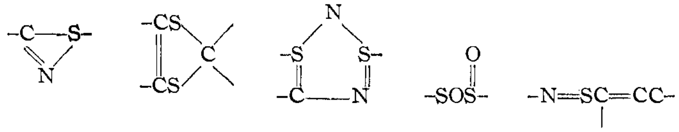
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

Some New Fluorocarbon–Sulfur Systems

BY J. S. JOHAR[1] AND R. D. DRESDNER

Received August 28, 1967

New fluorocarbon derivatives containing the groups

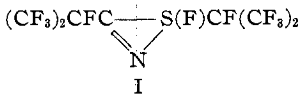


were prepared and isolated in various CsF-catalyzed reactions between fluorocarbon olefins and the iminosulfur difluorides, SF_4, and SOF_2. The formation of a new imine, $CF_3N{=}C(CF_3)C_2F_5$, is also reported. Chemical and spectral analyses were used to assign the above structures.

A large number of papers reporting on fluoride ion catalyzed reactions have appeared in the chemical literature attesting to the value of this contribution to fluorine chemistry. A considerable bibliography on the subject can be found in a review article[2] and several papers.[3] No less than three papers on the same subject were presented at the fourth International Symposium on Fluorine Chemistry held in Estes Park, Colo., July 1967.

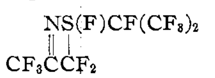
The purpose of this study was to extend the work on fluoride ion catalyzed heterogeneous reactions involving fluorocarbon olefins and various sulfur fluorides, including homologs of the fluorocarbon iminosulfur difluorides. The conditions and results of the various reactions over solid powdered CsF are summarized in Table I.

One reaction between $CF_3N{=}SF_2$ and $CF_3CF{=}CF_3$ described previously[3c] was repeated in order to isolate and identify a second product [besides $CF_3N{=}S(F)CF(CF_3)_2$]. It had the molecular formula $C_7F_{15}NS$ and the probable structure

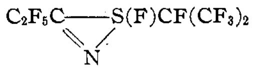


I

This assigned structure suggested a reevaluation of a compound isolated[3c] in the reaction between $C_3F_7N{=}SF_2$ and $CF_3CF{=}CF_2$ which had the molecular formula $C_6F_{13}NS$ and was assigned the probable structure



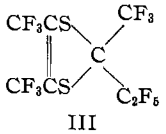
It is reasonable to presume that a more probable structural assignment is



which obviates a necessity for proposing C–N bond rupture. The presence of C_3F_8 in the product mixture suggests that both of the proposed three-membered ring heterocyclics are generated *via* F^- elimination from α-carbon atoms after F^- addition to the sulfur atoms in an intermediate species. The loss of "excess" fluorine from the sulfur occurs as C_3F_6 is oxidized to C_3F_8.

The interactions between fluorocarbon olefins and the various iminosulfur difluorides indicate some interesting steric effects. For example, although $CF_3N{=}SF_2$ reacts readily with $CF_3CF{=}CF_2$ at 100° or less,[3c] it fails to react appreciably with a mixture of *cis*- and *trans*-perfluorobutene-2 below 280°. Above 280°, the product formed is $CF_3N{=}C(CF_3)C_2F_5$ (II). The thermal stability limit for $CF_3N{=}SF_2$ under the condition at which the reaction was conducted is 300°.

When perfluorobutene-2 and $C_2F_5N{=}SF_2$ were heated together over solid CsF, no reaction was observed to occur below 280°. At 295° a reaction was observed. This was above the temperature at which $C_2F_5N{=}SF_2$ is stable. The main product isolated other than CF_3CN, a decomposition fragment of the iminosulfur difluoride, was the same as that isolated when SF_4 was allowed to react with perfluorobutene-2 or perfluorobutyne-2, namely



III

It will be noted (Table I) that the butyne undergoes reaction at a much lower temperature than butene. The only other identified product from these reactions was C_4F_{10}, indicating that the unsaturated fluorocarbons were acting as reducing agents. The reactions involving SF_4 are strikingly different from those observed in a previous study by Rosenberg and Muetterties[3b] in which $(CF_3)_2CFSF_3$ and $[(CF_3)_2CF]_2SF_2$ were formed when SF_4 and $CF_3CF{=}CF_2$ were allowed

---

(1) The material for this paper was abstracted from the Ph.D. dissertation of J. S. Johar and was presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, 50 (1965).

(3) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **1**, 287 (1964); (b) R. M. Rosenberg and E. L. Muetterties, *ibid.*, **3**, 756 (1962); (c) R. D. Dresdner, J. S. Johar, J. Merritt, and C. S. Patterson, *ibid.*, **4**, 678 (1965); (d) R. D. Dresdner, F. N. Teumac, and J. A. Young, *J. Org. Chem.*, **10**, 3524 (1965).

TABLE I

SUMMARY OF REACTIONS

Reactants				Max temp, °C	Time, hr	Products	Mole
Olefins	Mole	Sulfur compounds	Mole				
$CF_3CF{=}CF_2$	0.27	$CF_3N{=}SF_2$	0.64	83	115	$CF_3N{=}S(F)CF(CF_3)_2$ + I	0.15 + 0.007
$CF_3CF{=}CFCF_3$	0.17	$CF_3N{=}SF_2$	0.17	282	96	II	0.080
$CF_3CF{=}CFCF_3$	0.30	$C_2F_5N{=}SF_2$	0.17	293	97	III	0.075
$CF_3CF{=}CFCF_3$	0.29	SF_4 (technical)	*Ca.* 0.37	265	12	III + IV	0.065 (total)
$CF_3CF{=}CFCF_3$	0.23	SOF_2	0.54	202	120	IV	0.054
$CF_3C{\equiv}CCF_3$	0.07	$SOF_2 + SF_4$	0.064 + 0.051	80	24	III + IV	0.011 + 0.012
$CF_3C{\equiv}CCF_3$	0.10	$CF_3N{=}SF_2$	0.13	70	10	V + VIII	0.032 + trace
$CF_3C{\equiv}CCF_3$	0.11	$C_2F_5N{=}SF_2$	0.14	124	54	VI	0.093
$CF_3C{\equiv}CCF_3$	0.20	$C_3F_7N{=}SF_2$	0.13	150	72	VII	0.11

TABLE II

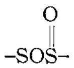
INFRARED SPECTRA

$C_7F_{15}NS$ (I)	$C_5F_{11}N$ (II)	$C_8F_{14}S_2$ (III)	$C_8F_{18}S_2O_2$ (IV)	$C_{10}F_{22}N_2S_2$ (V)	$C_6F_{13}NS$ (VI)	$C_7F_{15}NS$ (VII)	$C_5F_{11}NS$ (VIII)
1780 s (C═N) 1320–1240 vs (C—F) 1188 s 1165 s 1108 s 1020 w 1002 vs 900 w 810 m 753 m (S—F) 730 ms	1725 m (C═N) 1360 sh 1330 sh 1295 s 1225–1195 vs (C—F) 1105 m 1075 w 930 m 900 ms 865 m 740 m	1625 s (C═C) 1340 s 1300–1175 vs (C—F) 1065 s 925 s 865 s 835 ms 755 ms 750 vs 730 vs 725 vs 705 s 700 ms	1351 1333 vs (S═O)[a] 1300–1175 vs (C—F) 1145 vs 1095 vs 1058 ms 953 vs 932 vs 907 vs 875 vs 845 vs 763 vs 755 vs 733 vs (S—O—S)[b] 721 vs	1350 sh (N═S) 1334 s (C═S?) 1300–1160 (C—F) 1095 s 1083 s 1053 m 1042 sh 957 s 942 s 905 m 874 s 760 s 755 s 742 m 733 s 723 s	1724 vs (C═C) 1342 sh (N═S) 1282–1162 vs (C—F) 1105 vs[d] 1052 m[d] 950 s 924 m 883 s 863 s 760 s (S—F)[c,d] 743 s 724 s 718 s 700 s	1715 s (C═C) 1340 ms (N═S) 1280–1180 vs (C—F) 1132 s 1095 s 1008 s 954 s 918 s 880 ms 859 w 833 w 822 w 760 ms (S—F)[c,d] 746 s 733 s 721 s 694 w	1745 s (C═C) 1345 ms (N═S) 1335 ms, sh 1300–1180 s (C—F) 1090 m 1075 m 1015 s 942 m 909 w 875 ms 844 w 760 m (S—F)[c,d] 738 m 727 m

[a] S═O in SOF_2, 1331, 1341 cm^{-1}. [b] S—O—S in this region for $S_2O_5F_2$.[11] [c] S—F in $R_fN{=}S(F)CF(CF_3)_2$ at 757 cm^{-1}.[3c] [d] Midpoint of a sharp doublet.

to react over CsF at 150°. However, the literature[3b,4,5] presents evidence for the reduction of sulfur(IV) to sulfur(II). The fact that SF_4 reacts with CsF to form the salt $CsSF_5$[6] and does not desorb readily below 150° accounts for the minimum reaction temperature of 150° in reactions in which SF_4 is the electrophile.

The CsF-catalyzed reactions of SOF_2 with perfluorobutene-2 or with perfluorobutyne-2 gave rise to the same product $CF_3CF_2CF(CF_3)SOS(O)CF(CF_3)CF_2CF_3$ (IV), the former at 200°, the latter at about 80°. Any symmetrical structure involving the S_2O_2 grouping could be ruled out on the basis of the nmr results. Of the possible unsymmetrical structures only one



$$-SO\overset{\overset{O}{\|}}{S}-$$

was assignable on the basis of the ir evidence (see Table II). Although the O═S═O group in many molecules has characteristic absorptions near 1500 and 1250 cm^{-1}, as in SO_2F_2,[7] $C_5F_8(SO_3F)_2$,[8] or *sec*-$C_4F_9SO_3F$,[9] SOF_2 has a set of frequencies at 1331 and 1341 cm^{-1} and SOF_4 has a single absorption at 1383 cm^{-1} which has been assigned to one S═O unit on a sulfur atom.[10] A characteristic absorption for the SOS grouping in $S_2O_5F_2$ is reported[11] at 735 cm^{-1}. Oxygen singly bonded to sulfur in fluoroformylsulfuryl fluoride, $FC(O)OSO_2F$, is reported[12] at 757 cm^{-1}. Compound IV has a strong doublet absorption at 1351 and 1333 cm^{-1} as well as bands in the 750-cm^{-1} region suggesting along with the nmr evidence –SOS(═O)– rather than –SS(═O)$_2$– or –SOSO– bonding in IV.

In reactions involving SOF_2 and perfluorobutene-2 to form IV, a by-product which was extremely unstable was observed. As no C_4F_{10} was observed as the so-called oxidized product to account for the "excess"

---

(4) F. Loth and A. Michelis, *Ber.*, **27**, 2540 (1894).

(5) W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 551 (1960).

(6) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *ibid.*, **86**, 359 (1964).

(7) J. H. Simons, Ed., "Fluorine Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1950.

(8) J. M. Shreeve and G. H. Cady, *J. Amer. Chem. Soc.*, **81**, 4521 (1961).

(9) J. D. Delfino and J. M. Shreeve, *Inorg. Chem.*, **5**, 308 (1966).

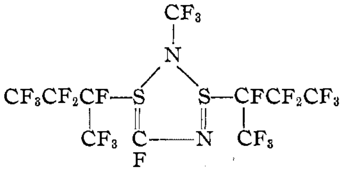
(10) F. B. Dudley, G. H. Cady, and D. F. Eggers, *J. Amer. Chem. Soc.*, **78**, 1553 (1956).

(11) H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 190 (1958).

(12) W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).

fluorine, SOF_2 may have been the reducing agent in this case.

The reactions between perfluorobutyne-2 and $C_2F_5N{=}SF_2$ and $C_3F_7N{=}SF_2$ over CsF were quite uncomplicated, resulting in the products $C_2F_5N{=}S(F)C(CF_3){=}CFCF_3$ (VI) and $C_3F_7N{=}S(F)C(CF_3){=}CFCF_3$ (VII). However, in the reaction involving $CF_3N{=}SF_2$, the main product had a molecular formula $C_{10}F_{22}S_2N_2$ and a probable structure



V

based on the available data. Here again the labile nature of the fluorine atoms on carbon adjacent to the N=S unsaturation has been dramatically demonstrated. Attempts to prepare the monomer $CF_3N{=}S(F)C(CF_3){=}CFCF_3$ (VIII) were not altogether unsuccessful. A very small amount was isolated from the products of a reaction run at 55° over a 4-hr period. However, only enough pure material was isolated to obtain a fairly well-resolved ir spectrum. Apparently, the rate of dimer formation was much more rapid than that of monomer formation.

Experimental Section

Materials.—Sulfur tetrafluoride was obtained from E. I. du Pont de Nemours and Co. or the Matheson Co., Inc. It was a technical grade containing variable amounts of SOF_2. By low-temperature fractionation of an SOF_2-enriched sample of SF_4, a quantity of SOF_2 containing only 3 mole % of impurity was obtained. Cesium fluoride was purchased from American Potash and Chemical Corp. Perfluorobutene was a 1:3 *cis–trans* mixture obtained from Matheson. Perfluorobutyne-2 was made from 2,3-dichlorohexafluorobutene-2 purchased from the Hooker Chemical Co. several years ago. The homologous fluorocarbon iminosulfur difluorides were prepared essentially by the method of Smith, *et al.*[5]

Apparatus.—Infrared spectra were obtained with a Perkin-Elmer Model 137B Infracord spectrometer. The F^{19} nmr spectra were obtained with a Varian DP-60 spectrometer at 56.4 Mc. Trifluoroacetic acid was used as the external reference. However, all chemical shifts reported have been converted to Φ values by adjusting the δ values. All nmr spectral assignments were made on the basis of relative peak areas, spin-spin interactions, the relative magnitude of coupling constants, and comparison with known Φ values in other related compounds. Some molecular weights were obtained by using a Bendix Model 14-107 time-of-flight spectrometer. This was possible when the parent ion was stable as it was in most cases. Some molecular weights obtained in this manner were compared with those obtained from vapor densities. Vpc analyses and separations were performed with a noncommercial unit using several columns packed with silicone or silicone gum on Chromosorb P.

General reaction procedure is described in a previous paper.[3c]

Thermal Stability of Reactants.—Each of the several reactants used in this study was checked for thermal and chemical stability over the catalyst under conditions similar to those generated during the various reactions. $CF_3N{=}SF_2$ was stable up to 300° for 80 hr at 24 atm. However, vacuum conditions at 200° were needed to desorb the last traces of material from the solid catalyst. $C_2F_5N{=}SF_2$ remained stable up to 285° at 24 atm. However, at 300° and 24.4 atm slow decomposition to SF_4 and CF_3CN was observed, *some of the* SF_4 *forming* $CsSF_5$ *with the catalyst.* $C_3F_7N{=}SF_2$ began to decompose at 250° although it was stable at 200° for several days at 10 atm. The decomposition products were SF_4 and C_2F_5CN. Both $CF_3CF{=}CFCF_3$ and $CF_3C{\equiv}CCF_3$ were stable over CsF to at least 300°.

All of the reactions studied under catalytic conditions were also attempted in the absence of a catalyst. In each instance no significant amount of reaction was observed.

Reaction of $CF_3N{=}SF_2$ and $CF_3CF{=}CF_2$ over CsF.—In a reaction similar to that reported,[3c] 41 g of $CF_3N{=}SF_2$ and 96 g of $CF_3CF{=}CF_2$ were condensed into the 500-ml reactor containing 100 g of dried, powdered CsF. The system was heated slowly to 83° and maintained there for 115 hr when heating was discontinued. The volatile products were transferred to a vacuum system. They amounted to 136 g, of which 53 g was $CF_3CF{=}CF_2$ and 45 g the previously reported $CF_3N{=}S(F)CF(CF_3)_2$. A minor product which boiled at 75.5° was isolated by vpc and amounted to 3.0 g. Its ir spectrum showed a strong absorption at 1780 cm^{-1} associated with the C=N stretch and another medium one at 753 cm^{-1} associated with S—F. This compound had a molecular weight of 415 (mass spectrometry), the same as that for an isomer of $C_7F_{15}NS$.

Anal. Calcd for $C_7F_{15}NS$: C, 20.24; N, 3.37. Found: C, 20.39; N, 3.34.

The nmr spectrum is [Φ (area)]: $(\mathit{CF_3})_2\mathrm{CFC}$ [80.3 (6.0)], $(\mathit{CF_3})_2\mathrm{CFS}$ [76.0 (6.1)], $(\mathrm{CF_3})_2\mathit{CF}\mathrm{C}$ [178.5 (1.1)], $(\mathrm{CF_3})_2\mathit{CF}\mathrm{S}$ [149.4 (1.2)], and $\mathrm{S}\mathit{F}$ [6.0 (0.9)]. The yield of compound I did not exceed 4%.

Reaction of $CF_3N{=}SF_2$ with $CF_3CF{=}CFCF_3$ over CsF.—$CF_3N{=}SF_2$ (26 g) and $CF_3CF{=}CFCF_3$ (34 g) were heated in the reactor over CsF at 225° for 12 hr. No reaction was observed based on an ir spectrum of a portion of the reactor contents. Some reaction occurred at 235°. Reaction was relatively rapid at 280°. This temperature was maintained for 96 hr. Only 50 g of volatile mixture could be removed from the reactor at 25°. These were 6.9 g of $CF_3N{=}SF_2$, 17.0 g of $CF_3CF{=}CFCF_3$, 23.0 g of II, and 3.0 g of unidentified material. On heating the reactor to 400° under vacuum some 6–8 g of a very reactive, volatile substance was obtained. It decomposed slowly to elemental sulfur and other residues. The new product which was chromatographically pure boiled at 36.6° and had molecular weights of 279 (vapor density) and 283 (mass spectrometry). This is consistent with a formula $C_5F_{11}N$.

Anal. Calcd for $C_5F_{11}N$: F, 73.85; C, 21.20; N, 4.95. Found: F, 74.00; C, 20.84; N, 5.00.

The nmr spectrum is [Φ (area)]: $\mathit{CF_3}\mathrm{N}$ [59.6 (2.9)], $\mathit{CF_3}\mathrm{C{=}N}$ [65.7 (3.1)], $\mathit{CF_3}\mathrm{CF_2}$ [82.3 (3.0)], and $\mathrm{CF_3}\mathit{CF_2}$ [116.7 (2.0)]. The yield of II was 60% based on the $CF_3N{=}SF_2$ used.

Reaction of $C_2F_5N{=}SF_2$ and $CF_3CF{=}CFCF_3$ over CsF.—$C_2F_5N{=}SF_2$ (35 g) and $CF_3CF{=}CFCF_3$ (61 g) were heated in the reactor over CsF to 282° in a 25-hr period to a maximum pressure of 24.2 atm. At 293° the pressure rose to 29.1 atm but fell to 24.5 atm after 72 hr. Heating was stopped and the products were removed and analyzed. They were 28 g of $CF_3CF{=}CFCF_3$, 13 g of CF_3CN, 10 g of C_4F_{10}, 32 g of a new product, and 3 g of residues. No $C_2F_5N{=}SF_2$ was recovered. The 10 g of material not removed with the volatile materials was pumped from the reactor at 400°. The new product (III) boiled at 135°, had a refractive index of 1.3354 at 20°, and had a molecular weight of 426 (mass spectrometry). This is consistent with a formula $C_8F_{14}S_2$.

Anal. Calcd for $C_8F_{14}S_2$: F, 62.44; C, 22.54; S, 15.02. Found: F, 62.14; C, 22.91; S, 14.97.

The nmr spectrum is [Φ (area)]: $\mathit{CF_3}\mathrm{C}$ [56.6 (5.8)], $\mathit{CF_3}\mathrm{C}$ [71.8 (3.0)], $\mathit{CF_3}\mathrm{CF_2}$ [78.5 (3.0)], $\mathrm{CF_3}\mathit{CF_2}$ [108.4 (2.0)]. These data coupled with the ir data are consistent with structure III.

Reaction of Technical Grade SF_4 and $CF_3CF{=}CFCF_3$ over CsF.—SF_4 (40 g) (plus SOF_2) and $CF_3CF{=}CFCF_3$ (57 g) were heated over CsF to 252° to a maximum pressure of 22.6 atm. At a temperature of 265°, the pressure dropped slowly to 15.3 atm within 12 hr. The volatile materials were removed from the reactor and on analysis were found to be 28 g of $CF_3CF{=}CF$-

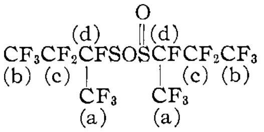
CF_3, 18 g of C_4F_{10}, 18 g of SF_4 and SOF_2, 29 g of a new product, 4 g of residues, and a small undetermined quantity of an unstable material. Chromatograms of the new product in several columns under a variety of conditions indicated that it consisted of two materials in the mole ratio of 3:1 which could not be completely resolved. The mixture was shown to be $C_8F_{14}S_2$ (III) and $C_8F_{18}S_2O_2$ (IV) in the mole ratio of about 3:1 on the basis of the ir spectra of the mixture (see below) and the two purified materials.

Reaction of SOF_2 and $CF_3CF{=}CFCF_3$ over CsF.—SOF_2 (41 g) and 47 g $CF_3CF{=}CFCF_3$ (47 g) were heated in the reactor over CsF to 202° and a maximum pressure of 28.0 atm in 16 hr. The temperature was held at this condition for 120 hr as the pressure fell to 13.2 atm. The products were removed, analyzed, and found to be 38 g of $CF_3CF{=}CFCF_3$, 13 g of SOF_2, 10 g of residues, and 25 g of a liquid product. About 15 g of material was pumped from the reactor at 400°. It was unstable and reactive to glass, forming SOF_2 and SiF_4. No C_4F_{10} was isolated. The new product was obtained about 95% pure on fractionation in a spinning-band column and further purified by preparative-scale vpc. It boiled at 149° and had a refractive index of 1.3318 at 20° and a molecular weight of 534 (mass spectrometry). These data are consistent with a molecular formula $C_8F_{18}S_2O_2$.

Anal. Calcd for $C_8F_{18}S_2O_2$: F, 64.05; C, 18.00; S, 11.99. Found: F, 64.47; C, 18.29; S, 12.33.

The nmr spectrum of this material was quite complex. It consisted of four pairs of peaks, all complex multiplets. One pair of CF_3 peaks was resolved, another pair of CF_3 peaks was not, and a pair of CF_2 peaks was incompletely resolved, whereas a pair of CF peaks was resolved. These data suggested two *sec*-C_4F_9 groups in slightly different magnetic environments. It was not possible to tell which C_4F_9 group was which, but tentative assignments could be made to each type of CF_3 group.

The nmr spectrum of compound IV



$$\underset{(b)}{CF_3}\underset{(c)}{CF_2}\overset{(d)}{\underset{\underset{(a)}{CF_3}}{CF}}SO\overset{\overset{O}{\|}}{S}\overset{(d)}{\underset{\underset{(a)}{CF_3}}{CF}}\underset{(c)}{CF_2}\underset{(b)}{CF_3}$$

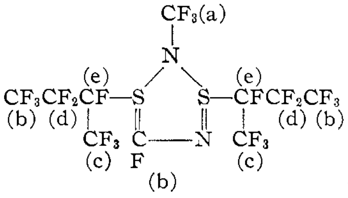
is [Φ (area)]: a,a [79.9 (3.0), 74.0 (3.1)], b,b [centered at 79.5 (6.0)], c,c [centered at 117.3 (3.9)], d,d [broad bimodal peak centered at 162.3 (2.0)]. The yield of IV based on the perfluorobutene used was not less than 80%.

Reaction of Technical SF_4 (with SOF_2) and $CF_3C{\equiv}CCF_3$ over CsF.—A mixture estimated chromatographically to consist of approximately equimolar amounts of SOF_2 and SF_4 weighing 14 g and 11.0 g of $CF_3C{\equiv}CCF_3$ were heated over CsF to 80° and a pressure of 8.7 atm. After 24 hr at this temperature, the pressure had fallen to 3.0 atm. The products were removed and gave the following analysis: 4 g of $CF_3C{\equiv}CCF_3$, 3 g of C_4F_{10}, 12 g of a mixture containing about equimolar amounts of III and IV, and 1.5 g of residues. In order to remove the final traces of material from the reactor, it was heated to 200° under vacuum and 5 g of an intensely blue volatile material was trapped at −196°. It was held under vacuum for 24 hr at −78° and it turned red. On slow warming to room temperature, a colorless reactive gas formed. A part of this gas mixture was identified as SOF_2 and SF_4 from an ir spectrum.

Reaction of $CF_3N{=}SF_2$ and $CF_3C{\equiv}CCF_3$ over CsF.—$CF_3N{=}SF_2$ (20 g) and $CF_3C{\equiv}CCF_3$ (15.6 g) were heated over CsF to 50° and a pressure of 3.0 atm. As the reaction appeared to be exothermic, the system equilibrated at 70° and 3.3 atm. After 10 hr, the pressure had dropped to 1.0 atm. The products were removed, analyzed, and found to be 9 g of $CF_3N{=}SF_2$, 3 g of $CF_3C{\equiv}CCF_3$, 20 g of a liquid product, and 3 g of residues. The liquid product, after purification, boiled at 167° and had a refractive index of 1.3315 at 20° and molecular weights of 630 (mass spectrometry). This is consistent with a molecular formula $C_{10}F_{22}N_2S_2$.

Anal. Calcd for $C_{10}F_{22}N_2S_2$: F, 66.35; C, 19.06; N, 4.44; S, 10.15. Found: F, 67.27; C, 19.45; N, 4.58; S, 10.10.

The nmr spectrum of this compound was very complex. One pair of CF_3 peaks was resolved, a second peak of CF_3 was not resolved but had a relative area of 7.1, suggesting the presence of a CF peak, a pair of CF_2 peaks was resolved, and a single CF_3 peak downfield appeared to be bonded to nitrogen. As in the case of compound IV this compound had two *sec*-C_4F_9 groups in different magnetic environments. The nmr spectrum of compound V



is [Φ (area)]: a [59.9 (3.0)], b,b,b [centered at 79.9 (7.12)], c,c [73.3, 74.1 (6.12)], d,d [116.0, 117.1 (4.0)], e,e [centered at 161.0 (2.05)]. The yield of V based on the perfluorobutyne used was 74%. Attempts to isolate the monomer $CF_3N{=}S(F)\text{-}C(CF_3){=}CFCF_3$ (VIII) by varying the mole ratio of reactants, temperatures, and reaction times were partially successful. A very small quantity of what appeared to be pure monomer was isolated by vpc. The ir spectrum of this substance is listed in Table II. There was insufficient material to evaluate any other properties.

Reaction of $C_2F_5{=}SF_2$ and $CF_3C{\equiv}CCF_3$ over CsF.—$C_2F_5N{=}SF_2$ (28 g) and $CF_3C{\equiv}CCF_3$ (17.0 g) were heated in the reactor over CsF to 124° and held for 54 hr, during which time the pressure fell from 8.7 to 3.2 atm. The products were removed and analyzed. There were 2 g of $CF_3C{\equiv}CCF_3$, 7 g of $C_2F_5N{=}SF_2$, 34 g of a liquid product, and 2 g of residues. The purified liquid product boiled at 98° and had a refractive index of 1.3158 at 20° and molecular weights of 368 (vapor density) and 365 (mass spectrometry). This is consistent with a molecular formula $C_6F_{15}NS$.

Anal. Calcd for $C_6F_{15}NS$: F, 67.67; C, 19.73; N, 3.84; S, 8.77. Found: F, 66.90; C, 19.90; N, 4.07; S, 10.48.

The nmr spectrum for VI is [Φ (area)]: $\mathit{CF_3}CF_2$ (72.6 (3.0)], $\mathit{CF_3}C{=}$ [7.3.3 (2.9)], $\mathit{CF_3}CF$ [80.1 (3.1), $CF_3\mathit{CF_2}$ [117.3 (1.9)], CF [164.1 (1.0)], $S\mathit{F}$ [36.4 (1.0)]. It will be noted that the $CF_2{=}N$ resonance is in the same upfield position as a normal $-CF_2-$ in a fluorocarbon group. This is attributed to the paramagnetic effect of the $C{=}C$ group. The yield of VI was almost 100% based on the perfluorobutyne used.

Reaction of $C_3F_7N{=}SF_2$ and $CF_3C{\equiv}CCF_3$ over CsF.—$C_3F_7N{=}SF_2$ (32 g) and $CF_3C{\equiv}CCF_3$ (32.8 g) were heated over CsF to 150° and a pressure of 7.8 atm. This temperature was maintained for 72 hr while the pressure fell to 6.2 atm. The products were removed, analyzed, and found to be 15.5 g of $CF_3C{\equiv}CCF_3$, 46.0 g of a liquid product, and 3.5 g of residues. No $C_3F_7N{=}SF_2$ was recovered. The purified liquid product boiled at 111° and had a refractive index of 1.3142 at 20° and molecular weights of 420 and 423 (vapor density) compared to 415 (theoretical) for $C_7F_{15}NS$ (VII).

Anal. Calcd for $C_7F_{15}NS$: C, 20.24; S, 7.71. Found: C, 20.68; S, 8.00.

The nmr spectrum for VII is [Φ (area)]: $\mathit{CF_3}CF_2$ [83.6 (3.1)], $\mathit{CF_3}C$ [73.4 (2.7)], $\mathit{CF_3}CF$ [8.03 (3.3)], $CF_3\mathit{CF_2}$ [118.7 (2.14)], $\mathit{CF_2}N$ [118.0 (2.14)], CF [163.8 (1.1)], SF [31.3 (1.0)]. Note again that the chemical shift of the CF_2N fluorines is upfield with a value equal to that of its neighboring CF_2 fluorines. Compound VII was prepared in 85% yield based on the total use of $C_3F_7N{=}SF_2$.

Acknowledgments.—The authors are most grateful to Dr. W. S. Brey, Jr., for obtaining and assisting in the interpretation of all nmr spectra and to Dr. R. J. Hanrahan for obtaining, after considerable experimentation, mass spectra containing parent ions.