of nitrogen trifluoride and trifluoramine oxide and Dr. F. E. Brinckman for carrying out purification procedures on the latter material. We gratefully acknowledge helpful discussions with Dr. W. H. Evans on the reliability and usefulness of pertinent thermodynamic data.

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Preparation and Reactions of Fluorosulfonyliminosulfuroxy Difluoride. XVII[1]

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FSO_2NSOF_2 was prepared by the direct fluorination of FSO_2NSO. A study of the reactions of FSO_2NSOF_2 with ammonia and several amines has resulted in the preparation and characterization of previously unreported compounds of the general formula FSO_2NSOFX where $X = NH_2$, $NHCH_3$, $N(CH_3)_2$, and $N(C_2H_5)_2$. Hydrolysis of FSO_2NSOF_2 in the presence of R_4PCl or R_4AsCl where $R = C_6H_5$ led to salts containing the imidodisulfurylfluoride ion. The compounds have been isolated and identified by infrared, nmr, and elemental analyses.

Introduction

Recently the preparation of FSO_2NSOF_2[2] was reported as resulting from the reaction of FSO_2NH_2 and SOF_4 in the presence of NaF; however, the chemistry of this compound was not discussed.

This investigation reports the preparation of FSO_2NSOF_2 in nearly quantitative yield by the direct fluorination of FSO_2NSO.[3] Additional characterization of this compound was completed. Hydrolysis of FSO_2NSOF_2 with tetraphenylphosphonium chloride and tetraphenylarsonium chloride led to salts containing the imidodisulfuryl fluoride ion. The intermediate ion, $(FSO_2)_2N^{\ominus}$, which can also be obtained from $(FSO_2)_2NH$,[4,5] suggests a probable mechanism for this hydrolysis. Compounds of the general formula FSO_2NSOFX where $X = NH_2$, CH_3NH, $(CH_3)_2N$, and $(C_2H_5)_2N$ resulted from reaction with NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(C_2H_5)_2NH$.

Experimental Section

Reagents.—Fluorine, tetraphenylphosphonium chloride, tetraphenylarsonium chloride, and the amines were obtained from Kali Chemie, A.G., or Fluka, A.G. These reagents were used without further purification. FSO_2NSO was prepared by the reaction of $SOCl_2$ with FSO_2NH_2.[3]

General Methods.—All reactions of FSO_2NSOF_2 were carried out in Pyrex flasks under an atmosphere of nitrogen. Prior to use the nitrogen was dried over a column of P_4O_{10}. Because the compounds could be extremely toxic, all reactions were performed in a well-ventilated hood.

Infrared spectra (Table I) were recorded using a Leitz infrared spectrophotometer. The spectra of liquids were obtained in the liquid phase as capillary films with potassium bromide windows and in the solid phase as potassium bromide pellets.

Nuclear magnetic resonance spectra (Table II) were recorded using a Varian A-56/60 spectrometer. Tetramethylsilane and trichlorofluoromethane were used as external standards. Vapor pressure data for FSO_2NSOF_2 were measured in a conventional glass vacuum apparatus using a quartz spiral monometer.

Elemental analyses (Table III) were performed by Beller Microanalytical Laboratory, Goettingen, Germany. Boiling points of liquids and melting points of solids are given in Table III.

Preparation of Fluorosulfonyliminosulfuroxy Difluoride, FSO_2NSOF_2.—Fluorine at the rate of 20 cm^3/min was bubbled through 50 ml of FSO_2NSO in a quartz trap at room temperature. The material was simultaneously subjected to ultraviolet radiation from a lamp[6] placed 1–2 cm distant from the trap. Two additional quartz traps at $-80°$ were connected to the trap, the first to collect any products which were carried out of the irradiated trap by the flow of fluorine, and the second to exclude moisture from the air. After 72 hr, distillation of the material in the two traps over a column packed with glass helices of 30-cm length and 1-cm diameter gave a 92% yield of the product, bp 72°. The material was identified by ir and nmr spectra.[2] A boiling point of 71.5° was found by extrapolation of a plot of log P(mm) *vs.* $1/T$. The data are [T (°C), P (mm)]: -15, 7.5; -10, 11; -5, 15.5; 0, 20; 5, 30; 10, 40; 15, 52.5; 19.5, 65.5. The vapor pressure curve from these data was found to be of the form $\log P(\text{mm}) = (-2062/T) + 8.860$. The values for ΔH and ΔS were calculated to be 9.4 kcal/mol and 27.3 cal/mol deg.

Preparation of Fluorosulfonyliminosulfuroxyamino Fluoride, $FSO_2NSOFNH_2$.—The reaction was carried out in a three-neck 2-l. flask equipped with a Dry Ice condenser maintained at $-80°$, a stirring motor, and a nitrogen T adapter. To 33.3 g (0.181 mol) of FSO_2NSOF_2 dissolved in 1 l. of dry ethyl ether was added 11.6 g (0.683 mol) of ammonia over a period of 30 min through the Dry Ice condenser. The flask was maintained at about $-80°$. After the addition was complete, the flask was slowly warmed to room temperature. The solid was removed by filtration under dry nitrogen. The solvent of the resulting solution was removed by means of a water pump vacuum and the residue was distilled in oil pump vacuum. Other products formed which were seen by an nmr spectrum of the crude product mixture, could not be isolated; yield, 1.5 g (0.0084 mol).

Preparation of Fluorosulfonyliminosulfuroxymethylamino Fluoride, $FSO_2NSOFNHCH_3$.—To a mixture of 37 g (0.20 mol) of FSO_2NSOF_2 and 500 ml of dry ethyl ether, 12.5 g (0.40 mol) of CH_3NH_2 was added using a dropping flunnel. The addition was carried out over a period of 1 hr. The flask was maintained at

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[1] Paper XVI: H. W. Roesky, *Inorg. Nucl. Chem. Letters*, **5**, 173 (1969).

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[6] Philips, 500 W, Type 57300 ZB.

Table I

Infrared Spectra (cm^{-1})

$FSO_2NSOFNH_2$	$FSO_2NSOFNHCH_3$	$FSO_2NSOFN(CH_3)_2$
$\sim$3310 s	$\sim$3300 s	$\sim$2980 w
$\sim$3100 m	$\sim$2980 m	1460 s
$\sim$2990 m	$\sim$2800 m	1410 vs
1540 s	1415 vs, w, sh	1350 vs
1408 vs	1342 vs	1285 s
1360 vs	1210 vs	1210 vs
1225 vs	1168 vs	1150 vs
1170 vs	1088 vs	1055 s
1005 s	995 w	995 vs
848 vs	895 s	835 vs
795 vs	840 vs	775 vs
733 s	785 vs	697 vs
615 m	733 s	606 s
560 m	617 m	552 vs
535 m	572 vs	498 w
	542 s	478 m
	515 w	458 w
	472 w	

$FSO_2NSOFN(C_2H_5)_2$	$(C_6H_5)_4PN(SO_2F)_2$	$(C_6H_5)_4AsN(SO_2F)_2$
$\sim$3000 m	1590 w	1488 w
$\sim$2950 w	1490 m	1440 s
$\sim$2900 w	1440 s	1385 vs
1470 s	1385 vs	1370 s
1410 vs	1370 s	1340 w
1338 vs	1340 m	1318 w
1300 w	1320 w	1292 w
1210 vs	1290 w	1220 m
1148 vs	1220 s	1181 vs
1090 s	1182 vs	1163 m
1064 s	1163 s	1108 s
1020 vs	1110 vs	1080 m
970 m	1025 w	1020 w
935 w	995 m	996 m
834 vs	825 s	850 w
787 vs	752 s	825 s
687 vs	722 vs	742 vs
605 vs	687 vs	687 vs
552 vs	572 vs	572 vs
480 m	528 vs	476 s
460 w		460 s

Table II

The ^1H and ^{19}F Nmr Spectra

Compound	Chem shift, ppm SO₂F	SOF	NH	CH	Area ratio for fluorine	J_{F-F}, cps	J_{F-H}, cps
$FSO_2NSOFNH_2$	−57.8	−68.2	−6.9	. . .	1.0:1.0	8.5	4.8
$FSO_2NSOFNHCH_3$	−58.0	−57.0	−6.43	−3.18	1.0:1.0	8.5	3.0[a]
$FSO_2NSOFN(CH_3)_2$	−58.6	−50.4	. . .	−3.25	1.0:1.0	8.2	3.4
$FSO_2NSOFN(C_2H_5)_2$	−58.7	−62.0	. . .	−1.39[b]	1.0:1.0	8.0	2.8[c]

[a] J_{CH_3-F}. [b] δ_{CH_2} −3.67. [c] J_{CH_2-F}. $J_{H-H} = 7.3$.

Table III

Elemental Analyses

Compound	% C Calcd	% C Found	% F Calcd	% F Found	% N Calcd	% N Found	% H Calcd	% H Found	% S Calcd	% S Found	Bp, °C (mm) [mp]
$FSO_2NSOFNH_2$	. . .	. . .	21.09	20.8	15.56	15.4	1.12	1.3	35.59	35.3	82 (0.01)
$FSO_2NSOFNHCH_3$	6.19	6.5	19.57	20.0	14.42	14.4	2.07	2.0	33.03	32.0	90–94 (0.01)
$FSO_2NSOFN(CH_3)_2$	11.54	12.0	18.25	18.0	13.45	13.3	2.91	3.1	30.80	30.3	59–60 (0.01)
$FSO_2NSOFN(C_2H_5)_2$	20.34	20.8	16.08	15.8	11.85	11.4	4.27	4.4	27.14	27.4	70–72 (0.01)
$(C_6H_5)_4PN(SO_2F)_2$	55.49	55.4	7.31		2.70		3.88	4.0	12.34	12.1	[189]
$(C_6H_5)_4AsN(SO_2F)_2$	51.16	51.3	6.74		2.48		3.58	3.6	11.38	11.1	[171]

−60°. The mixture was then allowed to warm to room temperature. Separation and purification of the product was accomplished in the same manner as described above; yield, 8 g (0.041 mol).

Preparation of Fluorosulfonyliminosulfuroxydimethylamino Fluoride, $FSO_2NSOFN(CH_3)_2$.—A 51-g (0.28-mol) sample of FSO_2NSOF_2 and 400 ml of dry ethyl ether were placed in a flask cooled to −60°. In an analogous method to that described above, 25 g (0.51 mol) of $(CH_3)_2NH$ was added, the solvent was removed under vacuum, and the product was purified by distillation; yield, 48 g (0.23 mol).

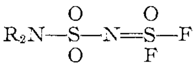
Preparation of Fluorosulfonyliminosulfuroxydiethylamino Fluoride, $FSO_2NSOFN(C_2H_5)_2$.—A sample of 37 g (0.20 mol) of FSO_2NSOF_2 dissolved in 400 ml of dry ethyl ether was treated with 29.2 g (0.40 mol) of $(C_2H_5)_2NH$. The same conditions and purification methods as described in the previous two reactions were used; yield, 34 g (0.14 mol).

Preparation of Tetraphenylphosphoniumimidodisulfuryl Fluoride, $(C_6H_5)_4PN(SO_2F)_2$.—A solution containing 0.01 mol of FSO_2NSOF_2 in 50 ml of water was placed in a beaker. A small molar excess of a 5% solution of $(C_6H_5)_4PCl$ was added slowly under stirring at room temperature. A white solid, recovered by filtration, was immediately formed. The solid was recrystallized from ethyl alcohol and dried under vacuum; yield, 4 g (0.008 mol).

Preparation of $(C_6H_5)_4AsN(SO_2F)_2$.—A 0.01-mol sample of a 5% solution of $(C_6H_5)_4AsCl$ was added to an aqueous solution of FSO_2NSOF_2 in the same manner as described in the previous reaction. Filtration and recrystallization gave 2 g (0.0035 mol) of the product.

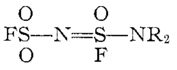
Results and Discussion

The reaction of N-sulfinylfluorosulfonylimide, $FSO_2\text{-}N{=}S{=}O$, with fluorine under uv irradiation gave fluorosulfonyliminosulfuroxydifluoride, FSO_2NSF_2. The oxidation from sulfur(IV) to sulfur(VI) by elemental fluorine is nearly quantitative. Selective substitution of one fluorine atom by another group takes place with ease in ether below 0°. The reaction of amines with FSO_2NSOF_2 produced only one of the two possible isomers which could be either



$R_2N\text{—}\overset{O}{\underset{O}{S}}\text{—}N{=}\overset{O}{\underset{F}{S}}\text{—}F$

I



$F\overset{O}{\underset{O}{S}}\text{—}N{=}\overset{O}{\underset{F}{S}}\text{—}NR_2$

II

An unambiguous structural assignment could be made by ^{19}F and ^1H nmr investigations. The ^{19}F nuclear magnetic resonance measurements (Figure 1) of $FSO_2NSOFN(CH_3)_2$ showed a doublet and two septuplets with chemical shifts at −58.6 and −50.4 ppm. The doublet is assigned to the fluorine in the FSO_2 group and the septuplet to the sulfur oxide group. The rela-

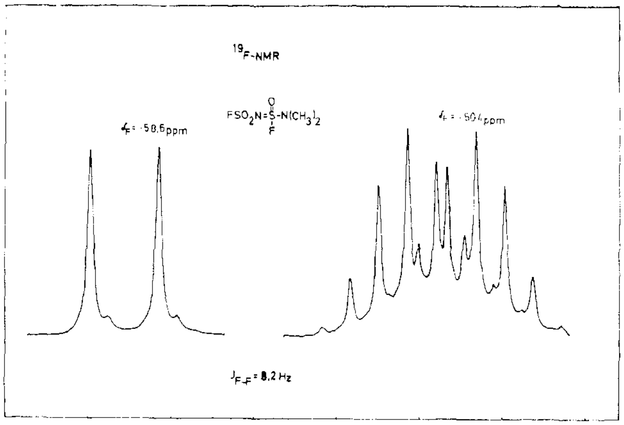
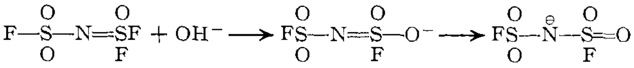


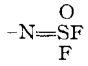
Figure 1.

tive intensities were 1:1, as would be expected for isomer II. The reaction of ammonia with FSO_2NSOF_2 produced several compounds as indicated by an ^{19}F nmr spectrum of the crude product mixture. Fractional distillation yielded only isomer II in a pure form, but in a small amount. A complete characterization of the other isomers was not attempted. The FSO_2 resonance in all of the compounds is essentially nonvarying. The FS shift is similar to other fluorosulfonyl compounds, *e.g.*, FSO_2NCO[7] (-61.0 ppm) and FSO_2NSO[3] (-59.2 ppm). Interaction occurs between the fluorosulfonyl group and the fluorine atom bonded to the sulfur oxide group. It can be seen that substitution of a proton for an alkyl group on the nitrogen causes a shift (ppm) to higher field (NH_2, -68.2; $N(C_2H_5)_2$, -62.0; $NHCH_3$, -57.0; $N(CH_3)_2$, -50.4). Hydrolysis of FSO_2NSOF_2 is rapid in the presence of excess water yielding the known ion $^{\ominus}N(SO_2F)_2$,[4] which could be trapped with bulky organic cations. The initial attack is also on a fluorine atom at the sulfur oxide group



$$F{-}\overset{O}{\underset{O}{S}}{-}N{=}\overset{O}{\underset{F}{S}}F + OH^- \longrightarrow F\overset{O}{\underset{O}{S}}{-}N{=}\overset{O}{\underset{F}{S}}{-}O^- \longrightarrow F\overset{O}{\underset{O}{S}}{-}\overset{\ominus}{N}{-}\overset{O}{\underset{F}{S}}{=}O$$

with rearrangement to structure II which was identified by comparison with a sample prepared by the literature method.[4] Hydrolysis of



$$-N{=}\overset{O}{\underset{F}{S}}F$$

compounds, through this mechanism, should provide a general method for the preparation of fluorosulfonyl derivatives. The substituted sulfur oxide products have hydrolytic stability comparable to other compounds containing the FSO_2 group, *e.g.*, $(CF_3)_2NOSO_2F$.[8]

The infrared spectra of these compounds have many bands; however, some assignments can be made. As is to be expected the N—H stretching and NH_2 deformation frequencies for $FSO_2NSOFNH_2$ are essentially nonvariant and appear at about 3300 and 1540 cm^{-1}, respectively. This agrees well with FSO_2NH_2.[7] The bands in the 1409–1415-cm^{-1} region for all of the compounds are assigned to asymmetric SO_2 stretches. The S=N stretching assignments in the molecules are complicated by the presence of S=O stretches and SO_2 symmetric stretches. The compounds show bands in the S—F stretching region but exact assignments are difficult.

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