

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF IDAHO, MOSCOW, IDAHO 83843

## Some Chemistry of Difluoraminocarbonyl Fluoride, $\text{NF}_2\text{CFO}$ . The Preparation of Perfluorourea, $(\text{NF}_2)_2\text{CO}$ , and Difluoraminocarbonyl Chloride, $\text{NF}_2\text{C}(\text{O})\text{Cl}$ . New Preparations for $\text{NF}_2\text{OCF}_3$ and $\text{NF}_2\text{Cl}$ <sup>1</sup>

BY GEORGE W. FRASER AND JEAN'NE M. SHREEVE

Received March 1, 1967

Reactions of  $\text{NF}_2\text{CFO}$  with  $\text{CF}_3\text{OF}$  or with  $\text{Al}_2\text{Cl}_6$  and  $\text{HCl}$  yield  $\text{NF}_2\text{OCF}_3$  or  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , respectively. The reactions of  $\text{NF}_2\text{CFO}$  with  $\text{KF}$  and  $\text{CsF}$  to give  $\text{KOCF}_2\text{NF}_2$ ,  $\text{KOCN}_2\text{F}_6$ ,  $\text{KOCN}_2\text{F}_5$ ,  $\text{CsOCF}_2\text{NF}_2$ ,  $\text{CsOCN}_2\text{F}_6$ , and  $\text{CsOCN}_2\text{F}_5$  are discussed. Decomposition of  $\text{KOCF}_2\text{NF}_2$  with  $\text{Cl}_2$  yields  $\text{NF}_2\text{Cl}$  and pyrolysis of  $\text{KOCN}_2\text{F}_5$  at  $95^\circ$  yields  $(\text{NF}_2)_2\text{CO}$ . Spectra and properties of  $(\text{NF}_2)_2\text{CO}$  and  $\text{NF}_2(\text{O})\text{Cl}$  are given.

This paper describes some of the chemistry of difluoraminocarbonyl fluoride,  $\text{NF}_2\text{CFO}$ , whose preparation and properties have been reported in a previous note.<sup>2</sup> Reaction of  $\text{NF}_2\text{CFO}$  with trifluoromethyl hypofluorite,  $\text{CF}_3\text{OF}$ , at room temperature yields difluoraminooxyperfluoromethane,  $\text{NF}_2\text{OCF}_3$ , a compound previously prepared by the reaction of tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ , with trifluoromethyl hypofluorite<sup>3,4</sup> and by the basic hydrolysis of difluoraminotrifluoromethoxytetrafluorosulfur(VI),  $\text{CF}_3\text{OSF}_4\text{NF}_2$ .<sup>4</sup> Several recent reports<sup>5-7</sup> indicate that anhydrous aluminum chloride, with or without a solvent or hydrogen chloride catalyst, is an effective chlorinating agent for replacement of certain labile fluorines in various types of compounds; and by an analogous reaction under mild conditions  $\text{NF}_2\text{CFO}$  is easily converted to the previously unreported difluoraminocarbonyl chloride,  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ . Reports of the formation of simple anionic complexes between the alkali metal fluorides and carbonyl fluoride<sup>8,9</sup> or hexafluoroacetone<sup>10,11</sup> suggested the analogous preparation of  $\text{KOCF}_2\text{NF}_2$  from  $\text{KF}$  and  $\text{NF}_2\text{CFO}$ . This adduct is a useful intermediate for a preparation of chlorodifluoramine,  $\text{NF}_2\text{Cl}$ ,<sup>12</sup> and  $\text{KOCN}_2\text{F}_5$ . Pyrolysis of the latter is the only known route to perfluorourea,  $(\text{NF}_2)_2\text{CO}$ , some of whose properties have already been described.<sup>13</sup>

### Results and Discussion

Trifluoromethyl hypofluorite,  $\text{CF}_3\text{OF}$ , slowly attacks difluoraminocarbonyl fluoride,  $\text{NF}_2\text{CFO}$ , at room temperature in Pyrex glass. After several hours the

(1) Taken from the Ph.D. thesis of G. W. Fraser and presented in part at the 3rd International Symposium on Fluorine Chemistry, Munich, 1965, and at the Symposium on Inorganic Fluorine Chemistry, Ann Arbor, Mich., June 1966.

(2) G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).

(3) W. H. Hale, Jr., and S. M. Williamson, *ibid.*, **4**, 1342 (1965).

(4) J. M. Shreeve, L. C. Duncan, and G. H. Cady, *ibid.*, **4**, 1516 (1965).

(5) W. S. Solomon, L. A. Dee, and D. W. Schults, *J. Org. Chem.*, **31**, 1551 (1966).

(6) M. Lustig, *Inorg. Chem.*, **5**, 1317 (1966).

(7) D. P. Babb and J. M. Shreeve, *ibid.*, **6**, 351 (1967).

(8) D. C. Bradley, M. E. Redwood, and C. J. Willis, *Proc. Chem. Soc.*, 416 (1964).

(9) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

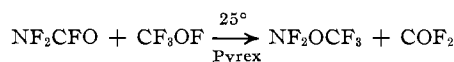
(10) D. P. Graham and V. Weinmayr, *J. Org. Chem.*, **31**, 957 (1966).

(11) A. G. Pittman and D. L. Sharp, *ibid.*, **31**, 2316 (1966).

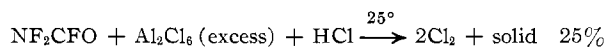
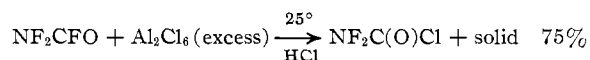
(12) For other preparations of  $\text{NF}_2\text{Cl}$ , see, for example: (a) W. C. Firth, Jr., *Inorg. Chem.*, **4**, 254 (1965); (b) C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 108 (1963), and references cited therein.

(13) G. W. Fraser and J. M. Shreeve, *Chem. Commun.*, 532 (1966).

starting materials initially in equimolar ratio appear to be completely consumed, and while considerable degradation and attack on the glass is evident, difluoraminooxyperfluoromethane,  $\text{NF}_2\text{OCF}_3$ , is easily isolated from the product mixture in yields approaching 40%. The presence of anhydrous  $\text{CsF}$  does not alter the yield appreciably

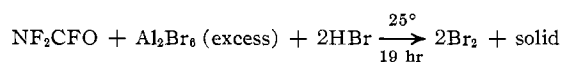
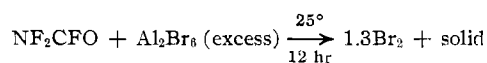


Difluoraminocarbonyl fluoride reacts very slowly with  $\text{Al}_2\text{Cl}_6$  at room temperature, but the rate of reaction is greatly increased by the presence of equivalent amounts of anhydrous  $\text{HCl}$ , whereupon the  $\text{NF}_2\text{CFO}$  is completely consumed within a matter of hours. The disappearance of  $\text{HCl}$  and the formation of  $\text{Cl}_2$  and difluoraminocarbonyl chloride,  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , suggest that the two major reactions occur simultaneously



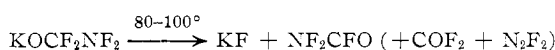
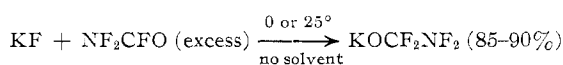
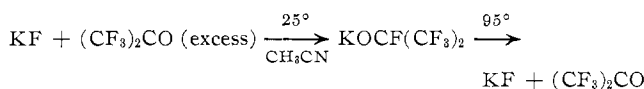
Side reactions usually lead to the formation of small amounts of  $\text{SiF}_4$ ,  $\text{COF}_2$ ,  $\text{COClF}$ , and occasionally  $\text{COCl}_2$ . The solid phase has not been characterized, but is generally suitable for subsequent preparation of more  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ .

Difluoraminocarbonyl fluoride is completely consumed within 12 hr upon contact with  $\text{Al}_2\text{Br}_6$  at room temperature, the only major volatile product being  $\text{Br}_2$ . The solid product has not been characterized other than to note that it has some tendency to absorb  $\text{HBr}$  at room temperature. If the reaction is repeated in the presence of 2 equiv of  $\text{HBr}$ , all gases are completely consumed with liberation of nearly the theoretical amount of  $\text{Br}_2$ . The pink, translucent residue from this reaction has little tendency to absorb more  $\text{HBr}$  and releases  $\text{NH}_3$  upon basic hydrolysis, but has not been otherwise characterized. Similar reactions at low

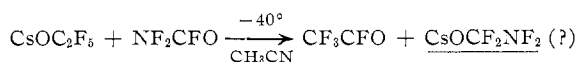
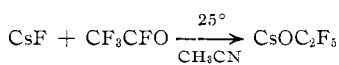


temperatures lead to the formation of significant amounts of  $\text{COBr}_2$  along with the  $\text{Br}_2$ , but under no conditions has there been found evidence of difluoroaminocarbonyl bromide,  $\text{NF}_2\text{C}(\text{O})\text{Br}$ .

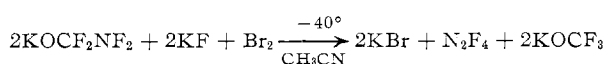
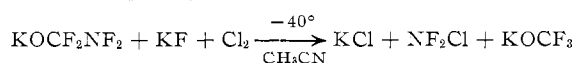
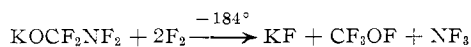
First attempts to prepare the adducts  $\text{KOCF}_2\text{NF}_2$  and  $\text{CsOCF}_2\text{NF}_2$  by reactions of anhydrous  $\text{KF}$  or  $\text{CsF}$  with equivalents or excesses of  $\text{NF}_2\text{CFO}$  led to little or no reaction at room temperature without solvent, to attack on the solvent in acetonitrile solutions at room temperature, and to partial degradation of the gas to  $\text{COF}_2$  in acetonitrile solutions at  $-40^\circ$ . If the  $\text{KF}$  is pretreated with hexafluoroacetone,  $(\text{CF}_3)_2\text{CO}$ , however, with the formation and subsequent thermal decomposition of the adduct  $\text{KOCF}(\text{CF}_3)_2$  as outlined below, it will rapidly absorb gaseous  $\text{NF}_2\text{CFO}$  at room temperature or  $0^\circ$  to form a nonvolatile product stable under vacuum which releases the  $\text{NF}_2\text{CFO}$  semiquantitatively upon warming. The product appears to be the simple salt  $\text{K}^+\text{OCF}_2\text{NF}_2^-$ .



An analogous reaction with pretreated  $\text{CsF}$  and  $\text{NF}_2\text{CFO}$  led to partial degradation of the gas to  $\text{COF}_2$ , and little or no  $\text{CsOCF}_2\text{NF}_2$  was believed to have formed. A solid product insoluble in acetonitrile, thermally stable, and strongly oxidizing, which may be  $\text{CsOCF}_2\text{NF}_2$ , was observed in semistoichiometric reactions of the type

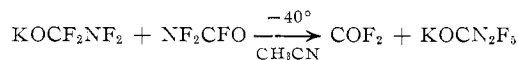
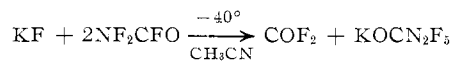


The salt  $\text{KOCF}_2\text{NF}_2$  is chemically reactive but has been found to have little synthetic value. Fluorination might be expected to lead to the unreported difluoro-(difluoroamino)methyl hypofluorite,  $\text{NF}_2\text{CF}_2\text{OF}$ , but under all conditions examined leads only to  $\text{CF}_3\text{OF}$  and  $\text{NF}_3$ . Similarly, chlorination of  $\text{KOCF}_2\text{NF}_2$  in the presence of  $\text{KF}$  yields chlorodifluoroamine,  $\text{NF}_2\text{Cl}$ , in 68% yield, a reaction which has some synthetic interest. The reaction of  $\text{KOCF}_2\text{NF}_2$  with  $\text{Br}_2$  yields tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ , instead of the unreported bromodifluoroamine,  $\text{NF}_2\text{Br}$ .

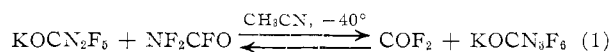


Granular anhydrous  $\text{KF}$  or pretreated  $\text{KF}$  reacts (slowly or rapidly, respectively) with 2 equiv of  $\text{NF}_2\text{CFO}$  in acetonitrile solution at  $-40^\circ$ , and the salt  $\text{KOCF}_2\text{NF}_2$  reacts rapidly with 1 equiv of  $\text{NF}_2\text{CFO}$  under the same conditions. In any case the reaction

is usually semistoichiometric. From synthetic data the nonvolatile product appears to be approximately  $\text{KOCN}_2\text{F}_5$  and is believed to be primarily the salt  $\text{K}^+\text{O}^-\text{CF}(\text{NF}_2)_2^-$



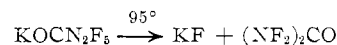
The solute ( $\text{KOCN}_2\text{F}_5$ ) from either of these reactions will react with more  $\text{NF}_2\text{CFO}$  with partial conversion of the gas to  $\text{COF}_2$ . An equilibrium reaction is indicated, for if the solute is treated several times with  $\text{NF}_2\text{CFO}$  in succession, synthetic data indicate that the nitrogen to carbon and potassium ratio approaches but does not rise significantly above 3:1:1, and the reaction is readily reversible with partial conversion of pure  $\text{COF}_2$  to  $\text{NF}_2\text{CFO}$



The final product has the approximate empirical formula  $\text{KOCN}_3\text{F}_6$  and is believed to be primarily the salt  $\text{K}^+\text{OC}(\text{NF}_2)_3^-$ . A cursory examination of the reactions of anhydrous  $\text{CsF}$  with excess  $\text{NF}_2\text{CFO}$  under the same conditions indicated that the formation of (apparently)  $\text{CsOCN}_2\text{F}_5$  and  $\text{CsOCN}_3\text{F}_6$  is completely analogous.

The postulated salts  $\text{M}^+\text{OCF}_2\text{NF}_2^-$ ,  $\text{M}^+\text{OCF}(\text{NF}_2)_2^-$ , and  $\text{M}^+\text{OC}(\text{NF}_2)_3^-$ , where  $\text{M}^+$  is  $\text{K}^+$  or  $\text{Cs}^+$ , are all hydrolytically and at least in part thermally unstable, sometimes explosively so. None has been isolated pure, and analytical and spectral data on them are unavailable.

Small samples (less than 0.5 mmole) of  $\text{KOCF}_2\text{NF}_2$  have always decomposed smoothly to  $\text{KF}$  and  $\text{NF}_2\text{CFO}$  upon heating, but solid samples of (approximately)  $\text{KOCN}_2\text{F}_5$  (0.3 mmole or less) explode violently when heated to  $70^\circ$ , and slow decomposition at lower temperatures does not yield appreciable amounts of perfluorourea,  $(\text{NF}_2)_2\text{CO}$ . If, however, the sample of  $\text{KOCN}_2\text{F}_5$  is sufficiently impure with  $\text{KOCF}_2\text{NF}_2$  (the recommended molar ratio of  $\text{KOCN}_2\text{F}_5$  to  $\text{KOCF}_2\text{NF}_2$  being no higher than 1:1), it may usually be decomposed at  $95^\circ$  without exploding. Characterization of the gas mixture thus liberated indicates that approximately 25% of the  $\text{KOCN}_2\text{F}_5$  decomposes to  $(\text{NF}_2)_2\text{CO}$  and  $\text{KF}$ , while the remainder yields  $\text{COF}_2$ ,  $\text{N}_2\text{F}_2$ , and probably  $\text{NF}_2\text{CFO}$ . The absence of tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ , in this gas mixture indicates that the  $(\text{NF}_2)_2\text{CO}$  probably does not arise from radical recombination, *e.g.*,  $\text{NF}_2\cdot + \cdot\text{C}(\text{O})\text{NF}_2$ .



Fluorine-19 nuclear magnetic resonance spectra of pure  $\text{NF}_2\text{CFO}$ ,  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , and  $(\text{NF}_2)_2\text{CO}$ , with external  $\text{CCl}_3\text{F}$  reference, were run in sequence under identical conditions. The chemical shifts of the signals assigned to the  $\text{NF}_2$  fluorine nuclei were  $-28.7$ ,  $-40.4$ , and  $-30.8$  ppm, respectively. Internally referenced  $\text{NF}_2\text{CFO}$  shows the corresponding signal at  $\phi^* -33.1$ .

Banks, *et al.*,<sup>14</sup> report for N,N-difluorourea,  $\text{NF}_2\text{C}(\text{O})\text{-NH}_2$ ,  $\phi^*$  *ca.*  $-33$ , Freeman<sup>15</sup> reports for N,N-difluoroacetamide,  $\text{NF}_2\text{C}(\text{O})\text{CH}_3$ ,  $\phi^*$  *ca.*  $-30$ , and Koshar, *et al.*,<sup>16</sup> report for bis(difluoramino)difluoromethane,  $(\text{NF}_2)_2\text{CF}_2$ ,  $\phi^*$   $-19.0$ . It is interesting to note that all reported compounds containing the  $\text{NF}_2\text{C}(\text{O})$ - structure show the  $\text{NF}_2$  resonance in the narrow range of  $\phi^*$  *ca.*  $-30$  to  $-40$ .

### Experimental Section

**Starting Materials.**—The preparation and purification of difluoraminoacetyl fluoride has already been described.<sup>2</sup> Hexafluoroacetone (Pierce Chemical Co.) and anhydrous hydrogen bromide (Matheson Co., Inc.) were used without purification. Anhydrous hydrogen chloride was prepared from concentrated sulfuric acid and sodium chloride and was dried by fractional condensation at  $-80^\circ$ . Anhydrous aluminum chloride (J. T. Baker Chemical Co.) and anhydrous aluminum bromide (Fisher Scientific Co.) were purified as needed by sealing the desired amount into a side arm on the reaction bulb, subliming the volatile material into the bulb under dynamic vacuum, and sealing off and removing the nonvolatile residue in the side arm. Fisher Certified reagent acetonitrile was used without purification except to store it at autogenous pressure over calcium hydride (Metal Hydrides, Inc.) at room temperature in a vessel from which it could be taken as needed directly into the vacuum system. Cesium fluoride (anhydrous, 99%, K & K Laboratories) and potassium fluoride (anhydrous granular reagent, Allied Chemical) were dehydrated as needed by stirring in a porcelain crucible over a flame and immediately transferring while hot the desired amount into the clean, tared reaction bulb for weighing. Carbonyl fluoride was prepared from carbon monoxide (Matheson Co., Inc.) and fluorine (Allied Chemical) and was purified by fractional codistillation.<sup>17</sup> It was not completely free of carbon dioxide. Trifluoroacetyl fluoride was prepared by allowing trifluoroacetyl chloride (K & K Laboratories) to react with an excess of anhydrous cesium fluoride in acetonitrile solution at room temperature. The  $\text{CF}_3\text{CFO}$  was liberated by the decomposition of its adduct,  $\text{CsOC}_2\text{F}_5$ , at  $95^\circ$  after evaporation of the solvent, and no purification was necessary. Trifluoromethyl hypofluorite was obtained from Dr. Claude Merrill (Dow Chemical Co.) and was purified by filtration at  $-184^\circ$ .

**General Procedure.**—Most reactions were run in 25- or 50-ml Pyrex bulbs which were fitted with a stopcock by means of 14/20  $\text{F}$  ground joints. Gases and volatile liquids were handled in conventional glass vacuum apparatus under conditions of high vacuum. A Kel-F oil (Grade KF-3, Minnesota Mining and Manufacturing Co.) null-point pressure transducer was used in handling gases highly corrosive to mercury. Gaseous starting materials and purified products were weighed and/or measured quantitatively by  $PVT$  data. Except where noted, all acetonitrile solutions with nitrogen-fluorine solutes were kept at  $-35 \pm 5^\circ$  to prevent attack on the solvent. Reactions involving such solutions were worked up by pumping out the gas at  $-40^\circ$  through a series of traps at  $-80$  and  $-184^\circ$ . Part or all of the solvent was then removed by warming the reaction bulb to  $0^\circ$  while pumping through the traps. For a continuing reaction sequence in solution, the solvent ( $-80^\circ$  trap) was then returned to the reaction bulb while the gas ( $-184^\circ$  trap) was freed of any remaining solvent by fractional condensation at  $-80^\circ$  prior to quantitative measurement. When necessary, gaseous products were separated by fractional codistillation<sup>17</sup> using an unpacked 12-ft, 1/8-in. o.d. aluminum fractionating column coiled to fit into a half-pint dewar flask.

(14) R. E. Banks, R. N. Haszeldine, and J. P. Lulu, *J. Chem. Soc., Sect. C*, 1514 (1966).

(15) J. P. Freeman, *Advances in Chemistry Series*, No. 36, American Chemical Society, Washington, D. C., 1962, p 129.

(16) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(17) G. H. Cady and D. P. Siegwirth, *Anal. Chem.*, **31**, 618 (1959).

Infrared spectra ( $5000\text{--}625\text{ cm}^{-1}$ , 3-min scan) of  $\text{NF}_2\text{CFO}$ ,  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , and  $(\text{NF}_2)_2\text{CO}$  were obtained on a Beckman IR5A spectrophotometer using a gas cell with NaCl windows and a path length of 50 mm. High-resolution  $\text{F}^{19}$  nuclear magnetic resonance spectra of these three compounds were taken at room temperature using a modified Varian DP-60 spectrometer (56.4 Mc/sec) by sealing the pure liquids in capillaries (*ca.* 1.5-mm o.d.) which were floated in the external reference,  $\text{CCl}_3\text{F}$ , in standard 5-mm tubes.

**Caution!** Nitrogen-fluorine-containing materials are strong oxidizing agents and in the presence of acetonitrile constitute potential safety hazards. Handling and freezing of such mixtures must always be done with adequate precautions. Solids (*e.g.*, salts) which contain or may contain nitrogen-fluorine groups or the nonvolatile residues from chemical decomposition of such solids must never be heated indiscriminately, for many have been found to be highly explosive. All pyrolyses must have adequate shielding, and disposal of such solids may be accomplished behind a shield with wet acetonitrile followed with water.

**Spectra of  $\text{NF}_2\text{CFO}$ .**—The infrared spectrum (10 mm pressure) is (in  $\text{cm}^{-1}$ ): 1900 (s), 1210 (s), 1035 (m), 960 (m), 835 (w), triplet, 765 (m), triplet. The  $\text{F}^{19}$  nmr spectrum, referenced externally with  $\text{CCl}_3\text{F}$ , shows:  $-28.7$  ppm ( $\text{NF}_2$ , broad and unresolved) and  $+15.1$  ppm ( $\text{CFO}$ , sharp 1:2:1 triplet,  $J = 19$  cps). The peak area ratio is approximately 3:1. The  $\text{F}^{19}$  nmr spectrum, referenced internally with  $\text{CCl}_3\text{F}$  solvent, shows ( $\phi^*$ ) resonances at  $-33.1$  and  $+11.5$ , but is otherwise identical. These data differ slightly from those originally published.<sup>2</sup>

**Preparation of  $\text{NF}_2\text{OCF}_3$ .**—To a clean 250-ml Pyrex reaction bulb were added 0.41 mmole of  $\text{NF}_2\text{CFO}$  and 0.41 mmole of  $\text{CF}_3\text{OF}$ . After 3 hr at room temperature, the gaseous products (1.00 mmole) were approximately  $\text{COF}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{SiF}_4$ , and  $\text{NF}_2\text{OCF}_3$ , and considerable white solid (fluorosilicates?) had formed in the bulb. The gaseous products were shaken for a few minutes at room temperature with moist soda lime pellets to remove acidic gases. The yield of  $\text{NF}_2\text{OCF}_3$ , after drying by fractional condensation at  $-80^\circ$ , was 0.156 mmole, 38%. It was identified by infrared spectrum, boiling point ( $-63^\circ$ ), and gas density molecular weight.<sup>3,4</sup>

**Preparation of  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ .**—Approximately 1 g of  $\text{Al}_2\text{Cl}_6$  was sublimed into a 50-ml Pyrex reaction bulb, and HCl (0.67 mmole) and  $\text{NF}_2\text{CFO}$  (0.70 mmole) were added. After 8 hr at room temperature, the gaseous products were separated by fractional codistillation. The major components were HCl,  $\text{Cl}_2$ , and  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ . [In some preparations, lesser amounts of  $\text{FCOCl}$  and  $\text{NF}_2\text{CFO}$  were also found. Reaction times of 24 hr often resulted in the formation of  $\text{COCl}_2$ , which could not be separated from the  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ .] The yield was 0.533 mmole ( $PVT$ ) of  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , 61.7 mg, mol wt = 116 [calcd for  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ , 115.5], 76% based on  $\text{NF}_2\text{CFO}$ .

The infrared spectrum (25 mm pressure) of  $\text{NF}_2\text{C}(\text{O})\text{Cl}$  is (in  $\text{cm}^{-1}$ ): 1840 (s), 1800 (ms), 1073 (m), 948 (s), 905 (vs), 770–755 (w), doublet, 645–635 (m), doublet. The  $\text{F}^{19}$  nmr spectrum shows a single, broad resonance at  $-40.4$  ppm. Experimental vapor pressure data are as follows [ $T$  ( $^\circ\text{K}$ ),  $P$  (mm)]: 189, 6; 213, 19; 222, 70; 234, 142. These data suggest a Clausius-Clapeyron curve given by:  $\log P(\text{mm}) = -1350T^{-1} + 7.92$ . The extrapolated normal boiling point is  $-5^\circ$ . The corresponding enthalpy of vaporization is 6.17 kcal mole $^{-1}$ ; the entropy of vaporization ( $-5^\circ$ ) is 23.0 eu. When gaseous  $\text{NF}_2\text{C}(\text{O})\text{Cl}$  was held over water at  $0^\circ$ , its infrared bands disappeared from the vapor phase within a matter of minutes with the formation of the well-known absorption bands of  $\text{HNF}_2$  and  $\text{CO}_2$ . The resulting solution gave positive tests for  $\text{Cl}^-$  and  $\text{F}^-$ .  $\text{NF}_2\text{C}(\text{O})\text{Cl}$  (10 mg) was hydrolyzed in acidified aqueous KI solution for 1 hr at room temperature. *Anal.* Found: 0.0360 oxidizing equiv (as  $\text{I}_3^-$ )/g. Calcd for  $\text{NF}_2\text{C}(\text{O})\text{Cl}$ : 0.0346. At room temperature,  $\text{NF}_2\text{C}(\text{O})\text{Cl}$  attacks mercury slowly to form  $\text{NF}_2\text{CFO}$  as the primary volatile product, is stable in Pyrex, and does not react with  $\text{N}_2\text{F}_4$  or  $\text{NF}_2\text{Cl}$ . Ultraviolet irradiation with  $\text{N}_2\text{F}_4$  through a Pyrex filter results in slow degradation to  $\text{FCOCl}$ .

**Attempted Bromination of  $\text{NF}_2\text{CFO}$ .**—Approximately 1 g of  $\text{Al}_2\text{Br}_6$  was sublimed into a 50-ml Pyrex reaction bulb, and  $\text{HBr}$  (0.58 mmole) and  $\text{NF}_2\text{CFO}$  (0.32 mmole) were added. The color of  $\text{Br}_2$  started to develop immediately upon warming. After 19 hr at room temperature, the volatile material was removed by pumping ( $1 \mu$ ) for 10 hr at room temperature through a U trap cooled to  $-184^\circ$ . The yield was 0.02 mmole not condensable at  $-80^\circ$  ( $\text{CO}_2$  and  $\text{SiF}_4$ ) and 0.101 g (0.63 mmole) of  $\text{Br}_2$  containing a trace of  $\text{COBr}_2$ , which was identified by its infrared spectrum.<sup>18</sup> The pinkish, translucent residue in the bulb, upon treatment with 0.90 mmole of  $\text{HBr}$  for 38 hr at room temperature, absorbed 0.04 mmole. It was not characterized.

**Pretreatment of  $\text{KF}$ .**—In most reactions a clean, dry 50-ml Pyrex bulb and 14/20  $\text{F}$  stopper were tared and the desired amount of granular, dehydrated  $\text{KF}$  was added and weighed in air. The stopper was then replaced by a stopcock and the  $\text{KF}$  was rehydrated by flaming out under dynamic vacuum. Anhydrous  $\text{CH}_3\text{CN}$  and a molar excess of  $(\text{CF}_3)_2\text{CO}$  were condensed into the bulb. After the  $\text{KF}$  had completely dissolved (about 8 hr at room temperature with occasional swirling), all volatile materials were pumped out rapidly at about  $50^\circ$  and the deposited  $\text{KF}$  was then pumped on for at least 5 min at  $95^\circ$ . The solvent and  $(\text{CF}_3)_2\text{CO}$  were recovered essentially unchanged and were separable by fractional condensation at  $-80^\circ$ . Typically, 21.0 mg (0.361 mmole) of  $\text{KF}$ , when treated with 0.80 g of  $\text{CH}_3\text{CN}$  and 0.23 g (1.4 mmoles) of  $(\text{CF}_3)_2\text{CO}$  for 13 hr, gained 0.4 mg in weight.

**Preparation of  $\text{KOCF}_2\text{NF}_2$ .**—The apparatus was a 50-ml Pyrex bulb with a 1.25-mm Teflon needle valve (Fischer and Porter Co.) and a small, open side arm. The apparatus was tared, hot dehydrated  $\text{KF}$  was added through the side arm, and the latter was pulled off to seal the bulb. Reweighing indicated that 21.0 mg (0.36 mmole) of  $\text{KF}$  had been added. After pretreatment of the  $\text{KF}$  with  $(\text{CF}_3)_2\text{CO}$ , the apparatus was reweighed and was found to have gained 0.4 mg.  $\text{NF}_2\text{CFO}$  [52.6 mg, 0.533 mmole ( $PVT$ ), mol wt = 98.7] was condensed in and allowed to react with the  $\text{KF}$  (without solvent) for 23.5 hr at  $0^\circ$ . After removal of unreacted gas [0.23 mmole, mol wt = 97, infrared analysis indicated  $\text{NF}_2\text{CFO}$  with a trace of  $\text{COF}_2$ ; frequently traces of  $(\text{CF}_3)_2\text{CO}$  are also found at this step], the apparatus was reweighed. The  $\text{KF}$  gained 30.4 mg in weight. This solid product was decomposed by heating the bulb to  $85^\circ$  with a water bath (*behind a shield!*) for 5 min while pumping the liberated gas through a U trap cooled to  $-184^\circ$ . Reweighing indicated that the solid lost 31.2 mg during pyrolysis. The liberated gas (0.32 mmole, mol wt = 97) was identified by infrared analysis as  $\text{NF}_2\text{CFO}$  with traces of  $\text{COF}_2$  and  $\text{N}_2\text{F}_2$ . These data indicate the formation of 0.31 mmole of  $\text{KOCF}_2\text{NF}_2$  (86% conversion of the  $\text{KF}$ ).

$\text{KOCF}_2\text{NF}_2$  is stable for at least short times under static vacuum at room temperature, but  $\text{NF}_2\text{CFO}$  is rapidly pumped off at  $80^\circ$ . Samples of 0.5 mmole or less have never exploded upon heating.  $\text{KOCF}_2\text{NF}_2$  is immediately hydrolyzed by water to  $\text{CO}_2$ ,  $\text{HNF}_2$ ,  $\text{N}_2\text{F}_2$ , etc., and liberates  $\text{I}_3^-$  from aqueous solutions of  $\text{KI}$ . It is highly soluble in acetonitrile at  $-40^\circ$ , but such a solution is not stable at room temperature. As a solid at temperatures as low as  $-184^\circ$  or in acetonitrile solution at  $-40^\circ$ ,  $\text{KOCF}_2\text{NF}_2$  is decomposed by  $\text{F}_2$  to  $\text{CF}_3\text{OF}$  and  $\text{NF}_3$ . In acetonitrile solution it yields  $\text{NF}_2\text{Cl}$  or  $\text{N}_2\text{F}_4$  in good yield when allowed to react with an equivalent amount of  $\text{Cl}_2$  or  $\text{Br}_2$ , respectively.  $\text{KOCF}_2\text{NF}_2$  as a solid at room temperature or in acetonitrile solution at  $-40^\circ$  is decomposed by  $\text{CF}_3\text{OF}$  to yield  $\text{CF}_3\text{ONF}_2$  or  $\text{NF}_3$ , respectively. An acetonitrile solution of  $\text{KOCF}_2\text{NF}_2$  is decomposed by  $\text{CF}_3\text{C(O)Cl}$  at  $-40^\circ$  liberating  $\text{CF}_3\text{CFO}$  and  $\text{NF}_2\text{CFO}$  with the precipitation of  $\text{KCl}$ , or is slowly decomposed by  $\text{NF}_2\text{Cl}$  at room temperature to  $\text{KCl}$ ,  $\text{N}_2\text{F}_4$ , and  $\text{COF}_2$ .

**Preparation of  $\text{NF}_2\text{Cl}$ .**—Approximately 0.1 g of dehydrated  $\text{KF}$  was pretreated with  $(\text{CF}_3)_2\text{CO}$  according to the procedure already described and then allowed to react with 0.92 mmole of

$\text{NF}_2\text{CFO}$  at  $0^\circ$  until the gas was absorbed. Approximately 0.5 ml of anhydrous  $\text{CH}_3\text{CN}$  was condensed in, the  $\text{KOCF}_2\text{NF}_2$  was dissolved at  $-40^\circ$ , and 0.91 mmole of  $\text{Cl}_2$  was frozen onto the solution. After being allowed to react for 0.5 hr at  $-40^\circ$ , the residual gas [78.4 mg, 0.91 mmole ( $PVT$ ), mol wt = 86,  $\text{Cl}_2$  and  $\text{NF}_2\text{Cl}$ ] was removed and separated by fractional codistillation. The yield of  $\text{NF}_2\text{Cl}$  was 0.62 mmole (68%), identified by gas density molecular weight, reactivity to mercury, and infrared spectrum.<sup>19</sup> After 7 hr at room temperature, the solution in the reaction bulb was evaporated to dryness and 0.14 mmole of  $\text{COF}_2$  was recovered. The solid residue was not characterized.

**$\text{KOCN}_2\text{F}_3$ .**—Material of this approximate empirical formula, two preparations of which are given below, may be isolated as a white solid by evaporating its acetonitrile solution at  $0^\circ$  and pumping off the remaining solvent for 1–2 min at  $40^\circ$ . It is highly soluble in acetonitrile, solutions of which are indefinitely stable at  $-40^\circ$  but slowly liberate  $\text{N}_2\text{F}_2$ , etc., with attack on the solvent at room temperature. An acetonitrile solution of  $\text{KOCN}_2\text{F}_3$ , when treated with  $\text{SiCl}_4$  at  $-40^\circ$ , liberates  $\text{NF}_2\text{Cl}$ ,  $\text{NF}_2\text{C(O)Cl}$ , etc., with the precipitation of  $\text{KCl}$ . Solid  $\text{KOCN}_2\text{F}_3$  slowly decomposes at room temperature to at least  $\text{NF}_2\text{CFO}$ ,  $\text{COF}_2$ , and  $\text{N}_2\text{F}_2$  and hydrolyzes violently or explosively when placed in water. Most samples explode violently when heated to  $70^\circ$ , but occasionally one will decompose quietly to  $(\text{NF}_2)_2\text{CO}$  (in part) and  $\text{KF}$ .

**Preparation of  $\text{KOCN}_2\text{F}_3$  from Pretreated  $\text{KF}$ .**—The apparatus was similar to that already described for the preparation of  $\text{KOCF}_2\text{NF}_2$ .  $\text{KF}$  (25.8 mg, 0.44 mmole) was pretreated with  $(\text{CF}_3)_2\text{CO}$  and then converted (86%) to  $\text{KOCF}_2\text{NF}_2$  according to the procedures already described. After pyrolysis of the latter to  $\text{KF}$ , reweighing indicated that the  $\text{KF}$  was lighter by 0.4 mg prior to the formation  $\text{KOCF}(\text{CF}_3)_2$ . The  $\text{KF}$  was then treated with  $\text{NF}_2\text{CFO}$  [87.4 mg, 0.880 mmole ( $PVT$ ), mol wt = 99.3] and 372.3 mg of anhydrous  $\text{CH}_3\text{CN}$  for 31.5 hr at  $-35 \pm 5^\circ$ . The residual gas was removed at  $-40^\circ$  (20 min) and the solvent was pumped off at  $0^\circ$  (15 min). After separation were recovered 362.6 mg of  $\text{CH}_3\text{CN}$  and 33.8 mg of gas [0.477 mmole ( $PVT$ ), mol wt = 70.9]. The latter was identified by infrared analysis as  $\text{COF}_2$  containing a small amount of unreacted  $\text{NF}_2\text{CFO}$  and on the basis of its molecular weight was estimated to be 0.41 mmole (27 mg) of  $\text{COF}_2$  and 0.07 mmole (7 mg) of  $\text{NF}_2\text{CFO}$ . Thus the gas had decreased in mass by 53.6 mg during reaction and 9.7 mg of  $\text{CH}_3\text{CN}$  was not recovered. By direct weighing of the residue (partially crystallized to a white solid) in the apparatus, the  $\text{KF}$  had gained in weight by 65.5 mg. From the observed composition of the residual gas in the reaction, the composition of the solid product appeared to be (element, mmoles): K, 0.44; O, 0.40; C, 0.40; N, 0.81; F, 2.05; and 0.24 mmole of  $\text{CH}_3\text{CN}$ ; this corresponds to the empirical formula  $\text{K}_{1.1}\text{O}_{1.0}\text{C}_{1.0}\text{N}_{2.0}\text{F}_{3.1}$ . This  $\text{KOCN}_2\text{F}_3$  readily dissolved in a small amount of  $\text{CH}_3\text{CN}$  at  $0^\circ$ . About 0.5 ml of  $\text{H}_2\text{O}$  was frozen onto the solution, and upon warming to room temperature, no visible reaction occurred. (Previous experiments showed that solid  $\text{KOCN}_2\text{F}_3$  hydrolyzes violently or explosively in water to  $\text{HNF}_2$ ,  $\text{N}_2\text{F}_2$ ,  $\text{CO}_2$ , etc.) All volatile material in the reaction bulb was then transferred *in vacuo* to a bulb containing acidified aqueous  $\text{KI}$  solution, and the  $\text{I}_3^-$  liberated at room temperature was titrated with standard thiosulfate solution. *Anal.* Found: 3.01 mequiv. Calcd for 0.44 mmole of  $\text{KOCN}_2\text{F}_3$ : 3.52 mequiv; calcd for 0.40 mmole of  $\text{KOCN}_2\text{F}_3$ : 3.20 mequiv.

**Preparation of  $\text{KOCN}_2\text{F}_3$  from Untreated  $\text{KF}$ .**—In a 25-ml reaction bulb 15.3 mg (0.26 mmole) of dehydrated granular  $\text{KF}$  was weighed out and treated with 0.52 mmole ( $PVT$ ) of  $\text{NF}_2\text{CFO}$  and 421.5 mg of anhydrous  $\text{CH}_3\text{CN}$  for 26 hr at  $-35 \pm 5^\circ$ , by which time the  $\text{KF}$  had completely dissolved. The residual gas was removed, measured, and returned to the reaction. After an additional 21 hr it was again removed and measured, and there was found no appreciable change in its quantity or composition (0.30 mmole,  $\text{COF}_2$  with a small amount of unreacted  $\text{NF}_2\text{CFO}$ ). The solvent was pumped off for 20 min at  $-25^\circ$ , and

(18) B. Schneider and J. Štokr, *Collection Czech. Chem. Commun.*, **26**, 1221 (1961).

(19) See ref 12b, p 113.

all but 26 mg was recovered. After sitting 30 min at room temperature, the solid product in the reaction bulb released 21 mg of  $\text{CH}_3\text{CN}$  and 0.02 mmole of gas ( $\text{COF}_2$ ,  $\text{N}_2\text{F}_2$ , and  $\text{NF}_2\text{CFO}$ ). An additional 25 hr at room temperature released 0.035 mmole of gas of similar composition, and 0.015 mmole of gas was pumped off when the solid was then warmed to  $60^\circ$  for a few minutes. In a few minutes at  $75^\circ$  the solid released ca. 3 mg of  $\text{CH}_3\text{CN}$  and 0.20 mmole of gas [ $\text{COF}_2$ ,  $\text{N}_2\text{F}_2$ ,  $\text{NF}_2\text{CFO}$ , and  $(\text{NF}_2)_2\text{CO}$ ], and subsequent heating to  $95^\circ$  liberated 0.08 mmole of gas of similar composition.

**Preparation of  $\text{KOCN}_2\text{F}_6$ (?).**—In a typical reaction 42.3 mg (0.73 mmole) of KF was pretreated with  $(\text{CF}_3)_2\text{CO}$  according to the procedure already described and was then treated with 0.79 mmole of  $\text{NF}_2\text{CFO}$  at  $0^\circ$  for 12.5 hr. Characterization of the residual gas indicated the formation of 0.65 mmole of  $\text{KOCF}_2\text{NF}_2$  (89% conversion). This product was treated *in situ* with 1.58 mmoles of  $\text{NF}_2\text{CFO}$  and 756.3 mg of anhydrous  $\text{CH}_3\text{CN}$  for 52 hr at  $-35 \pm 5^\circ$ . The residual gas in the system, after 28 and 52 hr, respectively, was: 119 mg, 1.53 mmoles, mol wt = 77.8; 118 mg, 1.54 mmole, mol wt = 76.6. On the basis of molecular weight, this gas mixture was estimated to be 1.03 mmoles (68 mg) of  $\text{COF}_2$  and 0.51 mmole (50 mg) of  $\text{NF}_2\text{CFO}$ ; this was qualitatively confirmed by infrared analysis. Consequently the solute (which was not isolated) has the apparent composition (element, mmoles): K, 0.73; O, 0.69; C, 0.69; N, 1.72; F, 3.83; this corresponds to the empirical formula  $\text{K}_{1.1}\text{O}_{1.0}\text{C}_{1.0}\text{N}_{2.5}\text{F}_{5.6}$ . These data are consistent with the assumption that the solute is 0.4 mmole of  $\text{KOCN}_2\text{F}_6$  and 0.3 mmole of  $\text{KOCN}_3\text{F}_6$ .

When this solution was treated with 0.9 mmole of  $\text{NF}_2\text{CFO}$  for 24 hr, the residual gas was found to be 0.3 mmole of  $\text{COF}_2$  and 0.5 mmole of  $\text{NF}_2\text{CFO}$ . Treatment of the resulting solution with 0.9 mmole of  $\text{COF}_2$  for 23 hr yielded 0.7 mmole of  $\text{COF}_2$  and 0.3 mmole of  $\text{NF}_2\text{CFO}$ , and subsequent treatment of the solution with 0.8 mmole of  $\text{NF}_2\text{CFO}$  for 72 hr yielded 0.3 mmole of  $\text{COF}_2$  and 0.5 mmole of  $\text{NF}_2\text{CFO}$ . These values are approximate and were determined by fractional codistillation of the residual gas. This solution of (approximately)  $\text{KOCN}_3\text{F}_6$  was then treated with 1.48 mmoles of  $\text{CF}_3\text{CO}$  for 25.5 hr at  $-35 \pm 5^\circ$ . The residual gas, after separation by fractional codistillation, was 1.47 mmoles of pure  $\text{CF}_3\text{CFO}$ .

$\text{KOCN}_3\text{F}_6$  is deposited as a white solid by evaporation of its acetonitrile solution. It is highly soluble in acetonitrile at  $-40^\circ$  and neither the solid nor solution is stable at room temperature. Its chemistry has not been studied other than to note that in acetonitrile solution at  $-40^\circ$  it reacts rapidly with  $\text{Cl}_2$  and liberates  $\text{NF}_2\text{Cl}$ ,  $\text{NF}_2\text{CFO}$ ,  $\text{NF}_2\text{C(O)Cl}$ , and probably  $(\text{NF}_2)_2\text{CO}$ , although the latter could not be isolated from the gas mixture for positive identification.

**Preparation of  $(\text{NF}_2)_2\text{CO}$ .**—In a 50-ml Pyrex reaction bulb 20.0 mg of KF (0.34 mmole) was pretreated with  $(\text{CF}_3)_2\text{CO}$  according to the procedure already described. It was then treated with 0.39 mmole of  $\text{NF}_2\text{CFO}$  at  $0^\circ$  (no solvent) for 13 hr, and the residual gas [0.08 mmole, essentially  $(\text{CF}_3)_2\text{CO}$  and  $\text{COF}_2$ ], was removed.  $\text{NF}_2\text{CFO}$  (0.16 mmole) and about 0.5 ml of anhydrous  $\text{CH}_3\text{CN}$  were condensed onto the solid ( $\text{KOCF}_2\text{NF}_2$ ) and the reaction was kept at  $-40^\circ$  for 2 hr. The residual gas (after removal from  $\text{CH}_3\text{CN}$ , 0.16 mmole of  $\text{COF}_2$ ) was pumped off at  $-40^\circ$  and the solvent was pumped off at  $0^\circ$  (ca. 10 min). The residue in the bulb was pumped on for 2 min at  $40^\circ$ , whereupon it crystallized to a white solid and liberated 0.02 mmole of gas ( $\text{NF}_2\text{CFO}$  and  $\text{COF}_2$ ) and 0.13 mmole of  $\text{CH}_3\text{CN}$ . The solid was then pyrolyzed by heating the bulb to  $95^\circ$  with a water bath for 2–3 min while pumping the liberated gases through a U trap cooled with liquid nitrogen. (*Caution!* Adequate shielding is necessary, as such a solid occasionally explodes violently when heated.) The trap was then warmed to  $-80^\circ$  and volatile material was distilled out into a storage tube, leaving 0.09 mmole of  $\text{CH}_3\text{CN}$ .

The residual KF in the bulb was then used directly for several subsequent one-step preparations. Typically, 0.50–0.55 mmole of  $\text{NF}_2\text{CFO}$  and 0.5 ml of  $\text{CH}_3\text{CN}$  were condensed in, and after a reaction time of 3–5 hr at  $-40^\circ$  the product was worked up and pyrolyzed exactly as described above. Pretreatment of the KF

with  $(\text{CF}_3)_2\text{CO}$  and preliminary formation of  $\text{KOCF}_2\text{NF}_2$  [to ensure adequate removal of residual  $(\text{CF}_3)_2\text{CO}$  from the system] was used only for "new" KF.

The gas mixtures from two or three pyrolyses were combined for separation by fractional codistillation. Generally, first a small sample of  $\text{NF}_2\text{CFO}$  was put through the apparatus to dry the column, etc. The gaseous products from a typical pyrolysis were: 0.15 mmole of a low-boiling fraction (primarily *cis*- $\text{N}_2\text{F}_2$ ,  $\text{COF}_2$ , and  $\text{CO}_2$ ), 0.17 mmole of  $\text{NF}_2\text{CFO}$ , a trace of  $\text{HNF}_2$ , and 0.05 mmole of  $(\text{NF}_2)_2\text{CO}$ . Based on the estimated content of  $\text{KOCF}(\text{NF}_2)_2$  in the solid, the yield of  $(\text{NF}_2)_2\text{CO}$  appeared to be 25–30%.

The infrared spectrum (20 mm pressure) of  $(\text{NF}_2)_2\text{CO}$  is (in  $\text{cm}^{-1}$ ): 1860 (s), 1150 (m), 978 (s), 926 (vs), 885 (m), 848 (m), doublet, 720 (m), broad. The  $\text{F}^{19}$  nmr spectrum shows a single, broad resonance at  $-30.8$  ppm. The gas density molecular weight was  $131 \pm 1$  (calcd, 132). Infrared analysis indicated that the gas reacts instantly with water vapor at room temperature to form only  $\text{CO}_2$  and  $\text{HNF}_2$ .  $(\text{NF}_2)_2\text{CO}$  (13.4 mg) was hydrolyzed in acidified aqueous KI solution at room temperature. *Anal.* Found: 0.0592 oxidizing equiv (as  $\text{I}_3^-$ )/g. Calcd for  $(\text{NF}_2)_2\text{CO}$ : 0.0606. The pure compound forms a cracked glass at  $-196^\circ$  and boils near  $-20^\circ$  (estimated by fractional codistillation<sup>17</sup>). It may be handled in conventional glass vacuum apparatus and does not attack mercury at room temperature.

**Preparation of  $\text{CsOCF}_2\text{NF}_2$ (?).**—Dehydrated CsF (60.0 mg, 0.39 mmole) was allowed to react with 0.64 mmole of  $\text{CF}_3\text{CFO}$  and 1.85 g of  $\text{CH}_3\text{CN}$  at room temperature for 24 hr. The unreacted gas was 0.30 mmole of  $\text{CF}_3\text{CFO}$ , indicating the formation of 0.34 mmole of  $\text{CsOCF}_2\text{F}_6$ .  $\text{NF}_2\text{CFO}$  (0.39 mmole) was frozen onto this solution, and after being allowed to react 25 hr at  $-40^\circ$ , the solvent was pumped off completely at  $-25^\circ$ . The gas recovered from the reaction (0.40 mmole), after separation by fractional codistillation, was found to be 0.11 mmole of (essentially)  $\text{COF}_2$  and 0.27 mmole of  $\text{CF}_3\text{CFO}$ . The solid product was slowly heated to  $100^\circ$  while pumping but liberated only micromolar amounts of  $\text{COF}_2$ ,  $\text{N}_2\text{F}_2$ ,  $\text{CF}_3\text{CFO}$ , and  $\text{CH}_3\text{CN}$ . It was apparently insoluble in  $\text{CH}_3\text{CN}$  and liberated considerable  $\text{I}_3^-$  from aqueous KI solution.

**Reaction of  $\text{NF}_2\text{CFO}$  with CsF.**—Dehydrated CsF (64.3 mg, 0.42 mmole) was allowed to react with  $\text{NF}_2\text{CFO}$  [106.7 mg, 1.09 mmoles (*PVT*), mol wt = 97.9] and 291.2 mg of anhydrous  $\text{CH}_3\text{CN}$ . After 4 hr at  $-40^\circ$  the CsF had completely dissolved, and after 5.5 hr the gas was removed. On the basis of infrared analysis and molecular weight [46.4 mg, 0.639 mmole (*PVT*), mol wt = 72.6], it was found to be approximately 0.51 mmole (34 mg) of  $\text{COF}_2$  and 0.13 mmole (13 mg) of  $\text{NF}_2\text{CFO}$ . Consequently, the composition of the nonvolatile solute appeared to be (element, mmoles): Cs, 0.42; O, 0.44; C, 0.44; N, 0.95; F, 2.25; this corresponds to the empirical formula  $\text{Cs}_{1.0}\text{O}_{1.0}\text{C}_{1.0}\text{N}_{2.5}\text{F}_{5.2}$ . After this solution was treated with 0.36 mmole (*PVT*) of  $\text{NF}_2\text{CFO}$  for 20 hr at  $-40^\circ$ , the residual gas was separated and found to be a mixture of  $\text{COF}_2$  and  $\text{NF}_2\text{CFO}$  [33.1 mg, 0.390 mmole (*PVT*), mol wt = 84.9] and was estimated to be 0.17 mmole (11 mg) of  $\text{COF}_2$  and 0.22 mmole (22 mg) of  $\text{NF}_2\text{CFO}$ . The net reaction to this point was therefore the consumption of 1.09 mmoles of  $\text{NF}_2\text{CFO}$  by 0.42 mmole of CsF with the formation of 0.67 mmole of  $\text{COF}_2$ . Consequently the composition of the solute now appeared to be (element, mmoles): Cs, 0.42; O, 0.42; C, 0.42; N, 1.09; F, 2.35; this corresponds to the empirical formula  $\text{Cs}_{1.0}\text{O}_{1.0}\text{C}_{1.0}\text{N}_{2.6}\text{F}_{5.6}$ .

**Acknowledgments.**—This work was supported in part by the Advanced Research Projects Agency through a contract monitored by the Office of Naval Research. G. W. F. was a National Science Foundation predoctoral fellow during 1965–1967. The authors wish to thank Mr. B. J. Nist of the University of Washington for some of the nuclear magnetic resonance spectra.