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Organic Fluoronitrogens. XI.[1] Hydroxy Addition Compounds of Fluorimines

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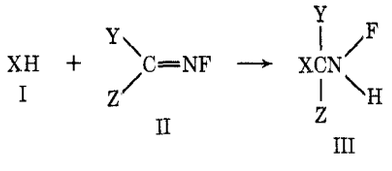
The reaction of *N*-fluorimines with hydroxy compounds yields saturated adducts possessing the NFH function. The adducts undergo a number of reactions depending on structure. These include loss of HF or HNF_2 to give new fluorimines, and fluorination to yield NF_2 derivatives. The addition of alcohols to pentafluoroguanidine (1) followed by fluorination of the resulting adduct affords a high-yield route to $C(NF_2)_3$ compounds.

Recent brief publications[2-4] on addition reactions of *N*-fluorimino (>C=NF) compounds prompted us to describe our rather extensive work in this area. This paper will deal with the addition of OH compounds to *N*-fluorimines and some of the reactions of the adducts; an accompanying paper[5] will consider the addition of NH compounds to *N*-fluorimines.

The *N*-fluorimines to be considered are listed in Table I.[6-9] Most of the reactions and discussion will concern compounds **1** and **4**.

Adducts are formed according to the following general equation.

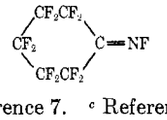


X = RO, R_2C=NO, RCOO, etc.

The ease of addition is a function of the nucleophilicity of the addend I and the structure of the fluorimine II. Methyl alcohol reacts at room temperature with **1**, **2**, and **3**, while heat or a basic catalyst is required to prepare the methyl alcohol adduct of **4** or **5**. Negatively substituted alcohols (*e.g.*, CF_3CH_2OH) and carboxylic acids require a basic catalyst for addition to **1**.

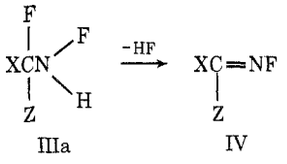
TABLE I

N-FLUORIMINO COMPOUNDS

Compd	Structure	No.	Bp, °C	Ref
Pentafluoroguanidine	$(F_2N)_2C$=NF	1	−2	*a*
Tetrafluoroformamidine	F_2NCF=NF	2	−29	*a*
N-Fluorotetrafluoroethylidine imine	CF_3CF=NF	3	−32	*b*
N-Fluorohexafluoroisopropylidine imine	$(CF_3)_2C$=NF	4	−12	*c*
N-Fluorodecafluorocyclohexylidine imine		5	60	*d*

[a] Reference 6. [b] Reference 7. [c] Reference 8. [d] Reference 9.

The adduct III is stable when Y and Z are perfluoroalkyl groups. For example, $C_2H_5OC(CF_3)_2NFH$ distills at 93–94°.[2] However, if Y (or Z) is F, the adduct III is not isolated; instead, a new fluorimine IV is the product resulting from the elimination of HF from the unstable intermediate IIIa.



To illustrate, when CH_3OH reacts with CF_3CF=NF (**3**) at room temperature, the intermediate adduct is not observed and conversion to $CH_3OC(CF_3)$=NF (**6**) is obtained within 5 min.

If Y (or Z) of III is the NF_2 group, the adducts are more stable than the IIIa type, but loss of HNF_2 may

(1) Previous publication in this series: R. A. Mitsch, *J. Org. Chem.*, **33**, 1847 (1968).

(2) K. N. Makarov, B. L. Dyatkin, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (8), 1924 (1968), describe the addition of alcohols and amines to $(CF_3)_2C$=NF.

(3) D. L. Ross, C. L. Coon, and M. E. Hill, *J. Org. Chem.*, **35**, 3093 (1970), discuss the addition of methanol to $C_3F_7C(NF_2)$=NF and fluorination of the adduct.

(4) A. V. Fokin, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1), 199 (1970), describe the addition of methanol to $(F_2N)_2C$=NF and fluorination of the adduct.

(5) C. D. Wright and J. L. Zollinger, *J. Org. Chem.*, **38**, 1075 (1973).

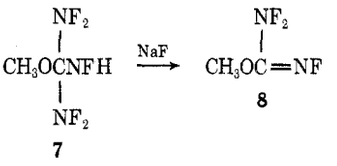
(6) R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967).

(7) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Amer. Chem. Soc.*, **86**, 1827 (1964).

(8) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *ibid.*, **82**, 5831 (1960).

(9) R. A. Mitsch, *ibid.*, **87**, 328 (1965).

also occur. The loss is spontaneous in some cases, but heating or treatment with basic reagents is usually required. For example, $(CH_3)_2CHOH$ and **1** yield a mixture of $(CH_3)_2CHOC(NF_2)_2NFH$ (**13**) and $(CH_3)_2CHOC(NF_2)=NF$ (**14**) in 1 day at room temperature. The adduct **7** (from CH_3OH and **1**) is stable for weeks



7 **8**

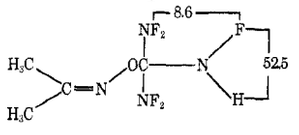
in glass at room temperature, but passage over NaF pellets in a stream of N_2 at about 25° results in complete conversion to methoxytrifluoroformamidine (**8**).

Fluorine and proton nmr spectroscopy were the most useful analytical tools for following the course of reactions and assigning product structures.[10] This is illustrated in Table II for the acetone oxime adduct of **1**.

TABLE II

NMR SPECTRUM OF $(CH_3)_2C=NOC(NF_2)_2NFH$ (**30**)

	Peak	Type	Assignment	Area ratio
Fluorine, ϕ	−20.5	Doublet	NF_2	4
	133.1	Double quintet	NFH	1
Proton, τ	0.90	Doublet	NFH	1
	7.94	Singlet	CH_3	3
	8.02	Singlet	CH_3	3
J values, Hz				



The NFH group is a doublet in both the ^{19}F and ^1H spectra. The wide splitting (52.5 Hz) present in this doublet in both spectra is characteristic of F and H attached to the same atom. The fivefold structure of each of these doublet peaks in the ^{19}F nmr spectrum arises from interaction with the F of the NFH group by the four F atoms of the NF_2 groups. The rather narrow splitting (8.6 Hz) observed is of the expected order of magnitude for F atoms separated by three atoms. The presence of two methyl group peaks in the ^1H nmr spectrum of **30** is expected from the geometry of the molecule.

Table III lists some representative adducts of **1** along with yields and ^{19}F nmr absorptions. Additional reaction details and analytical data are reported in the Experimental Section for selected derivatives listed in Table III. Chemical shifts and spin–spin couplings of most adducts are similar to the values found for **30** discussed above. In many adducts of **1**, however, the NF_2 and NFH absorptions are collapsed into broad singlet peaks and do not show the splittings observed in **30**. It should also be noted that the position of the NFH peak in alcohol adducts of **1** is sensitive to the solvent system. For example, the NFH peak of **7** is at ϕ 144.6 when excess CH_3OH is present and at 138.9 when free of CH_3OH.

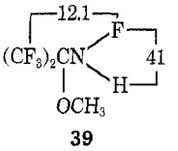
(10) J. P. Freeman in "Advances in Fluorine Chemistry," Vol. 6, J. C. Tatlow, R. D. Peacock, and H. H. Hyman, Ed., Butterworths, London, 1970, p 313.

In addition to the alcohols listed in Table III, C_2H_5OH, n-C_3H_7OH, c-$C_6H_{11}OH$, $OCH_2CH_2CH_2CH_2OH$, $HO(CH_2)_{11}NH_2\cdot HClO_4$, and $HO(CH_2)_9COOH$ also formed adducts with **1** in high yields. Reaction of **1** with $(CH_3)_3COH$ gave no reaction at room temperature and mainly decomposition products on heating or catalysis. The reaction of m-cresol and **1** resulted in an explosion. Negatively substituted phenols gave adducts (**20** and **21**).

Besides the base-catalyzed reaction of CH_3COOH and **1**, HCOOH and C_6H_5COOH also formed addition products. However, CF_3COOH failed to react under similar conditions. Degradation products and byproducts in the reaction of CH_3COOH with **1** included CH_3COF, HNF_2, and $FC(NF_2)_2NFH$ (**38**). The latter compound appears to arise from the addition of HF to **1**. ^{19}F nmr absorptions at ϕ −21.8 (s, 4, NF_2), 133.8 (t, 1, CF), and 136.4 (d, J = 53 Hz, 1, NFH) are consistent with the assigned structure. **38** was observed frequently in reactions involving pentafluoroguanidine (**1**).

The fluorimine **4** did not react with alcohols unless heated or catalyzed. In the presence of trimethylamine, several alcohols and acetone oxime formed saturated addition products in high conversions.

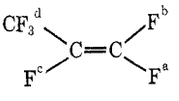
These are listed in Table IV along with yields and ^{19}F nmr data. As in the case with adducts of **1**, the NFH absorption is a complex doublet at high field. The broad doublet splitting is due to the H and the multiplet to the CF_3 groups. The CF_3 groups are split into a doublet by NF. The spin–spin coupling constants (hertz) are shown for **39**.



39

Reaction of lower aliphatic alcohols with **2** or **3** are rapid at room temperature, yielding mainly new fluorimines by loss of HF from the unstable adducts, as discussed earlier. Both syn and anti isomers are obtained in the reaction of **3** with CH_3OH or n-C_4H_9OH. The pure isomers isolated from the CH_3OH reaction by glpc were carefully analyzed. Structure, nmr absorption (ϕ, τ), and splitting (hertz) are shown along with other physical property data in Table V.

The absolute structure assignments for **6a** and **6b** are based on the analogous structure



where J_{ad} = 8.3 and J_{bd} = 21.7 Hz.[11] The corresponding spin–spin coupling constants for **6a** and **6b** are 8.8 and 24.6 Hz, respectively (Table V).

The reaction of CF_3CH_2OH and **3** required pyridine catalysis at room temperature. The major product (67%) was $CF_3CH_2OCF(CF_3)NFH$ (**45**), as evidenced by the characteristic complex multiplet in the ^{19}F nmr at ϕ 138.2 due to NFH and the sharp peak at 130.3 for the CF group. About 33% of the product was $CF_3CH_2OC(CF_3)=NF$ (**46**) (isomer a, probably syn) with ^{19}F

(11) H. M. McConnell, et al., J. Chem. Phys., 24, 479 (1956).

TABLE III
HYDROXY ADDUCTS OF $(F_2N)_2C{=}NF$ (1)[a]

Registry no.	Reactant	Product[b]	No.	Yield,[c] %	Fluorine nmr absorptions, ϕ[d] NF_2	NFH	=NF
67-56-1	CH_3OH	$CH_3OC(NF_2)_2NFH$	7	90	−20.6	138.9	
71-36-3	n-C_4H_9OH	n-C_4H_9OA[b]	9	88	−21.1	138.1	
		n-$C_4H_9OC(NF_2){=}NF$	10	~10	−42.8		44.3
112-53-8	n-$C_{12}H_{25}OH$	n-$C_{12}H_{25}OA$	11	90	−20.8	137.2	
		n-$C_{12}H_{25}OC(NF_2){=}NF$	12	~10	−42.7		44.0
67-63-0	$(CH_3)_2CHOH$	$(CH_3)_2CHOA$	13	61	−21.0	137.4	
		$(CH_3)_2CHOC(NF_2){=}NF$	14	18	−42.6		43.0
100-51-6	$C_6H_5CH_2OH$	$C_6H_5CH_2OA$	15	70	−21.3	137.3	
		$C_6H_5CH_2OC(NF_2){=}NF$	16	10	−42.8		40.6
107-21-1	$HOCH_2CH_2OH$	$HOCH_2CH_2OA$	17	90	−20	142	
	$HOCH_2CH_2OH$[e]	$AOCH_2CH_2OA$	18	80	−21.7	142.2	
75-89-8	CF_3CH_2OH[f]	CF_3CH_2OA	19	60	−21.7	138.5	
120-47-8	p-$C_2H_5OOCC_6H_4OH$[f]	p-$C_2H_5OOCC_6H_4OA$	20	90	−22.0	138.9	
100-02-7	p-$NO_2C_6H_4OH$	p-$NO_2C_6H_4OA$	21	80	−23.2	138.6	
107-07-3	$ClCH_2CH_2OH$	$ClCH_2CH_2OA$	22	70	−21.2	138.9	
556-52-5	OCH_2CHCH_2OH	OCH_2CHCH_2OA	23	90	−20.9	142.3	
107-18-6	$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OA$	24	80	−21	141.7	
107-19-7	$CH{\equiv}CCH_2OH$	$CH{\equiv}CCH_2OA$	25	70	−21.3	142	
46-35-5	CH_3OOCCH_2OH	CH_3OOCCH_2OA	26	80	−21.6	140.7	
1679-53-4	$HOOC(CH_2)_9OH$	$HOOC(CH_2)_9OA$	27	80	−21	143.6	
38092-76-1	$HClO_4 \cdot H_2NCH_2CH_2OH$[e,f]	$HClO_4 \cdot H_2NCH_2CH_2OA$	28	80	−22	141.4	
15588-62-2	$HClO_4 \cdot H_2NOH$[e,f]	$HClO_4 \cdot H_2NOA$	29	30	−31	113	
127-06-0	$(CH_3)_2C{=}NOH$	$(CH_3)_2C{=}NOA$	30	90	−20.5[g]	133.1[g]	
2580-79-2	$+C(NH_2){=}NOH]_2$	$+C(NH_2){=}NOA]_2$	31	80	−22.3	138.3	
1794-86-1	$Cl_2C{=}NOH$[f]	$Cl_2C{=}NOA$	32	80	−23.4	137.5	
31767-13-2	$CH_3OOCCH{=}NOH$	$CH_3OOCCH{=}NOA$	33	70	−22.6	137.6	
5146-68-9	$COCH_2CH_2CONCH_2OH$	$COCH_2CH_2CONCH_2OA$	34	90	−22.0	139.6	
64-19-7	CH_3COOH[h]	CH_3COOA	35	70	−23	132	
7722-84-1	HOOH (98%)	HOOA	36	70	−22.5	139.5	
75-91-2	$(CH_3)_3COOH$[f]	$(CH_3)_3COOA$[i]	37	80	−22.9	140.3	

[a] In a typical reaction, the anhydrous OH reagent was treated with a 10–30% excess of 1 for 1 day at room temperature in a sealed nmr tube, with internal $CFCl_3$ reference, and, if needed, a solvent (usually CH_3CN) and catalyst. [b] The products are nonvolatile liquids or solids. By-products such as HNF_2, $FC(NF_2)_2NFH$ (38), and small amounts of $ROC(NF_2){=}NF$ are not reported. A = $C(NF_2)_2NFH$. [c] Based on ^{19}F nmr analysis of reaction mixture. [d] Chemical shifts are in parts per million relative to $CFCl_3$ as internal reference.[16] Position of NFH peak is sensitive to the solvent system. [e] Large excess of 1. [f] Urea catalyst. [g] See text for detailed nmr analysis. [h] CH_3COOK catalyst, reaction 5 min at 0°. [i] Stable at −78°, unstable at 25°.

nmr peaks at ϕ 38.3 (=NF), 71.3 (CCF_3), and 76 (CH_2CF_3) in appropriate ratios. A weak absorption at ϕ 67.8 (CCF_3) may be due to a small amount of isomer b.

The reaction of CH_3OH and **2** gave a rapid room-temperature conversion to the same isomer of the fluorimine **8** as obtained from the reaction of the adduct **7** and NaF (above), by elimination of HF from the unstable intermediate adduct.

$$\underset{\mathbf{2}}{F_2NCF{=}NF} + CH_3OH \longrightarrow [CH_3OCF(NF_2)NFH] \xrightarrow[66\%]{-HF} \underset{\mathbf{8}}{CH_3OC(NF_2){=}NF}$$

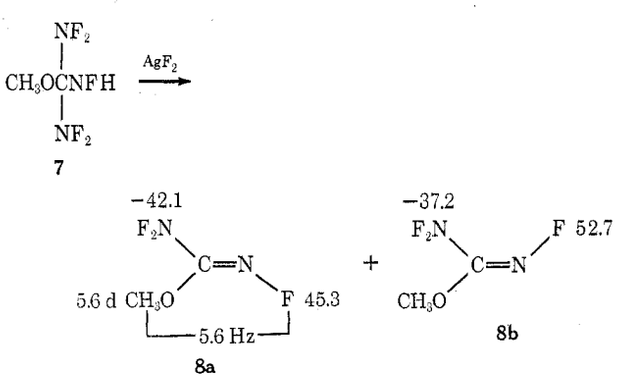
Other products isolated in this reaction include CH_3OCONF_2 (7%) and $(CH_3O)_2C{=}O$ (15%). These products are apparently derived from **8** *via* successive hydrolysis and methanolysis steps.

$$\underset{\mathbf{8}}{CH_3OC(NF_2){=}NF} \xrightarrow{H_2O} CH_3O\overset{O}{\overset{\|}{C}}NF_2 \xrightarrow{CH_3OH} CH_3O\overset{O}{\overset{\|}{C}}OCH_3$$

The reaction of isopropyl difluorocarbamate with isopropyl alcohol to yield diisopropyl carbonate has been reported.[12a]

(12) (a) V. Grakauskas and K. Baum, *J. Amer. Chem. Soc.*, **91**, 1679 (1969); (b) R. A. Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *J. Heterocycl. Chem.*, **2**, 371 (1965).

Reactions of Adducts. Conversion to Fluorimines.—The most characteristic reaction of fluorimine adducts derived from **1**, **2**, or **3** is loss of HF or HNF_2 to yield new fluorimines, *e.g.*, **6**, **8**, and **14**. As noted in the earlier discussion, these derivatives may form spontaneously, by heating or by treatment with basic reagents. As described earlier, only one geometric isomer of **8** (**8a**) was formed when **7** was passed over a

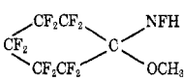


bed of NaF pellets or **2** was treated with CH_3OH. However, when **7** was treated with AgF_2 at 0°, both syn and anti isomers were obtained.

Isomer a, compound **8a**, has been assigned the syn ($CH_3O/{=}NF$) configuration shown on the basis of a com-

TABLE IV

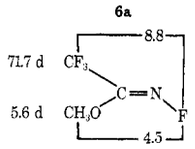
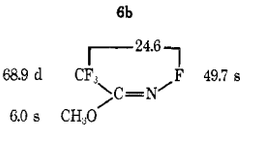
ADDUCTS OF 4[a] AND 5[b]

Fluorimine	Reactant	Product	No.	Yield, %	^{19}F Nmr spectra, ϕ[c] CF$_3$	NFH
4	CH_3OH	$(CF_3)_2C(OCH_3)NFH$	39	80	73.6	143.4
4	$(CH_3)_2CHOH$	$(CF_3)_2C[OCH(CH_3)_2]NFH$	40	70	73.8	142.8
4	n-C_4H_9OH	$(CF_3)_2C(OC_4H_9)NFH$	41	100	73.7	144.6
4	$(CH_3)_2C{=}NOH$	$(CF_3)_2C[ON{=}C(CH_3)_2]NFH$	42	100	72.8	140.6
4	CF_3CH_2OH[d]	$(CF_3)_2C(OCH_2CF_3)NFH$	43	80	76.5 82.2 (CF_3CH_2)	138
5	CH_3OH[b]		44	60	110–145 (ring)	150[e]

[a] Reactions were run overnight at room temperature in sealed glass nmr tubes with excess of OH reagent, plus $(CH_3)_3N$ catalyst and $CFCl_3$ solvent (except as noted in d). [b] Run as in a, except no catalyst and reaction heated for 16 hr at 53°. [c] NFH absorption may be a few parts per million high because of excess OH compound; see text. [d] CH_3CN solvent. No adduct with $CFCl_3$ solvent. [e] ^{1}H nmr peaks: τ 1.5 (NH), 6.2 (CH_3).

TABLE V

PROPERTIES OF THE ISOMERS OF 6

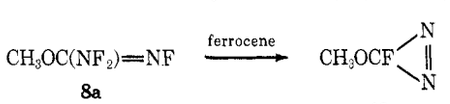
No.	6a	6b
Structure and nmr (ϕ, τ)		
Isomer	a	b
Config	syn	anti
Ratio	1	3
T_R[a]	336	370
Bp, °C[b]	47	50
Mp, °C	−96	−90
Ir, μ (C=N)	6.09	6.01
Mol wt[c]	150	152

[a] Relative to $CFCl_3$ = 100 on column C (Experimental Section) at 50°. [b] Extrapolated to 760 mm from vapor pressure data. [c] From mass spectral effusion rates on m/e 76. Formula weight = 145. (See Experimental Section for elemental analysis and mass spectral data.)

parison of the nmr spectral data (ϕ, τ) with that given for the syn (CH_3O/=NF) isomer of $CF_3C(OCH_3)$=NF (**6**) (Table V). The ^{1}H nmr peaks for CH_3 in **6a** and **8a** are both doublets (split by F in C=NF) and are identical in chemical shift (τ 5.6) and nearly identical in coupling constants (4.5 *vs.* 6 Hz). ^{19}F nmr absorptions for F in the C=NF group also give support for the assigned structures. The syn isomers **6a** and **8a** have peaks at ϕ 46.7 and 45.3, respectively, while both the anti isomers **6b** and **8b** have absorptions at a slightly higher field, ϕ 49.7 and 52.7, respectively. Additional data on these isomers are reported in the Experimental Section.

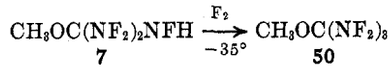
A partial conversion to the two geometric isomers of $CF_3CO_2CH_2CH_2OC(NF_2)$=NF (**47**) formed during gas chromatography of $CF_3CO_2CH_2CH_2OC(NF_2)_2NFH$ (**48**) (from **17** and trifluoroacetic anhydride) at 100°. Most of **48** survived this separation procedure.

The alkoxy trifluoroformamidine compounds undergo the reductive defluorination cyclization reaction described by Mitsch.[1] This is illustrated by the conversion of **8a** to fluoromethoxydiazirine (**49**) in 90% yield.



The characterization of **49** has been reported,[12b] but the synthetic route has not been described before.

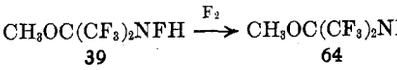
Fluorination. Preparation of Tris(difluoroamino)-methyl Compounds.—A very general reaction of fluorimine adducts containing the NFH group is fluorination with elemental fluorine to convert this function to the NF_2 group. Under suitable conditions (dilute F_2, low temperature, solvents) good conversion to the corresponding NF_2 compound is obtained with no replacement of other H atoms in the molecule by F. Adducts of **1** are converted by this process to compounds containing the highly fluorinated tris(difluoramino)methyl, $C(NF_2)_3$, group. For example see below.



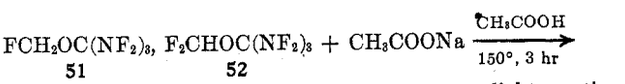
The ^{19}F *nmr spectrum* of **50** shows only a single broad peak at ϕ −22.2. More concentrated F_2 and higher temperatures yield, in addition to **50**, the more highly fluorinated compounds $FCH_2OC(NF_2)_3$ (**51**) and $F_2CHOC(NF_2)_3$ (**52**). The presence of F atoms in the methyl group shifts the ^{19}F nmr peaks (NF_2) to lower field: ϕ −23.5 for **51** and −24.5 for **52**.

The preparation of several $C(NF_2)_3$ compounds is summarized in Table VI. Fluorination conditions, yields, and ^{19}F nmr chemical shifts are given. Purification was effected by glpc or column chromatography (solids). Additional data and analytical results are reported in the Experimental Section.

Fluorination of **39** gave the NF_2 derivative **64**, a liquid, bp 63°.



In contrast with the relatively unstable alcohol adducts of **1**, the $C(NF_2)_3$ derivatives have remarkably good stability if protected from reducing agents. For example, thermal stability is indicated by the isolation of $(F_2N)_3COCH_2CH_2OC(NF_2)_3$ (**54**) by chromatography at 100°. Chemical stability is illustrated by the sealed-tube reactions of mixtures of **50**, **51**, and **52** shown below.


slight reaction

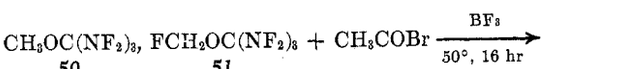

no reaction

TABLE VI

TRIS(DIFLUORAMINO)METHYL COMPOUNDS FROM THE FLUORINATION OF PENTAFLUOROGUANIDINE (1) ADDUCTS[a]

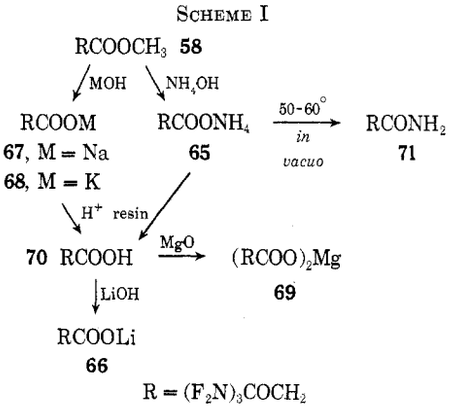
Fluorination			Product			
Adduct[b]	% F_2[c]	Temp range, °C	Formula[d]	No.	Yield, %	^{19}F nmr, ϕ, NF_2
7	2.7	−35	$CH_3OC(NF_2)_3$	50	30	−22.2
7	4.3	−20	CH_3OT[d]	50	10	−22.2
			FCH_2OT	51	30	−23.5
			F_2CHOT	52	25	−24.5
17	6	−20 to −10	$HOCH_2CH_2OT$	53	70	−23.6
18	5	−23 to 25	$TOCH_2CH_2OT$	54	80	−23
23	8	−20	OCH_2CHCH_2OT	55	70	−23.1
22	3	−45	$ClCH_2CH_2OT$	56	70	−23.1
34	5	−23 to 25	$COCH_2CH_2CONCH_2OT$	57	80	−24.3
26	5	0	CH_3OOCCH_2OT	58	80	−23.1
28	4	−23 to 0	$HClO_4 \cdot H_2NCH_2CH_2OT$	59	80	−24.0
33	3	−23 to 25	$CH_3OOCCH{=}NOT$	60	70	−24.0
30	3	−35	$(CH_3)_2C{=}NOT$	61	70	−24.4
			$FCH_2C(CH_3){=}NOT$	62	Small	−26.2
32	10	−30	$Cl_2C{=}NOT$	63	35	−25.2

[a] Fluorinations were conducted in CH_3CN or CF_3CH_2OH solvent in most cases. Adducts 7 and 30 were fluorinated without solvent [b] From Table III. [c] Diluted with N_2. [d] T = $C(NF_2)_3$.

Heating a mixture of **50** and **51** with $AlCl_3$ at 150° for 16 hr caused the decomposition of **50**, but **51** survived, apparently owing to its lower electron density at the ether oxygen when compared with **50**. *Caution.* Although moderate thermal and chemical stability is indicated by the above information, these $C(NF_2)_3$ compounds are still powerful oxidizing agents and are also sensitive to impact. (See Experimental Section.)

Tris(difluoramino)methyl compounds possessing other reactive functional groups have been subjected to a number of chemical reactions with high retention of the $C(NF_2)_3$ structure. Methyl [tris(difluoramino)-methoxy]acetate (**58**) has been transformed to the free acid and several of its salts. Heating the ammonium salt afforded the corresponding amide. These reactions are shown in Scheme I. Except for amide

SCHEME I



formation all reactions were run at room temperature, usually in alcohol or water. Further data are reported in Table IX.

Reaction of $(F_2N)_3COCH_2CH_2OH$ (**53**) with $(CF_3CO)_2O$ gave a good conversion to the trifluoroacetyl derivative **72**.

The perchlorate salt **59** (Table VI) was readily converted to the free amine $(F_2N)_3COCH_2CH_2NH_2$ (**73**) by reaction with base. Other salts were prepared by neutralization of **73** with the appropriate acid. In this manner, salts containing the following anions were prepared: Cl^-, Br^-, NO_3^-, HF_2^-, SO_4^{2-}, and $C_2O_4^{2-}$. In addition to these, a salt, mp 83–88°, bearing the $C(NF_2)_3$ group in both cation and anion was prepared. (See Table X).

$$59 + 68 \xrightarrow{CH_3OH} (F_2N)_3COCH_2CH_2NH_3^+ {}^-OOCCH_2OC(NF_2)_3 + KClO_4$$
79

The Cl atoms in $(F_2N)_3CON{=}CCl_2$ (**63**) were easily displaced by nucleophilic reagents. Thus, reaction with $(CH_3)_2NH$ at 25° gave the corresponding bis(dimethylamino) compound (nmr and ir), and treatment with $NaOCH_3$ afforded the expected methoxy derivative **80**.

$$63 + NaOCH_3 \xrightarrow[6\text{ hr, }25°]{CFCl_3} (F_2N)_3CON{=}C(OCH_3)_2$$
80

Other Adduct Reactions.—Heating the adduct **39** with acetic anhydride at 80–90° gave no evidence for formation of the *N*-acetyl derivative. Instead, a gradual conversion to the starting imine **4** and methyl acetate took place, indicating that an equilibrium exists between **39** and the starting materials which is shifted to the left as CH_3OH forms the acetate.

$$(CF_3)_2C{=}NF + CH_3OH \rightleftharpoons CH_3OC(CF_3)_2NFH$$
4 **39**

Reaction of **7** with acetyl chloride or Cl_2 in a sealed tube at room temperature gave a partial conversion to a chloro compound **81**. Methyl acetate was a by-product in the first reaction. Cleavage of ethers by acid chlorides to yield esters and alkyl chlorides is

$$CH_3OC(NF_2)_2NFH + CH_3COCl \longrightarrow \underset{7}{} \qquad ClC(NF_2)_2NFH + CH_3COOCH_3$$
81

known;[13] however, zinc chloride was required as catalyst. ^{19}F nmr absorptions for **81** are at ϕ − 31.2 (NF_2) and 107.4 (NFH), the latter a double quintet, in

(13) R. C. Fuson, "Advanced Organic Chemistry," Wiley, New York, N. Y., 1950, p 178.

an area ratio of 4:1. The presence of Cl shifts the F peaks to lower field. The related compound $ClCF(NF_2)_2$, prepared from **38** and NO_2Cl, has NF_2 absorptions in the same region as **81**, ϕ − 30.9.[14] The adduct **7** reacts with gaseous formaldehyde in acetonitrile to give an 80% conversion to a mixture of the methylol and methylene derivatives in a ratio of about 2:1.

$$7 + CH_2O \xrightarrow[CH_3CN]{25^\circ} CH_3OC(NF_2)_2NFCH_2OH\ (\mathbf{82}) + [CH_3OC(NF_2)_2NF]_2CH_2\ (\mathbf{83})$$

A broad singlet peak in the ^{19}F nmr at ϕ − 23 was assigned to NF_2 of **82** and **83**, and absorptions at 85 and 79, both triplets ($J \cong 40$ Hz) with finer splittings ($J \cong 12$ Hz), were attributed to NF of **82** and **83**, respectively. Analogous reactions have been reported[12] for the *N*-fluorourethane, $C_2H_5OCONFH$. The resulting methylol derivative $C_2H_5OCONFCH_2OH$ has a ^{19}F nmr chemical shift for the NF group of ϕ 75, a triplet with $J = 32$ Hz, position and splittings in reasonable agreement with the values found for NF of **82**.

Reaction of **7** with NOF, CF_3COONO, or NO_2Cl resulted in the replacement of the NFH group with F to yield $CH_3OCF(NF_2)_2$ (**84**), with ^{19}F nmr peaks at ϕ

$$CH_3OC(NF_2)_2NFH\ (\mathbf{7}) \xrightarrow[-78^\circ]{NOF} CH_3OC(NF_2)_2N(NO)F \xrightarrow{25^\circ} CH_3OCF(NF_2)_2\ (\mathbf{84})$$

$$7 \xrightarrow[25^\circ]{NO_2Cl} CH_3OC(NF_2)_2N(NO_2)F \longrightarrow \mathbf{84} + CH_3OC(NF_2)_2NFCl\ (\mathbf{85})$$

− 18.9 (NF_2) and 120 (CF). The suspected unstable intermediates in these reactions are the NNO and NNO_2 compounds shown.

In the reactions of NOF with **7**, a stable blue color (due to the NNO intermediate) formed immediately at −78°, but, on warming to room temperature, the reaction mixture became irreversibly colorless and **84** was present. A second product in the NO_2Cl reaction was tentatively identified as $CH_3OC(NF_2)_2NFCl$ (**85**), ^{19}F nmr ϕ − 24.8 (NF_2) and 9.7 (NFCl). A similar chemical shift, ϕ 7.9, has been reported[15] for NFCl in the compound CF_3NFCl.

Experimental Section

Precautions.—Some of the fluoronitrogen compounds described in this paper are shatteringly explosive under certain conditions. All adducts and fluorinated adducts of **1** should be considered explosive, while derivatives of **3**, **4**, and **5** are less sensitive. Suitable protective equipment should be used during all phases of work with **1** and its derivatives. In regard to these latter compounds, we have operated within a quantity limit of 1 g in borosilicate glass vessels using poly(methylmethacrylate) shielding panels, face shields, ear plugs, and heavy leather gloves and jackets. For quantities greater than 1 g, remote handling is recommended. Some liquid products have exploded during phase changes (freezing, thawing, distillation) and impact. Besides exploding on impact, solids derived from **1** are also sensitive to abrasion or grinding. Although liquid nitrogen and liquid oxygen have been used as coolants for the transfer of small quantities of volatile fluoronitrogen compounds under vacuum, the use of nonflammable slush baths ($CFCl_3$, CCl_4, etc.) with temperatures above the melting point of the compound or mixture are preferred. A previous paper[6] in this series should be consulted for further precautions.

General.—The fluorimines **1** and **2** were prepared by the procedures reported.[6] The other fluorimines (**3**, **4**, and **5**) were synthesized by the reductive defluorination[9] of the appropriate difluoramino precursors or, in the case of **4**, the dehydrofluorination of a new compound, $(CF_3)_2CFNFH$ (**86**). Liquid alcohols were either distilled or predried over anhydrous $CaSO_4$ or molecular sieves. Other hydroxy compounds were commercial reagent chemicals or were synthesized and purified as required and noted in the appropriate experiment. Fluorine was obtained from the General Chemical Division of Allied Chemical Corp.

Nmr spectra were measured on a Varian V-4300-2 instrument operating at 40.0 MHz. Values for ^1H chemical shifts are given in τ units with respect to $(CH_3)_4Si$ as an internal reference, and values for the ^{19}F chemical shifts, employing $CFCl_3$ as internal reference, are given in ϕ units.[16] Infrared spectra were recorded by means of a Perkin-Elmer double-beam spectrophotometer, Model 21. A Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer was used to obtain the mass spectra and molecular weights by effusion rate measurements. An ionization potential of 70 eV and an ionization chamber temperature of 250° were employed. Gas–liquid partition chromatographic (glpc) analyses and separations were carried out on a Perkin-Elmer vapor fractometer, Model 154-D, equipped with a thermistor detector and modified gas sampling and back flush valves. Dry helium was used as the carrier gas. The various nitrogen–fluorine compounds eluting from the columns were collected in flame-dried borosilicate glass traps cooled with liquid nitrogen or appropriate nonflammable slush baths. Columns used for glpc are listed in Table VII.

TABLE VII
GAS CHROMATOGRAPHY COLUMNS

Column	Liquid phase	%	Support	Length, ft	Diameter, in.
A	LSX-30295[a]	20	Celite[b]	10	0.5
B	FS-1265[a]	20	Fluoropak 80[c]	3.3	0.5
C	FS-1265	33	Chromosorb P[b]	24	0.25
D	FS-1265	20	Chromosorb P	15	0.5
E	FS-1265	30	Anakrom ABS[d]	6	0.375
F	KF-8126[e]	33	Chromosorb P	6.5	0.5
G	KF-8126	33	Chromosorb P	18	0.5
H	SE-30[f]	20	Celite	10	0.25
I	SF-96[f]	25	Anakrom ABS	6.5	0.5
J	FC-45[e]	25	Celite	6.5	0.5

[a] Dow Corning. [b] Johns-Manville. [c] The Fluorocarbon Co. [d] Analab Co. [e] 3M Co. [f] General Electric Co.

Relative retention times (T_R) for compounds isolated by glpc were calculated according to the following equation.

$$T_R = (T_{compound} - T_{air})/(T_{ref} - T_{air}) \times 100$$

Elemental analyses were carried out using published procedures.[17] Analysis of some compounds proved difficult because of explosions and problems encountered in purifying unstable materials. In these cases, structure determinations were based upon nmr, ir, and mass spectral data.

Adducts of Pentafluoroguanidine (1) and Other Fluorimines.—Approximate yields and some ^{19}F nmr absorptions are presented in Table III for derivatives of **1** and in Table IV for derivatives of **4** and **5**.

Apparatus and Procedure.—On a small scale (0.05–0.2 g), the addition compounds were prepared in the borosilicate glass tubes (~1.5 ml capacity) used for nmr spectroscopy. In a typical reaction, the dry reactant, catalyst (if needed), solvent (if used), and $CFCl_3$ containing $Si(CH_3)_4$ (nmr internal reference compounds)

(14) D. H. Dybvig (3M Co.), U. S. Patent 3,358,028 (1967).
(15) J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *Inorg. Chem.*, **6**, 417 (1967).
(16) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959); G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).
(17) P. B. Olson and R. E. Kolb, *Michrochem. J.*, **12**, 117 (1967); P. B. Olson and R. T. Knafla, *ibid.*, **13**, 362 (1968); J. G. Gagnon and P. B. Olson, *Anal. Chem.*, **40**, 1856 (1968).

were placed in the nmr tube. Then 1, or other fluorimine, was added by vacuum transfer employing a liquid nitrogen bath (−196°) or a $CFCl_3$ slush bath (−110°). The latter bath is recommended for quantities of 1 over 0.2 g, since this fluorimine (mp −148°) frequently explodes during phase changes, as mentioned above. The tube was sealed off with a flame and the reaction mixture was allowed to warm over a period of several minutes to the desired reaction temperature (usually room temperature, ~25°) and maintained for the appropriate length of time. Heating was sometimes required. The course and extent of reaction was conveniently followed by fluorine nmr spectroscopy.

On a larger scale (0.5–1.0 g), a 2.5-cm diameter glass reactor of approximately 10 ml capacity, fitted with a poly(tetrafluoroethylene) needle valve was employed. A small poly(tetrafluoroethylene) coated magnetic stirring bar was often used in this reactor.

Reactions of adducts and their derivatives were also carried out in the glass reaction tubes described above.

Fluorination Apparatus and Procedure.—Method A: The adduct, essentially free of solvent, was placed in a shallow copper vessel in a 0.4-l. copper reactor. The reactor was purged with dry nitrogen and cooled to the desired temperature, and fluorine, diluted with nitrogen, was passed over the adduct. The effluent gas stream was conducted through copper tubing and (generally) a tube containing NaF pellets to remove HF, and then into a glass trap cooled with liquid air or oxygen where products were collected.

Method B: The apparatus consisted of a glass nmr tube having a 2.5-cm diameter glass bulb approximately 12.5 cm from the bottom, the latter connected to a poly(tetrafluoroethylene) needle valve through the center of which was inserted a poly(chlorotrifluoroethylene) capillary extending down into the nmr tube portion of the reactor. The fluorimine adduct (in trifluoroethanol or acetonitrile solvent) in the reactor was usually cooled to −24° with a CCl_4 slush bath; then fluorine gas (25–100% in excess of theoretical), diluted with nitrogen, was continuously recirculated through the solution at atmospheric pressure by means of a diaphragm-activated pump. The cooling bath was allowed to warm slowly to room temperature during the fluorination.

Method C: The reactor was either borosilicate glass or poly(chlorotrifluoroethylene) of 10 to 30 ml capacity in which a solution (acetonitrile) of the adduct was placed. The dilute (nitrogen) fluorine stream was passed into the cooled reaction mixture and the effluent gases were collected as in method A.

Methoxybis(difluoramino)fluoraminomethane (7).—Anhydrous methyl alcohol (0.057 g, 1.8 mmol) and 1 (0.48 g, 0.33 mmol) were condensed in a glass nmr tube (as described above). The sealed tube was allowed to stand at room temperature for 20 hr. Fluorine and proton nmr analyses revealed complete reaction of 1 with methyl alcohol to give the adduct 7, a liquid with vapor pressure of 11 mm at 22°. The ^{19}F nmr spectrum has only a singlet peak (area 4) at ϕ − 20.6 (NF_2) and a double quintet (area 1) centered at 138.9 (NFH), J_{FF} = 8.4, J_{HF} = 54.2 Hz. The proton nmr spectrum shows a singlet at τ 6.0 (CH_3O). The infrared spectrum of the adduct possesses the following peaks: 3.04 (m) NH, 3.38 (w) CH, 6.84 (m), 7.06 (m), 7.70 (s), 8.00 (m), 8.82 (m), 9.65–11.36 μ (vs) NF.

A sample was purified by glpc on column B at 25° (T_R = 3750, CH_2Cl_2 = 100). Some CH_3OH was present as an impurity (ir).

Anal. Calcd for 87% $C_2H_4F_5N_3O$·13% CH_3OH: C, 16.6; F, 45.7. Found: C, 16.5; F, 45.6.

Reaction of 7 with Metal Fluorides. Methoxytrifluoroformamidine (8).—The above adduct 7, prepared from 88 mg (2.74 mmol) of methyl alcohol and 0.45 g (3.0 mmol) of 1, pumped free of excess 1, was cooled to −110° under vacuum and then allowed to warm slowly to room temperature while the vapors were conducted through an evacuated U tube containing about 25 g of powdered anhydrous sodium fluoride. The resulting product gases were conducted into two evacuated traps connected in series, cooled to −78 and −110°, respectively. The −78° trap on warming was found to contain 1.9 mmol of 8 (isomer a) and the −110° trap contained an equivalent amount of difluoramine.

This same isomer was obtained in 66% yield by the reaction of the fluorimine 2 with CH_2OH (0.5 hr, 25°). Other reaction products isolated by glpc in this latter reaction were CH_3OCONF_2[18] (7%) and $(CH_3O)_2C{=}O$ (15%).

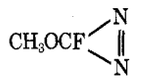
Both geometric isomers of 8 were obtained when 0.09 g (0.5 mmol) of 7 was charged to a 20-ml glass tube cooled to −78° containing 0.16 g of AgF_2. The tube was closed and allowed to warm gradually to 0° and kept there for 1.5 hr. The volatile reaction products were HNF_2, N_2F_4, and the syn and anti isomers of 8. The isomers were separated by glpc on column D at 60°. Properties are reported in Table VIII.

TABLE VIII
PROPERTIES OF $CH_3OC(NF_2){=}NF$ (8)

No.	Compd 8a	Compd 8b	Assignment
Isomer	a	b	
Configuration[a]	syn	anti	
Vapor pressure, 25°	72 mm		
Mol wt[b]	125		
^{19}F nmr, ϕ	−42.1	−37.2	$-NF_2$
	45.3	52.7	$=NF$
^1H nmr, τ	5.95 d (J = 3.5 Hz)		CH_3
Infrared spectra, μ	3.37	3.38	CH
	5.94	6.05	C=N
	7.93	7.51	COC
	10.97, 11.36	10.17, 11.27	NF and NF_2
T_R ($CFCl_3$ = 100)	804	686	
Analysis	c		

[a] $CH_3O/{=}NF$. [b] By mass spectral effusion rates. Theory, 128. [c] Calcd for $C_2H_3F_3N_2O$: C, 18.8; F, 44.5. Found: C, 19.2; F, 45.7.

Reaction of 8 with Ferrocene. Fluoromethoxydiazirine (49).—A mixture of 64 mg (0.05 mmol) of 8 (syn), 93 mg (0.50 mmol) of $C_{10}H_{10}Fe$, and 1.0 ml of xylene hexafluoride was stirred for 1 hr at 25°. The reaction mixture was fractionated under vacuum through traps at −35 and −196° connected in series. The −196° traps contained 0.47 mmol (92%) of almost pure 49. The compound was purified by glpc at room temperature on column F.



49

Elemental and spectral analyses, along with some chemical properties, have been reported.[7]

Reaction of 7 with NOF and CF_3COONO. Methoxybis(difluoramino)fluoromethane (84).—In a glass nmr tube containing 54 mg (0.30 mmol) of 7 and 0.08 ml of $CFCl_3$ was added 0.4 mmol of nitrosyl fluoride (from reaction of N_2F_4 and N_2O_4 at 25°) and the tube was sealed. A pale purple solution formed at once on mixing the reactants at −78°. The solution became colorless on warming to room temperature. The ^{19}F nmr spectrum, run within 1 hr, showed, besides a small amount of unreacted 7, absorptions at ϕ − 18.9 and 120.0 (ratio 4:1) assigned to NF_2 and F of $CH_3OCF(NF_2)_2$ (84), respectively. The ^1H nmr spectrum had one peak at τ 6.06 due to CH_3. This compound was also formed by the reaction (1 day at 0°) of 7 with excess trifluoroacetyl nitrite and as one of the products in the reaction (1.5 hr at 25°) of nitryl chloride and 7. The other nonvolatile product of the latter reaction may be $CH_3OC(NF_2)_2NFCl$ (85). ^{19}F nmr peaks are at ϕ − 24.8 (NF_2) and 9.7 (NF) in 4:1 ratio, ^1H nmr τ 5.93 (OCH_3).

A sample of 84 was purified by glpc using column A at 25° (T_R = 402, $CFCl_3$ = 100).

Anal. Calcd for $C_2H_3F_5N_2O$: C, 14.5; F, 57.2; mol wt, 166. Found: C, 14.2; F, 53.2; mol wt, 149 (by mass spectrometer effusion studies.) Some principal ions from mass spectral analysis include, m/e, ion (rel intensity), 15, CH_3^+ (150); 31, CH_3O^+ and/or CF^+ (76); 52, NF_2^+ (5); 62, $C_2H_3FO^+$ (10); 81, $C_2H_3F_2O^+$ (17); and 114, $C_2H_3F_3NO^+$ (9.8).

Heating 84 for 4.5 hr at 115° in anhydrous HBr (38% in acetic acid) caused only slight decomposition (nmr).

Reaction of 7 with Cl_2 or CH_3COCl. Chlorobis(difluoramino)fluoraminomethane (81).—Reaction of 54 mg (0.3 mmol) of 7 with 0.40 mmol of Cl_2 gas in a sealed nmr tube with 0.08 ml of $CFCl_3$ for 16 hr at 25° gave a partial conversion to a product identified as $ClC(NF_2)_2NFH$ (81): nmr ϕ − 31.2 (s, 4, NF_2), 107.4 (d, J_{FH} = 51 Hz, quintet, J_{FF} = 5.3 Hz, 1, NFH); τ 0.35 (d, J_{FH} = 50 Hz, NFH).

(18) R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 3912 (1961).

A similar reaction with acetyl chloride (2 hr, 25°) also gave a partial conversion to **81** plus methyl acetate.

Reaction of 7 with Formaldehyde. Methoxybis(difluoramino)hydroxymethylfluoraminomethane (82). Bis[methoxybis(difluoramino)methylfluoramino]methane (83).—Excess gaseous formaldehyde, produced by heating paraformaldehyde in mineral oil, was swept with a N_2 stream into a reactor containing a stirred solution of the adduct **7** (0.45 g, 2.5 mmol) in 1 ml of CH_3CN at 25°. After 0.5 hr, a liquid–solid mixture was present. The solid was paraformaldehyde (ir). ^{19}F nmr analysis of the liquid phase indicated an 80% conversion to a mixture of the methylol derivative **82**, $CH_3OC(NF_2)_2NFCH_2OH$, and the methylene compound **83**, $[CH_3OC(NF_2)_2NF]_2CH_2$, in a 2:1 ratio. ^{19}F nmr peaks were at ϕ − 23.0 (s, 8, NF_2 of **82** and **83**), 79.0 (t, $J \cong 40$ Hz, m, $J \cong 12$ Hz, 1, $NFCH_2NF$), 85.0 (t, $J \cong 39$ Hz, m, $J \cong 12$ Hz, 1, $NFCH_2OH$).

Fluorination of 7. Methoxytris(difluoramino)methane (50).—Employing method A, 0.8 g (4.4 mmol) of **7** was fluorinated with 80 mmol of F_2 (2.7% in N_2) at −35° over a period of 3 hr. The product, isolated from the −183° trap, was mainly $CH_3OC(NF_2)_3$ (**50**). This compound is a colorless, mobile liquid with a vapor pressure of about 70 mm at 25° [extrapolated bp ~75° (lit.[4] bp 70–71°)], mol wt calcd 199, found (mass spectral effusion rate) 193. The ^{19}F nmr spectrum has a single peak at ϕ − 22.2 (lit.[4] −24.2, external CF_3COOH reference), ^1H nmr τ 5.87 (CH_3). The infrared spectrum has absorptions at 3.35 (w), CH, 6.82 (m), 7.83 (s), 9.6–11.2 μ (s) NF.

This ether (**50**) did not react with $AlCl_3$ or 100% H_2SO_4 at room temperature, but decomposed slowly on warming (50–70°) with these reagents.

Fluoromethoxytris(difluoramino)methane (51) and Difluoromethoxytris(difluoramino)methane (52).—Again employing method A, 1.0 g (0.55 mmol) of **7** was fluorinated at −20° with 60 mmol of F_2 (4.3% in N_2) to yield the following distribution of products: 10% **50**, 30% $FCH_2OC(NF_2)_3$ (**51**), and 25% $F_2CHOC(NF_2)_3$ (**52**). The compounds were isolated by glpc on column A at 25°. T_R ($CFCl_3$ = 100) values: **50**, 637; **51**, 676; **52**, 310. Nmr: **51**, ϕ − 23.5 (s, 6, NF_2), 149.3 (t, J = 49.2 Hz, 1, FCH_2–), τ 4.16 (d, J = 49.2 Hz, FCH_2); **52**, ϕ −24.5 (s, 3, NF_2), 80.6 (d, J = 68.3 Hz, 1, F_2CH–), τ 3.04 (t, J = 68.3 Hz, F_2CH–). The mass spectrum of **52** includes these fragments, *m/e*, ion (rel intensity): 31, CF^+ (5.8); 33, NF^+ (5.0); 51, CHF_2^+ (100); 52, NF_2^+ (4.9); 80, CNF_2O^+ (3.6); 112, $C_2HF_3NO^+$ (0.7); 168, $CF_6N_3^+$ (0.9); 184, $CF_6N_3O^+$ (0.1).

2-(Hydroxy)ethoxybis(difluoramino)fluoraminomethane (17).—Ethylene glycol (0.32 g, 5.1 mmol), 3 ml of CH_3CN, and 0.76 g (5.1 mmol) of **1** were stirred overnight at room temperature. Most of **1** was consumed. The reaction mixture was analyzed by nmr: ϕ − 20 (s, 4, NF_2), 142 (d, 1, J = ~50 Hz, NFH); τ − 0.5 (d, 1, J = ~53 Hz, NFH), 5.6 (t, 2, CH_2OC), 6.25 (d, 2, CH_2OH), all consistent for $HOCH_2CH_2C(NF_2)_2NFH$ (**17**).

Reaction of 17 with Trifluoroacetic Anhydride. 2-(Trifluoroacetoxy)ethoxybis(difluoramino)fluoraminomethane (48) and 2-(Trifluoroacetoxy)ethoxytrifluoroformamidine (47).—Reaction of excess $(CF_3CO)_2O$ with an acetonitrile solution of **17** for 9 days at 25° followed by glpc on column E at 100° gave two main liquid fractions. The less volatile (T_R = 3290, CH_3CN = 100), major component was identified as $CF_3COOCH_2CH_2OC(NF_2)_2NFH$ (**48**): nmr ϕ − 21.3 (s, 4, NF_2), 39.1 (d, 1, NFH), 76 (s, 3, CF_3); τ 1.25 (NFH), 5.4 (CH_2); ir 3.08 (w) NH, 5.58 (s) C=O, 10.75–11.26 μ (s) NF. The other fraction (T_R = 1960, CH_3CN = 100) was identified as the two isomers of $CF_3COOCH_2CH_2OC(NF_2)$=NF (**47**) (see discussion of isomers of **6** and **8** in text): nmr ϕ − 43 (NF_2, syn RO/=NF), 40.8 (=NF, syn), −37.7 (NF_2, anti), 49.0 (=NF, anti), 75.7 (CF_3); τ 5.5 (CH_2); ir 3.37 (w) CH, 5.56 (s) C=O, 5.94 (m) C=N, 6.07 (m) C=N, 8.18 (s), 8.60 (vs) CO, 10.26–11.5 μ (m) NF.

Fluorination of 17. 2-(Hydroxy)ethoxytris(difluoramino)methane (53).—Employing fluorination method C, the adduct **17** prepared from 0.97 g (6.5 mmol) of **1** and 0.40 g (6.5 mmol) of $HOCH_2CH_2OH$ in 2 ml of CH_3CN was fluorinated at −30° using 30 mmol of F_2 (5% in N_2). The main reaction product isolated by glpc on column E at 100° (T_R = 550, CH_3CN = 100) was a colorless liquid, identified as $HOCH_2CH_2OC(NF_2)_3$ (**53**): nmr ϕ − 23.3 (s, NF_2), τ 5.49 (t, CH_2OC), 6.10 (t, $HOCH_2$), 5.97 (HO–); ir 3.00 (w) OH, 3.45 (w) CH, 7.93 (s), CO, 8.50 (m), 9.75–11.25 μ (s) NF.

Reaction of 53 with Trifluoroacetic Anhydride. 2-(Trifluoroacetoxy)ethoxytris(difluoramino)methane (72).—The CH_3CN solution of **53** from the previous reaction was mixed with 2.4 g (11.4 mmol) of $(CF_3CO)_2O$ and allowed to stir at room temperature overnight. The reaction mixture was fractionated by glpc on column E at 80° to yield, in addition to $CF_3COOCH_2CH_2OOCCF_3$ and $CF_3COOCH_2CH_2OH$, $CF_3COOCH_2CH_2OC(NF_2)_3$ (**72**) (T_R = 1380, CH_3CN = 100) as the principal product: nmr ϕ − 23.0 (s, 2, NF_2), 75.8 (s, 1, CF_3); τ 5.37 (s, CH_2); ir 3.37 (w) CH, 5.56 (s) C=O, 8.60 (vs), 10.33–11.22 μ (s) NF.

1,2-Bis[tris(difluoramino)methoxy]ethane (54).—The diadduct **18** was prepared by reaction of a tenfold molar excess of **1** with $HOCH_2CH_2OH$ in CH_3CN at room temperature for 10 days. Concentration of the reaction mixture gave **18** as an impact sensitive, viscous pale yellow oil: nmr ϕ − 21.7 (d, J = 52 Hz, 4, NF_2), 142.2 (d, J = 50 Hz, quintet, J = 10 Hz, 1, NFH); τ − 0.35 (d, J = 51 Hz, NFH), 5.4 (s, CH_2).

A sample of **18** dissolved in 0.5 ml of CF_3CH_2OH was fluorinated at −23 to 25° using method B and a 20% excess of F_2 (5% in N_2). Evaporation of the solvent gave $(F_2N)_3COCH_2CH_2OC(NF_2)_3$ (**54**) as a pale yellow, viscous oil, vapor pressure <1 mm at 25°. Purification by glpc at 100° on column H afforded a pure sample (T_R = 342, C_2Cl_4 = 100); nmr ϕ − 23.0 (s, NF_2), τ 5.3 (s, CH_2); ir 3.36 (m) CH, 6.85 (w), 7.20 (w), 8.11 (s) CO, 9.73 (s), 10.28–11.24 μ (s) NF.

Anal. Calcd for $C_4H_4F_{12}N_6O_2$: C, 12.1; F, 57.6; N, 21.2. Found: C, 13.3; F, 55.9; N, 22.0.

2-Chloroethoxytris(difluoramino)methane (56).—The adduct $ClCH_2CH_2OC(NF_2)_2NFH$ (**22**) prepared from 0.24 g (3 mmol) of $ClCH_2CH_2OH$ and 0.52 g (3.5 mmol) of **1** (1 ml of CH_3CN solvent, 18 mg of urea catalyst, stirred overnight at 25°) was fluorinated at −45° using method C and 15 mmol of F_2 (3% in N_2). The reaction mixture was fractionated by glpc on column I at 80° to give $ClCH_2CH_2OC(NF_2)_3$ (**56**) as a colorless liquid (T_R = 352, CCl_4 = 100), vapor pressure about 4 mm at 23°: nmr ϕ − 23.1 (s, NF_2), τ 5.40 (t, J = 5.5 Hz, CH_2O), 6.29 (t, J = 5.5 Hz, $ClCH_2$), 8.0 (CH_3CN impurity); ir 3.36 (w) CH, 6.82 (w), 6.96 (w), 7.12 (w), 8.00 (s) CO, 9.35 (w), 9.9–11.3 (s) NF, 14.70 μ (m).

Anal. Calcd for 96% $C_3H_4ClF_6N_3O$·4% CH_3CN: F, 43.8; N, 17.9; mol wt, 247.5. Found: F, 43.8; N, 17.9; mol wt, 248 (by mass spectral effusion rate on mass 65 peak).

Methyl[tris(difluoramino)methoxy]acetate (58).—The adduct $CH_3OOCCH_2OC(NF_2)_2NFH$ (**26**), prepared from 0.52 ml (7.4 mmol) of methyl glycolate and 1.2 g (7.9 mmol) of **1** (3 ml of CH_3CN, 20 mg of urea catalyst, reacted overnight at 25°), was fluorinated at 0° using method C and 46 mmol of F_2 (5% in N_2) over a 5.5-hr period. Volatile components were removed under vacuum. The residual liquid, vapor pressure <1 mm at 25°, was purified by glpc on column H at 80° to yield pure $CH_3OOCCH_2OC(NF_2)_3$ (**58**) (T_R = 218, C_2Cl_4 = 100); nmr ϕ −23.1 (NF_2), τ 5.14 (CH_2), 6.22 (CH_3); ir 3.36 (w) CH, 5.63 (s) C=O, 6.92 (m), 7.17 (m), 7.74 (m), 8.20 (s) CO, 9.50 (m), 10.66–11.23 μ (m) NF. *Anal.* Calcd for $C_4H_5F_6N_3O_3$: C, 18.7; F, 44.3. Found: C, 18.6; F, 44.0. Derivatives of **58** are listed in Table IX.

Tris(difluoramino)methoxyethylammonium Perchlorate (59) and Tris(difluoramino)methoxyethylamine (73).—The adduct $HClO_4$·$H_2NCH_2CH_2OC(NF_2)_2NFH$ (**28**), prepared by the reaction of 0.32 g (2 mmol) of ethanolammonium perchlorate and 0.6 g (4 mmol) of **1** (3 ml of CH_3CN solvent, 15 mg of urea catalyst, stirred for 2 days, 25°), was fluorinated (method C) with about 30 mmol of F_2 (5% in N_2) at −10°. The crude $HClO_4$·$H_2NCH_2CH_2OC(NF_2)_3$ (**59**) contained a carbonyl impurity by ir analysis. A 0.2-g sample of solid crude **59** dissolved in 10 ml of ice water was shaken with 100 ml of FC-75 fluorocarbon solvent (3M Co.) and 4 ml of saturated $NaHCO_3$ (aqueous). The FC-75 extract, containing the high-boiling liquid amine $H_2NCH_2CH_2OC(NF_2)_3$ (**73**), was titrated with 0.10 *N* $HClO_4$ (methyl red indicator). The isolated **59** product (60 mg), mp 208–210° dec, was free of carbonyl impurity: ir 3.15 (s) NH_2^+, 6.19 (m), 6.64 (m), 8.02 (s), 9.18 (vs) ClO_4^-, 9.9–11.3 μ (s) NF_2. ^{19}F nmr analysis showed a broad single peak at ϕ − 24.0. A sample for elemental analysis was prepared by first dissolving 1 g of the above product in 10 ml of ice water. This solution was extracted with 20 ml of ethyl acetate, and the extract was washed with 10 ml of ice water and concentrated to a volume of about 2 ml. This solution was added to about 60 ml of chloroform. The white crystals of **59** obtained after filtering and drying under vacuum weighed 0.40 g and melted at 218–220° dec. (The ir spectrum was essentially unchanged.) *Anal.* Calcd for $C_3H_7ClF_6N_4O_5$ (328.5): C, 10.97; F, 34.69; N, 17.06. Found: C,

TABLE IX

DERIVATIVES OF $(F_2N)_3COCH_2COOCH_3$ (58)

No.	Compd[a]	Synthesis[b]	Appearance	^{19}F Nmr, ϕ, NF_2	Ir, μ C=O
65	$RCOONH_4$	c	Solid, mp 85–88° dec	−23.9	6.14
66	RCOOLi	d	Hygroscopic solid		6.12
67	RCOONa	e	Solid		6.17
68	RCOOK	f	Needles		6.08
69	$(RCOO)_2Mg$	g	Solid, mp 220° dec		6.09
70	RCOOH	h	Liquid	−23.4	5.73
71	$RCONH_2$	i	Crystals, mp 90–92°		5.95

[a] R = $(F_2N)_3COCH_2$. [b] All reactions run on 15–30 mg of NF compound. [c] **58** in C_2H_5OH, excess 3% NH_4OH, 12 hr, 25°. [d] **70**, neutralize with methanolic LiOH. [e] **58**, saponify (3 days, 25°) with stoichiometric amount of 0.10 *N* NaOH (aqueous). [f] **58**, saponify (18 hr, 25°) with stoichiometric amount of 0.024 *N* KOH (C_2H_5OH). [g] **70** in CH_3OH plus stoichiometric amount of MgO, 25°. *Anal.* Calcd for $C_6H_4F_{12}MgN_6O_6$: C, 14.2; H, 0.8; Mg, 4.8. Found: C, 15.0; H, 1.2; Mg, 4.5. [h] **65** in CH_3OH percolated through acid ion exchange resin (Biorad AG 50). [i] **65** heated 50–60° at 0.1 mm. *Anal.* Calcd for $C_3H_4F_6N_4O_2$: C, 14.9; H, 1.67; F, 47.1; N, 23.1. Found: C, 16.1; H, 2.0; F, 46.5; N, 22.8.

11.14; F, 34.5; N, 17.4; equiv wt, 326. Salts of **73** are listed in Table X.

***O*-Tris(difluoramino)methylacetoxime (61).**—The adduct **30**, prepared by reaction of 0.154 g (2.1 mmol) of acetoxime and 0.42 g (2.8 mmol) of **1** for 0.5 hr at −78° and 0.5 hr at 25°, was fluorinated (method A) with 60 mmol of F_2 (2.7% in N_2) at −20° for 2 hr. The fluorinated products were volatilized from the fluorination chamber into the −183° trap with a stream of N_2 at room temperature. The products were then fractionated under vacuum through −35, −119, and −196° traps in series. The −35° trap contained $(CH_3)_2C{=}NOC(NF_2)_3$ (**61**) and a small amount of $FCH_2C(CH_3)C{=}NOC(NF_2)_3$ (**62**): nmr of **61** ϕ − 24.4 (NF_2), τ 7.92, 7.98 (syn and anti CH_3); nmr of **62** ϕ − 26.2 (NF_2), τ 7.81 (CH_3), 5.10 (d, CH_2F).

***O,O'*-Bis[bis(difluoramino)fluoraminomethyl]diaminoglyoxime (31).**—A mixture of 0.181 g (1.54 mmol) of diaminoglyoxime, 2.2 g of dioxane, and 0.95 g (6.4 mmol) of **1** was stirred at room temperature for 1 hr. Excess **1** and solvent were removed under reduced pressure (0.1 mm, 25°). The residual white solid was crystallized from benzene, mp 90° dec. Nmr and elemental analyses indicated the structure to be $+C(NH_2){=}NOC(NF_2)_2NFH]_2$ (**31**) with 0.5 mol of dioxane of crystallization: nmr ϕ − 21.2 (d, J = 8.6 Hz, 4, NF_2), 138.3 (d, J = 49.3 Hz, quintet, J = 8.4 Hz, 1, NFH); τ −1.13 (NFH), 3.38 (NH_2), 6.33 (CH_2 of dioxane). *Anal.* Calcd for $C_6H_{10}F_{10}N_{10}O_3$: C, 18.8; F, 38.0. Found: C, 19.6; F, 37.4, 38.6.

Conducting the synthesis in acetonitrile yields **31** free of complexing solvent. Recrystallization from CCl_4 affords a white solid, mp 69–71°, which is very sensitive to impact and slowly decomposes at 25°.

Anal. Calcd for $C_4H_6F_{10}N_{10}O_2$: C, 11.5; F, 45.7; N, 33.6. Found: C, 11.2; F, 43.2; N, 35.1.

***O*-Tris(difluoramino)methyldichloroformoxime (63).**—The adduct $Cl_2C{=}NOC(NF_2)_2NFH$ (**32**), prepared by treating 0.52 g (4.6 mmol) of $Cl_2C{=}NOH$,[19] 0.75 g (5.1 mmol) of **1**, and 25 mg of urea in 5 ml of CH_3CN at room temperature for 2 hr, was fluorinated (method C) with 37 mmol of F_2 (10% in N_2) at −30°. Separation of the reaction mixture by glpc on column E at 50° afforded a 40% yield of pure $(F_2N)_3CON{=}CCl_2$ (**63**) (T_R = 310, CH_3CN = 100) as a colorless liquid, vapor pressure about 5 mm at 25°. ^{19}F nmr showed a single peak for NF_2 at ϕ − 25.2; ir 6.29 μ (m) C=N; mass spectrum *m/e* (ions) 42 (CON^+), 52 (NF_2^+), 82 (CCl_2^+), 96 ($NCCl_2^+$).

Anal. Calcd for $C_2Cl_2F_6N_4O$: C, 8.6; N, 19.9; Cl, 25.2; F, 40.6; mol wt, 281. Found: C, 9.6; N, 19.9; Cl, 24.9; F, 41.4; mol wt, 270 (by mass spectral effusion rates).

(19) E. Gryzskiewicz-Trochimowski, K. Dymowski, and E. Schmidt, *Bull. Soc. Chim. Fr.*, 597 (1948).

Reaction of 63 with Sodium Methoxide. Dimethyl *N*-[Tris(difluoramino)methoxy]iminocarbonate (80).—To a solution of 0.282 g (1.0 mmol) of **63** in 15 ml of $CFCl_3$ was added 0.140 g (2.6 mmol) of $NaOCH_3$. The reaction mixture was stirred for 6 hr at room temperature and filtered through glass wool, and the filtrate was concentrated under vacuum at −30° to yield the product $(F_2N)_3CON{=}C(OCH_3)_2$ (**80**) as a pale yellow liquid, vapor pressure <1 mm at 25°: nmr ϕ − 24.0 (NF_2), τ 6.12 and 6.6 (syn and anti CH_3 groups); ir 6.18 μ (C=N). The mass spectrum was consistent with the assigned structure, including a parent peak at *m/e* 272.

Anal. Calcd for $C_4H_6F_6N_4O_3$: C, 17.6; F, 41.9; mol wt, 272. Found: C, 18.4; F, 40.6; mol wt, 277 (by mass spectral effusion rates).

Bis(difluoramino)fluoraminomethyl Hydroperoxide (36).—A mixture of 93 mg (2.8 mmol) of H_2O_2 (98% purity, FMC Corp.), 20 mg of urea catalyst, 2.0 ml of $CH_3COOC_2H_5$ solvent, and 0.95 g (6 mmol) of **1** was stirred at room temperature for 2 hr. Volatiles and part of solvent were removed from the pale yellow solution. ^{19}F nmr analysis of the residual liquid showed only peaks due to the adduct $HOOC(NF_2)_2NFH$ (**36**), ϕ − 22.5 (s, 4, NF_2), 139.5 (d, 1, NFH). (The same nmr absorptions were obtained when equimolar quantities of **1** and H_2O_2 were used, although yields were lower, indicating that the structure of **36** is a 1:1 adduct as shown.)

Acetoxybis(difluoramino)fluoraminomethane (35) and Bis(difluoramino)fluoraminofluoromethane (38).—A mixture of 0.08 ml (1.33 mmol) of glacial acetic acid (containing 5 mol % CH_3COOK catalyst), 45 mg (0.3 mmol) of **1**, and about 0.1 ml of CH_3OCH_3 was allowed to warm from −196° and the temperature was held at 0° for 5 min. ^{19}F nmr analysis run at − 28° showed about a 70% conversion to the adduct $CH_3COOC(NF_2)_2NFH$ (**35**): ϕ − 23 (s, 4, NF_2) and 132 (d, 1, NFH). Some CH_3COF and HNF_2 were also present. Longer reaction times or higher temperature caused decomposition of **35** and gave more of these by-products and also $F^aC(NF_2{}^b)_2NF^cH^d$ (**38**) (HF adduct of **1**): ^{19}F nmr ($CFCl_3$) ϕ −21.8 (s, 4, NF_2), 133.8 (t, J_{a-cd} = 16 Hz, 1, FC), 136.4 (d, $J_{c-d} \cong$ 57 Hz, m, J_{b-c} = small, 1, NFH). **38** was isolated by glpc on column J at 25° (T_R 280, $CFCl_3$ = 100): ir 3.02 (m) NH, 6.99 (m), 7.57 (m), 8.08 (m), 8.32 (m), 8.64 (w), 9.7–11.1 (s), NF, 11.8 μ (m); mol wt calcd 169, found (by mass spectral effusion rates) 170.

***N*-Fluorohexafluoroisopropylidine Imine (4).**—Using method C, without solvent, 12 mmol of $(CF_3)_2C{=}NH$[20] was fluorinated at −78° with 30 mmol of F_2 (5% in N_2). The −183° trap contained 3.9 mmol of a mixture of $(CF_3)_2C{=}NF$ (**4**), bp −12° (lit.[8] bp −13 to 11.7°), and $(CF_3)_2CFNF_2$ (**87**), bp 0° (lit.[8] bp −2 to 1°), which were separated by glpc on column G at 25° (T_R of **4** = 81, **87** = 102, CF_2Cl_2 = 100). The reactor contained 9.5 mmol of a liquid, bp about 45°, assigned the structure $(CF_3{}^a)_2CF^bNF^cH^d$ (**86**) [*Anal.* Calcd mol wt: 203. Found: 203 (by mass spectral effusion rates).]: nmr ϕ 75.9 (d, J_{a-c} = 11.9 Hz; d, J_{a-b} = 3.6 Hz; 6, CF_3), 134.7 (d, J_{c-d} = 57 Hz; d, J_{c-b} = 20.8 Hz; septet, J_{c-a} = 12.2 Hz; 1, NFH), 151.4 (d, J_{b-c} = 20.8 Hz; d, J_{b-d} = 14.2 Hz; septet, J_{a-b} = 3.1 Hz; 1, CF); ir 3.00 (w) NH, 7.63 (s), 7.95 (vs), 8.20 (s), 8.46 (s), 9.00 (m), 9.78 (m), 10.42 (m), 11.58 (m), 13.5–14.0 μ (s). Vaporizing **86** slowly through a bed of NaF pellets at 25° eliminated HF and gave a quantitative conversion to **4** [treatment of **87** with $(C_6H_5)_3P$ also yielded **4**].

Methoxybis(trifluoromethyl)difluoraminomethane (64).—The reaction mixture containing the adduct $(CF_3)_2C(OCH_3)NFH$ (**39**), prepared from 0.55 g (3 mmol) of **4** and 80 mg (2.5 mmol) of CH_3OH [1 ml of CH_3CN, 15 mg of $(CH_3)_3N$ catalyst, overnight, 25°], was fluorinated using method C at −20° with 15 mmol of F_2 (3% in N_2). The contents of the −183° trap (2.2 mmol) were separated by glpc on column F at 22.5°. The peak eluting at 15 min (air = 0.7 min) was trapped (about 1 mmol) and identified as $(CF_3)_2C(OCH_3)NF_2$ (**64**): bp (from vapor pressure data) 68°; mp *ca.* −82°; nmr ϕ − 19.2 (s, 1, NF_2), 70.7 (t, J = 12.6 Hz, 3, CF_3).

Anal. Calcd for $C_4H_3F_8NO$: F, 65.2; N, 6.0. Found: F, 64.6; N, 6.0.

***N*-Fluoromethoxytrifluoroethylidine Imine (6).**—A mixture of 0.33 g (2.5 mmol) of **3** ($CF_3CF{=}NF$) and 64 mg (2.0 mmol) of CH_3OH was allowed to stand at room temperature for 3 days. (The reaction was nearly complete after 5 min.) The products were separated by glpc on column C at 50°. Both geometric

(20) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

TABLE X
SALTS OF $(F_2N)_3COCH_2CH_2NH_2$ (73)[a]

No.	Salt[b]	Mp, °C[c]	Equiv wt Theory	Equiv wt Found	Anal., % Calcd C	Calcd F	Found C	Found F
59	$RCH_2NH_3^+ClO_4^-$	218–220	328.5	326	11.0	34.7	11.1	34.5
74	$RCH_2NH_3^+Cl^-$	120	264.5	258	13.6	43.1	13.5	42.4
75	$RCH_2NH_3^+Br^-$	96	309		12.7		11.6	
76	$RCH_2NH_3^+HF_2^-$ [d]	118	268					
77	$[RCH_2NH_3^+]_2SO_4^{2-}$	138	277	259	13.0		13.0	
78	$[RCH_2NH_3^+]_2C_2O_4^{2-}$ [e]	144	273	263	17.6		18.2	
79	$RCH_2NH_3^+{}^-OOCR$[f]	83–88	471 [ir 6.0 μ (C=O)]					

[a] Preparation of 73 described in the preceding example, except that pure 59 starting material was employed. [b] R = $(F_2N)_3COCH_2$. Salts, except where noted, were made by neutralization of FC-75 solutions of the free amine 73 (about 0.2 g) with the appropriate dilute (about 0.1 *N*), aqueous acid, concentration of the aqueous phase, and drying the solid in a vacuum desiccator. [c] The temperature at which most of the melting took place. [d] Titrated 73 with HF, but ir analysis supported the HF_2^- rather than the F^- salt. Hygroscopic solid which sublimed near the melting point. [e] Recrystallized from CH_3OH. [f] 0.1 mmol of $(F_2N)_3COCH_2COOK$ in 4 ml of CH_3OH plus 0.1 mmol of 59 in 1 ml of CH_3OH; $KClO_4$ was filtered off and the solution was evaporated.

isomers of $CH_3OC(CF_3)$=NF were isolated: isomer a (syn, CH_3O/=NF) (6a) and isomer b (anti) (6b) in a ratio of 1:3. Table V in the text lists many of the properties of these compounds. The mass spectra of 6a and 6b contain these ions (abundance).

m/e	15	28	31	69	76	126	145
6a	100	15	65.9	72.5	4.5	0	7.2
6b	100	12.9	68.0	54.6	4.2	3.0	2.6
Ion	CH_3^+	CO^+	CH_3O^+	CF_3^+	$C_2F_2N^+$	$C_3H_3F_3NO^+$	$C_3H_3F_4NO^+$

Anal. Calcd for $C_3H_3F_4NO$ (6b) (145.06): C, 24.8; F, 52.4. Found: C, 23.8; F, 52.4.

***N*-Fluoro-*n*-butoxytrifluoroethylidine Imine (88).**—A mixture of 40 mg (0.3 mmol) of 3, 37 mg (0.5 mmol) of dry n-C_4H_9OH, and about 0.2 ml of $CFCl_3$ was allowed to react overnight at room temperature. ^{19}F nmr analysis indicated the presence of the anti (8a) and syn (8b) isomers of n-$C_4H_9OC(CF_3)$=NF in a ratio of about 1:4, ϕ: (8a) 49.2 (=NF), 68.8 (CF_3); (8b) 44.1 (=NF), 71.5 (CF_3).

Registry No.—1, 10051-06-6; 2, 14362-70-0; 3, 758-35-0; 4, 2802-70-2; 5, 839-09-8; *syn*-6, 38088-66-3; *anti*-6, 38088-67-4; 7, 38087-75-1; *syn*-8, 38088-68-5; *anti*-8, 38088-69-6; 9, 38087-76-2; 10, 38087-77-3; 11, 38087-78-4; 12, 38087-79-5; 13, 38087-80-8; 14, 38087-81-9; 15, 38087-82-0; 16, 38087-83-1; 17, 38087-84-2; 18, 38165-82-1; 19, 38087-85-3; 20, 38087-86-4; 21, 38087-87-5; 22, 38087-88-6; 23, 38087-89-7; 24, 38087-90-0; 25, 38087-91-1; 26, 38165-83-2; 27, 38088-04-9; 28, 38088-05-0; 29, 38088-06-1; 30, 38088-07-2; 31, 38165-86-5; 32, 35431-00-6; 33, 38088-09-4; 34, 38088-10-7; 35, 38088-11-8; 36, 38088-12-9; 37, 38088-13-0; 38, 38088-14-1; 39, 38088-15-2; 40, 38088-16-3; 41, 38088-17-4; 42, 38092-35-2; 43, 38146-44-0; 44, 38092-36-3; 47, 38092-37-4; 48, 38092-38-5; 50, 26901-93-9; 51, 38092-40-9; 52, 38092-41-0; 53, 38092-42-1; 54, 38092,43-2; 55, 38092-44-3; 56, 38092-45-4; 57, 38092-46-5; 58, 38092-47-6; 59, 25448-61-7; 60, 38092-49-8; 61, 38092-50-1; 62, 38092-51-2; 63, 35431-01-7; 64, 38092-53-4; 65, 38165-87-6; 66, 38165-88-7; 67, 38092-54-5; 68, 38092-55-6; 69, 38092-56-7; 70, 38092-57-8; 71, 38092-58-9; 72, 38092-59-0; 73, 38165-85-4; 74, 38092-60-3; 75, 38092-61-4; 76, 38092-62-5; 77, 38092-63-6; 78, 38092-64-7; 79, 38092-65-8; 80, 35431-02-8; 81, 38092-67-0; 82, 38092-68-1; 83, 38092-69-2; 84, 38092-70-5; 85, 38092-71-6; 86, 22341-37-3; 87, 662-23-7; 88, 38092-74-9.

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