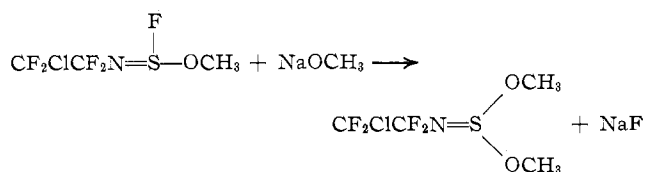
^a R. Mews and O. Glemser, unpublished results. ^b F. Seel, J. Boudier, and W. Gombler, *Chem. Ber.*, **102**, 443 (1969). ^c See ref 41.

Thus the double-bonded oxygen or nitrogen ligands can be introduced by analogous routes.

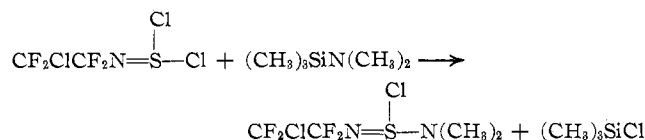
Fluorosulfinic esters $\text{O}=\text{S}(\text{F})\text{OR}$ are readily prepared by fluorine for chlorine exchange from chlorosulfinic esters³² or in the fluorination of sulfite esters by SF_4 or WF_6 .³³ The preparation of sulfur difluoride imides from the dichloride imides has been successful only for a few cases,³⁴ therefore we chose to derive alkoxy sulfur monofluoride imides directly from the fluoro derivatives.



But the second fluorine atom is also easily exchanged



While the chlorosulfinic amides³⁵ are reported to be distillable under reduced pressure, their imide analogs will decompose on heating above room temperature. They may, however, be obtained in high purity from the interaction



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since only the desired product is involatile at 20° and 0.5 Torr.

The last example shows, as anticipated from the comparison of $\text{O}=\text{SF}_2$ with $\text{RN}=\text{SF}_2$, that thionyl derivatives are thermally more stable than their imide analogs. It therefore appears unlikely for example that the imide counterparts of $\text{O}=\text{SClF}$ or even $\text{O}=\text{SBr}_2$ will be readily isolated. On the other hand the fair thermal stability of compounds $\text{O}=\text{S}(\text{R}_f)_2$,³⁶ $\text{R}_f\text{S}(\text{O})\text{NR}_2$,³⁷ or $\text{R}_f\text{S}(\text{O})\text{Cl}$ ³⁸ suggests that their nitrogen relatives may not be difficult to isolate.

It is possible, from a comparison of ir and nmr data of the oxide and imide series relatives, to roughly estimate the pertinent spectroscopic properties of unknown $\text{X}=\text{S}(\text{Y})\text{Z}$ compounds. The $\nu_{S=O}$ in thionyl derivatives is known to be affected not only by inductive and electromeric effects but also by steric factors associated with the substituents attached to the sulfur atom.^{39,40} Presumably steric factors are responsible for the absence of parallel behavior between the oxides and those sulfur(IV) imide analogs $\text{RN}=\text{S}(\text{Y})\text{Z}$ involving bulky R groups. Table II shows the $\nu_{S=N}$ to be less dependent on the Y and Z groups than the $\nu_{S=O}$. The first usually occurs as strong band in the region 1320-1350 cm^{-1} .⁴¹ In the parent difluorides $\text{O}=\text{SF}_2$ and $\text{R}_f\text{N}=\text{SF}_2$ there is a shift to somewhat higher wave numbers.

Table III shows both ν_{SF} and the ^{19}F chemical shift δ_{SF} vary in similar fashion in a series of related compounds. The SF stretching frequency in the OSF derivatives is slightly higher than in the NSF cases.

(36) (a) D. T. Sauer and J. M. Shreeve, *Chem. Commun.*, 1679 (1970); (b) E. W. Lawless, *Inorg. Chem.*, **9**, 2796 (1970).

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(39) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 191.

(40) Very good empirical formulas have been derived for the dependence of ν_{SO} on the sum of the electronegativities of the substituents X and Y in $\text{O}=\text{S}(\text{X})\text{Y}$ (R. Steudel, *Z. Naturforsch. B*, **26**, 750 (1971)).

(41) Recently for the 1,3-dioxolanes $[(\text{CF}_3)_2\text{CO}]_2\text{S}=\text{NF}_2$ (prepared by the reaction of R_fNSF_2 with $\text{Li}_2[(\text{CF}_3)_2\text{CO}]_2$) $\nu_{S=N}$ was found at 1380 cm^{-1} ($\text{R}_f = \text{CF}_3$) and 1405 cm^{-1} ($\text{R}_f = \text{C}_2\text{F}_5$): A. P. Conroy and R. D. Dresdner, *Inorg. Chem.*, **9**, 2739 (1970).

The nmr spectra show somewhat less shielding for the fluorine atom in the oxygen than in the nitrogen compounds.

The nmr spectra of the compounds $\text{RCF}_2\text{N}=\text{S}(\text{R})\text{F}$ [Figure 1] show AB structure for the CF_2 group. In RCXYNSF_2 derivatives the fluorine atoms in the NSF_2 group are magnetically nonequivalent.⁷⁻⁹ The observed temperature dependence of the nmr spectra may be accounted for in terms of a hindered rotation around the C-N axis. Conversely bulky substituents at the sulfur atom should also cause steric hindrance, and this should result in magnetic nonequivalence of the CF_2

fluorines. The same could be expected also for the compounds $\text{RCF}_2\text{N}=\text{S}\text{Cl}_2$, $\text{N}=\text{S}(\text{NR}_2)\text{Cl}$, and $\text{N}=\text{S}(\text{OR})_2$. Presumably coupling between the fluorine atoms attached to the C atom is not observed as a result of a high $J/\nu_0\delta_{\text{AB}}$ value.

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Characterization of the Trisulfur Radical Anion S_3^- in Blue Solutions of Alkali Polysulfides in Hexamethylphosphoramide

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Alkali polysulfides dissolve in hexamethylphosphoramide (HMPA) to give deep blue solutions. The blue species has been characterized as S_3^- by electrical transference, conductivity, and magnetic susceptibility measurements and by visible, ultraviolet, infrared, Raman, and electron spin resonance spectra.

Introduction

It has been known for a long time that a blue color develops when sulfur is heated with water and traces of some basic salt.^{1,2} Blue solutions are also formed by sulfur in alkali halide melts,^{3,4} in sulfur-doped borate glasses,⁵ by alkali polysulfides in basic solvents, e.g., dimethylformamide (DMF)^{6,7} and dimethyl sulfoxide (DMSO),⁸ or by electrochemical reduction of S_8 in DMSO.^{9,10} In all cases the blue species is characterized by a visible absorption band at ca. 620 nm. The identity of the blue species has been uncertain; Lux and coworkers claim the color is due to neutral molecules S_x ($x = 2-4$)^{6,8} while Giggenbach claims that it is due to the radical anion S_2^- .^{2,5,7} Giggenbach also suggests that the blue color of ultramarine can be attributed to S_2^- ,⁷ while other workers¹¹ propose that S_2^- and/or S_3^- is responsible for the color of the mineral. Merritt and Sawyer suggest that S_3^- is the species formed by electrochemical reduction of elemental sulfur in DMSO,⁹ but this has recently been disproved by Bonnaterre and Cauquis¹⁰ who show that the oxidation state of the sulfur in this system is $-1/3$; they propose S_3^{2-} . Gruen and coworkers⁴ agree that the blue species is sulfur ($-1/3$) but they attribute it to S_3^- .

The centers S_2^{-12} and S_3^{-13} have both been characterized by esr spectra of sulfur-doped alkali halide crystals and it has been shown by resonance Raman and infrared spectra¹⁴ that S_3^- is associated with a visible absorption band at 610 nm while S_2^- absorbs at 400 nm. ESR and Raman studies of ultramarine show that the blue color is due to S_3^- .¹⁴

During investigations of HMPA as a solvent for electrochemical reductions we observed that sulfur is sparingly soluble in HMPA to give a blue anionic species¹⁵ which showed the same characteristic structured absorption band at 620 nm as alkali polysulfides in DMF.⁷ Since the negatively charged species has been produced from elemental sulfur, the sulfur has either disproportionated or, more probably, been reduced by the solvent. Electrical transference experiments have shown that anionic species with characteristic visible absorption bands at 616 and 400 nm are formed when elemental sulfur dissolves in ethylenediamine.¹⁶ The 616-nm band was attributed to sulfur radical ions ($\cdot\text{S}-\text{S}_x-\text{S}^-$).¹⁶ To elucidate the controversial nature of the blue species we have studied its formation from polysulfides (i.e., sulfur in various mean oxidation states) in HMPA.

Experimental Section

Materials.—The air sensitive, blue solutions were always handled in a dry oxygen-free atmosphere (Vacuum Atmospheres drybox) and allowed to equilibrate for 24 hr before measurements were made. HMPA was obtained from Aldrich and vacuum

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