Organic Fluoronitrogens. XII.[1] Amino Addition Compounds of Fluorimines. Tetrakis(difluoramino)methane

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The addition of amino compounds to *N*-fluorimines to yield saturated and unsaturated products is described. Pentafluoroguanidine (**1**) and ammonia react at −110° to form the adduct $H_2NC(NF_2)_2NFH$ (**2**). On warming to 25°, **2** loses HNF_2 to yield $H_2NC(NF_2)=NF$ (**3**). Fluorination of **2** at low temperature affords the completely fluorinated derivative, $C(NF_2)_4$ (**4**), an explosive, oxidizing liquid.

A previous paper[1] described the addition of hydroxy compounds to *N*-fluorimines and the chemistry of the products. In this paper, NH adducts of fluorimines, especially pentafluoroguanidine (**1**),[2] will be considered. Many of the NF compounds discussed in this paper are explosive and all work was conducted on a small scale with appropriate shielding.

The principal reactions which occur when amino compounds are treated with **1** are shown below.

$$R_1R_2NH + \underset{\mathbf{1}}{(F_2N)_2C{=}NF} \longrightarrow \underset{\mathbf{A}}{R_1R_2NC(NF_2)NFH} \xrightarrow{-HNF_2} \underset{\mathbf{B}}{R_1R_2NC(NF_2){=}NF}$$

The double bond in **1** is very electron deficient and a large variety of amino compounds may be added. The rate of addition and the types of products formed (A and/or B) depend upon the nucleophilicity of the amino compound and the reaction conditions, as summarized in Table II. Amines such as ammonia, *p*-cyanoaniline, and *p*-trifluoromethylaniline add to **1** at low temperature to form saturated products of type A. Warming these adducts to room temperature causes loss of HNF_2 to yield the unsaturated derivatives of type B. More basic amines such as *n*-butylamine and dimethylamine react rapidly at low temperature, *e.g.*, −78°, to yield exclusively the unsaturated (B) derivatives. For example, ^{19}F nmr analysis of the reaction mixture from dimethylamine and **1** at −78° showed no evidence for the intermediate saturated adduct (A). Amino compounds of very low nucleophilicity, such as succinimide, require a basic catalyst for the addition reaction to take place. Polar solvents with low melting points such as acetonitrile, dimethyl ether, diethyl ether, and tetrahydrofuran were found useful to facilitate reaction and to prevent explosions initiated by exotherms.

The addition of anhydrous NH_3 to **1** takes place rapidly in CH_3OCH_3 solution at −110° to afford a high yield of the saturated adduct **2**, as determined by ^{19}F nmr and ir analyses.

$$NH_3 + \underset{\mathbf{1}}{(F_2N)_2C{=}NF} \xrightarrow{-110°} \underset{\mathbf{2}}{H_2NC(NF_2)NFH}$$

If **2** is allowed to warm to room temperature, HNF_2 is eliminated and 1,1,2-trifluoroguanidine (**3**) is formed in high yield.

$$\underset{\mathbf{2}}{H_2NC(NF_2)NFH} \xrightarrow{25°} \underset{\mathbf{3}}{H_2NC(NF_2){=}NF} + HNF_2$$

Tetrakis(difluoramino)methane.—Fluorination of **2** with a large excess of dilute F_2 at about −30° (neat) gave a mixture of products shown in the equation below, which were separated by glpc (peak area per cents observed were 20, 16, 14, <5, <5, and <5, respectively).

$$\underset{\mathbf{2}}{H_2NC(NF_2)NFH} \xrightarrow{F_2} \underset{\mathbf{4}}{C(NF_2)_4} + \underset{\mathbf{5}}{FC(NF_2)_3} + \underset{\mathbf{1}}{(F_2N)_2C{=}NF} + \underset{\mathbf{6}}{CF_2(NF_2)_2} + \underset{\mathbf{7}}{CF(NF_2){=}NF} + \underset{\mathbf{9}}{(F_2N)_3CNFH}$$

The most interesting product is the new compound[3] tetrakis(difluoramino)methane (**4**) in which all H atoms of **2** have been replaced by F. A small amount of the NFH compound **9**, an intermediate to **4**, was also isolated. The other products arise from cleavage of C–N bonds during fluorination, or, in the case of **1**, the fluorination of **3** (which forms easily from **2** as mentioned above). The compounds **5**,[2] **6**,[4] and **7**[2] have been reported. **4** was isolated by glpc and many of its properties were determined (Table I). It is an explosive (impact sensitive), oxidizing, volatile liquid, but, when manipulated with care, exhibited surprising stability (up to 175°). The presence of the strongly electronegative F atoms attached to N appears to stabilize the molecule much as do the O atoms in the analogous tetranitromethane, $C(NO_2)_4$.

The fluorination of **2** was observed to take place by a stepwise replacement of H atoms by F. The

$$\underset{\mathbf{2}}{H_2NC(NF_2)NFH} \xrightarrow{F_2} \underset{\mathbf{8}}{HFNC(NF_2)NFH} \xrightarrow{F_2} \underset{\mathbf{9}}{(F_2N)_3CNFH} \xrightarrow{F_2} \underset{\mathbf{4}}{C(NF_2)_4}$$

$$\mathbf{2} \rightarrow \underset{\mathbf{10}}{H_2NC(NF_2)_3}$$

(1) Previous publication in this series: J. L. Zollinger, *et al.*, *J. Org. Chem.*, **38**, 1065 (1973).

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

(3) Preparation of **4** is also disclosed by W. C. Firth, Jr., S. Frank, and M. D. Meyers, *ibid.*, **38**, 1088 (1973), by the fluorination of $(F_2N)_2C(NFH)$-NCO.

(4) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *ibid.*, **31**, 4232 (1966).

TABLE I

TETRAKIS(DIFLUORAMINO)METHANE (4)

Structural formula: $C(NF_2)_4$

Anal. Calcd for CF_8N_4: C, 5.45; F, 69.1; N, 25.45; mol wt, 220. Found: C, 5.8; F, 68.2; N, 26.0; mol wt,[a] 223.

Appearance: colorless liquid

Boiling point:[b] 40°

Melting point: −13.5 to −12.5°

Heat of vaporization: 6.5 kcal/mol

Trouton's constant: 21.1

T_R: 111[c]

^{19}F nmr (ϕ): −29.3, broad singlet (NF_2)

Density (25°):[d] 1.68 g/cc

Critical temperature:[e] 175°

Solubility: miscible with $CFCl_3$, CF_2Cl_2, CF_3CH_2OH, and N_2F_4

Impact sensitivity:[f] less than 33 kg-cm

DTA: 210° smooth exotherm starts; 250° maximum rate of exotherm.

Thermal stability: solutions of **4** in $CFCl_3$ in glass were unchanged after 12 hr at 125°; complete decomposition occurred after 12 hr at 165°.

[a] By mass spectral effusion rates. [b] Log P (mm) = 7.498 − 1449/T (−12 to 60°). [c] Relative retention time ($CFCl_3$ = 100) on a 0.5 in. × 20 ft glpc column of 20% FS-1265 (Dow-Corning) on firebrick at 25°. [d] Orthobaric liquid density: $d_t = 1.744 - 2.505 \times 10^{-3}t - 2.372 \times 10^{-6}t^2 - 2.338 \times 10^{-8}t^3$. [e] Meniscus disappearance in glass. Some decomposition. [f] As determined by dropping a 2-kg steel block on a sealed glass ampoule of **4**.

progress of the reaction in CH_3CN solution at −35° was monitored by glpc and ^{19}F nmr analysis of liquid samples withdrawn from the reactor during fluorination.

The intermediate products **8** and **9** were isolated by glpc and identified by ^{19}F nmr and ir analyses. **8** was also characterized by its mass spectrum and a molecular weight determination. The concentration of **8** reached a maximum after about 1 molar equiv of F_2 had been added. Compound **10**, a possible intermediate in the synthesis, was not observed.[5] The ^{19}F nmr spectrum expected for **10** would be a single broad absorption in the ϕ −25 region. The initial fluorination product, however, exhibited peaks at ϕ −23.6 (s) and 135.0 (d) in an area ratio of 2:1, consistent for structure **8**. These results indicate that the NH_2 group in **2** is more reactive toward F_2 than the NFH group. The monohydride **9** exhibits ^{19}F nmr absorptions at ϕ −26.4 (s) and 136.1 (complex) in a ratio of 6:1.

As H is replaced by F in the compound series **2**, **8**, **9**, **4**, the ^{19}F nmr absorption for the NF_2 group is observed to shift in increments of about 3 ppm to progressively lower field: −20.5, −23.6, −26.4, and −29.3.

Thermal stability increases as one progresses through the above series of compounds. Whereas **2** was converted to **3** on warming to room temperature, **8** and **9** were isolated by glpc at 50°. **8** was unchanged in $CFCl_3$ solution in glass on standing for 18 days at room temperature. Treatment of **9** with NaF or heating yields **1** by loss of HNF_2.

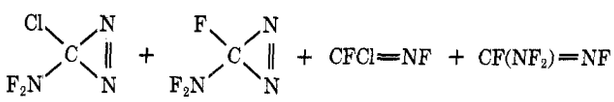
The acetone hydrazone adduct **20** in Table II was stable only at low temperatures. However, warming to room temperature did not yield the unsaturated product (type B) observed for other adducts, *e.g.*, **2**, but gave a mixture of products, including **23** and **24**,[6] resulting from apparent cleavage and rearrangement reactions.

$$\underset{\mathbf{20}}{(CH_3)_2C{=}NNHC(NF_2)_2NFH} \xrightarrow{25^\circ} \underset{\mathbf{23}}{FC(NF_2)_2NH_2} + \underset{\mathbf{24}}{F_2NCF_2NFH}$$

Other products identified in the reaction were HNF_2, N_2O, and acetone. **23** and **24** were isolated by glpc and characterized (see Experimental Section).

Unexpected products were also obtained in the reaction of semicarbazide hydrochloride and **1**.

$$\underset{\mathbf{1}}{H_2NCONHNH_2{\cdot}HCl} + (F_2N)_2C{=}NF \xrightarrow{25^\circ}$$



25 **26** **27** **7**

When the reaction was monitored by glpc, the concentration of **25** in the gas phase was observed to increase with time to a maximum at 6 hr, then decrease. After 18 hr, no **25** was present. The properties of **25** have been published,[7] but the synthetic route was not given. The diazirine **26** has been reported.[8] The syn and anti isomers of both **27**[9] and **7**[2] were detected among the products of the reaction.

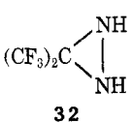
1,1,2-Trifluoroguanidine (**3**), originally isolated from the decomposition of **2**, was also formed when **7** and

$$\underset{\mathbf{7}}{CF(NF_2){=}NF} + NH_3 \xrightarrow{25^\circ} \left[H_2NC(NF_2)FNH \right] \xrightarrow{-HF} \underset{\mathbf{3}}{H_2NC(NF_2){=}NF}$$

NH_3 were allowed to react. The presumed intermediate adduct was not isolated but lost HF to yield **3**.

Additions of NH compounds to other *N*-fluorimines are summarized in Table III. No saturated adducts were observed in reactions of $CF_3CF{=}NF$[1] (**28**) with amines; instead, loss of HF occurred to yield $H_2NC(CF_3){=}NF$ (**30**) and $(CH_3)_2NC(CF_3){=}NF$ (**31**) in high yields from NH_3 and $(CH_3)_2NH$, respectively.

The addition of NH_3 to $(CF_3)_2C{=}NF$[1] (**29**) is mildly exothermic in ethyl ether solution and the product was a solid characterized as the diaziridine **32**, which



32

was recently reported.[10] **32** is formed in quantitative yield, apparently from a 1,3 elimination of HF from an intermediate adduct not isolated.

(5) Compound **10** has been prepared by the hydrolysis of $(F_2N)_2CNCO$: W. C. Firth, Jr., and S. Frank, *ibid.*, **38**, 1083 (1973).

(6) Compound **24** was isolated and characterized by R. J. Koshar. Another route to **24** has been reported, but no properties were given (U. S. Patent 3,410,853).

(7) R. A. Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *J. Heterocycl. Chem.*, **2**, 371 (1965).

(8) R. A. Mitsch, *J. Org. Chem.*, **33**, 1847 (1968).

(9) D. H. Dybvig, *Inorg. Chem.*, **5**, 1795 (1966).

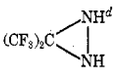
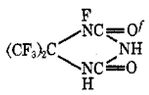
(10) (a) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965), synthesized **32** from $(CF_3)_2C{=}NH + HN_3$. (b) K. N. Makarov, B. L. Dyatkin, and I. L. Knunyants [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1924 (1968); *Chem. Abstr.*, **70**, 3878y (1969)] prepared **32** from **29** and NH_3.

TABLE II
ADDITION OF NH COMPOUNDS TO $(F_2N)_2C{=}NF$ (1)[a]

Reactant	Product[b]	No.	Conditions: Temp, °C	Conditions: Time, hr	Yield,[c] %	^{19}F Nmr absorptions, ϕ[d]: NF_2	NFH	=NF
NH_3	$H_2NC(NF_2)_2NFH$	2	−110	0.25	90	−20.5	135.1	
NH_3	$H_2NC(NF_2){=}NF$	3	25	24	80	−47.2		50.7
p-$CF_3C_6H_4NH_2$	*p*-$CF_3C_6H_4NH$-A[e]	11	25	0.25	60	−24	137	62 (CF_3)
	p-$CF_3C_6H_4NH$-T[f]	12			20	−45		38
p-$NCC_6H_4NH_2$	*p*-NCC_6H_4NH-A	13	25	0.25	60	−24d[g]	136 m[h]	
	p-NCC_6H_4NH-T	14			20	−45		34
n-$C_4H_9NH_2$	*n*-C_4H_9NH-T	15	0	0.1	50	−44		62.4
$(CH_3)_2NH$	$(CH_3)_2N$-T	16	−80	0.5	90	−40.8		61.7
$(CH_3)_3CNH_2$	*syn*-$(CH_3)_3CNH$-T[i]	17	25	0.5	50	−45.9		54.7
	anti-$(CH_3)_3CNH$-T	18			25	−41.6		61.2
$HClO_4 \cdot H_2NNH_2$	$HClO_4 \cdot H_2NNH$-A	19	25	20	60	−24.6	139.5	
$(CH_3)_2C{=}NNH_2$	$(CH_3)_2C{=}NNH$-A	20	−90	0.5	80	−20.4	138.2	
$CF_3CONHNH_2$	$CF_3CONHNH$-A	21	0	0.25	60	−22.4	141.2	75 (CF_3)
$COCH_2CH_2CONH$[j]	$COCH_2CH_2CON$-A	22	25	72	20	−25.1	121.5	

[a] In a typical reaction, the anhydrous amino compound is treated with 10–20 mol % excess of pentafluoroguanidine (1) in a sealed nmr tube with internal $CFCl_3$ reference and CH_3CN solvent at the temperature and time indicated. [b] The products are nonvolatile explosive solids or liquids. See Experimental Section for further properties of compounds **2** and **3**. [c] Yields were estimated from nmr data. [d] Chemical shifts are in parts per million relative to $CFCl_3$ as internal reference. [e] A is the $C(NF_2)_2NFH$ group. [f] T is the $C(NF_2){=}NF$ group. [g] Doublet, J_{FH} = 51.4 Hz. [h] Quintet, J_{FF} = 11.2 Hz. [i] Assignment of syn configuration [with respect to $(CH_3)_3CNH$ and =NF groups] is based on analogy with the isomers of $CH_3OC(NF_2){=}NF$ described in our previous paper.[1] [j] Triethylamine catalyst.

TABLE III
ADDITION OF NH COMPOUNDS TO OTHER FLUORIMINES[a]

Fluorimine	No.	Reactant	Temp, °C	Products	No.	Yield, %	^{19}F nmr, ϕ	Ir, μ
$CF(NF_2){=}NF$	7	NH_3	−78	$H_2NC(NF_2){=}NF$[b]	3	80	−47.2 (NF_2) 50.7 (NF)	5.85 (C=N)
$CF_3CF{=}NF$	28	NH_3	−78	$H_2NC(CF_3){=}NF$	30	95	70.5 (CF_3) 49.4 (NF)	3.02 (NH) 5.99 (C=N)
$CF_3CF{=}NF$	28	$(CH_3)_2NH$	−78	$(CH_3)_2NC(CF_3){=}NF$	31	90	65.5 (CF_3)[c] 45.9 (NF)	6.09 (C=N)
$(CF_3)_2C{=}NF$	29	NH_3	25		32	95	75.2 (CF_3)	3.05 (NH)
$(CF_3)_2C{=}NF$	29	$(CH_3)_2NH$	25	$(CH_3)_2C{=}NN(CH_3)_2$[b]	33	95	63.7, 52.0 (CF_3)	6.25 (C=N)
$(CF_3)_2C{=}NF$	29	HNCO[e]	25		35	50	74.1 (d, CF_3) 87.5 (m, NF)	5.75 (C=O)

[a] Reactions carried out in sealed tubes using excess fluorimine, and $CFCl_3$ as solvent and internal nmr reference. [b] See Experimental Section. [c] Doublet, J = 8.6 Hz. [d] Known compound[10] (see text). [e] $(CH_3)_3N$ catalyst. [f] Analogous compound, where NF is NH, reported[10a] from $(CF_3)_2C{=}NH$ plus 2HNCO. The multiplet for NF appears to be a sevenfold peak in the ^{19}F nmr spectrum of **35**, as would be expected from coupling with the six F atoms of the CF_3 groups, mp 109–110°.

The reaction of **29** and $(CH_3)_2NH$ afforded quantitative yields of $(CF_3)_2C{=}NN(CH_3)_2$ (**33**) formed by addition inverse to that seen in all other reactions in our studies.[11] **33** was thoroughly characterized and was synthesized independently as follows.

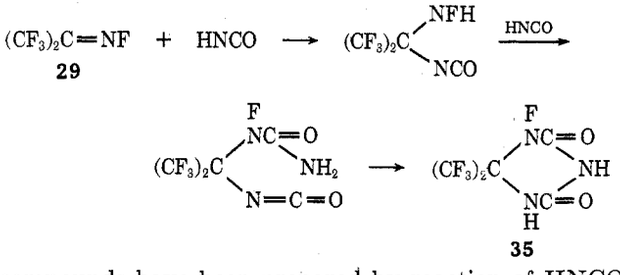
$$(CF_3)_2C{=}O + H_2NN(CH_3)_2 \longrightarrow (CF_3)_2C(OH)NHN(CH_3)_2 \xrightarrow{POCl_3} \mathbf{33}$$

Dimerization of **33** to the diazetidine **34** occurred either "spontaneously" in glassware or by catalysis with concentrated sulfuric acid. The nmr spectra

$$\underset{\mathbf{33}}{2(CF_3)_2C{=}NN(CH_3)_2} \xrightarrow{H_2SO_4} \underset{\mathbf{34}}{(CF_3)_2C(-NN(CH_3)_2)(-)C(CF_3)_2(-)NN(CH_3)_2}$$

of **34** contained only single peaks for H and F. The structure was further confirmed by mass spectral and elemental analyses.

Two moles of HNCO react with **29** to yield what is believed to be the cyclic product, **35**. Similar cyclic



compounds have been prepared by reaction of HNCO with **1**[12] and with $(CF_3)_2C{=}NH$.[10a] A possible path to **35** is shown.

(11) (a) Reference 10b reported the closely related reaction of **29** and $HN(C_2H_5)_2$ to yield $(CF_3)_2C{=}NN(C_2H_5)_2$, also involving an inverse addition. (b) **33** was recently reported by F. J. Weight, *J. Org. Chem.*, **37**, 1314 (1972).

(12) W. C. Firth, Jr., S. Frank, and E. J. Schriffert, *J. Org. Chem.* **38**, 1080 (1973).

Experimental Section

Precautions.—Many of the fluoronitrogen compounds described in this paper are shatteringly explosive under certain conditions. See the previous paper[1] for details concerning safety, starting materials, reaction procedures, equipment, compound purification, and analytical methods. Manufacturers of liquid phases and solid supports for glpc are listed in Table VII in ref 1.

Only the principal and structurally significant ions from mass spectral analyses are presented.

Derivatives of Pentafluoroguanidine (1) and Other Fluorimines.—Approximate yields and ^{19}F nmr absorptions are presented in Table II for NH derivatives of 1 and in Table III for derivatives of **28** and **29**. Many of the properties of $C(NF_2)_4$ (**4**) are given in Table I.

Preparation of Bis(difluoramino)fluoraminomethylamine (2) and 1,1,2-Trifluoroguanidine (3).—Pentafluoroguanidine (**1**, 0.46 g, 3.1 mmol) was added by vacuum transfer over a 1-min period to a stirred solution of anhydrous ammonia (0.05 g, 2.9 mmol) in 5 ml of dimethyl ether at −110° ($CFCl_3$ slush bath) in an approximately 10-ml capacity borosilicate glass reactor fitted with a polytetrafluoroethylene (ptfe) needle valve and a ptfe-coated magnetic stirring bar. The mixture was warmed to −63° ($CHCl_3$ slush bath) while solvent and unreacted **1** were removed under pump vacuum. After 0.5 hr the yellow liquid residue had a vapor pressure of less than 1 mm at −63° and was identified (nmr) as $H_2NC(NF_2)_2NFH$ (**2**), complexed with about three molecules of CH_3OCH_3. Nmr analysis was run quickly (to avoid decomposition) at 25° in CH_3CN solution with $CFCl_3$ and $Si(CH_3)_4$ as internal references. ^{19}F nmr peaks were found at ϕ −20.5 (singlet, area ~4) due to NF_2 and at 135.1 (double quintet, J_{FH} = 50.5, J_{FF} = 9.8 Hz, area 1) due to NFH. ^1H nmr analysis gave peaks at τ 1 assigned to NFH and 5.8 due to CH_3OCH_3. Absorptions assigned to **2** constituted over 90% of the peaks in the fluorine nmr spectrum.

Other products, which increased in amount slowly as the sample remained at room temperature (it was stable at −78°), were HNF_2 (ϕ 7), $CF(NF_2)_2NFH$ (HF adduct of **1**, reported[1] in previous work), and the major decomposition product, $H_2NC(NF_2)$=NF (**3**), from loss of HNF_2 by **2**. Compound **3** was purified by glpc on a 0.25 in. × 9 ft column (30% SF-96 on Anakrom ABS) at 75°, T_R = 121 ($CHCl{=}CCl_2$ = 100), vapor pressure approximately 2 mm at 25°: nmr (CH_3CN, $CFCl_3$) ϕ −47.2 (s, 2, NF_2), 50.7 (s, 1, =NF); τ 4.07 (broad singlet, NH_2); ir (liquid) 2.88 (s), 2.95 (s), 3.02 (s) and 3.17 (m) all due to NH_2, 5.85 (s) C=N, 6.28 (m), 7.34 (m), 9.65 (w), 9.95 (w), 10.90 (m), 11.65 (vs) NF, 14.25 μ (w); mass spectrum *m/e*, ion (rel intensity), 27, CHN^+ (42); 28, CH_2N^+ (81), 41, CHN_2^+ (16); 42, $CH_2N_2^+$ (72); 46, $CHFN^+$ (40), 56, $CH_2N_3^+$ (1.7); 61, $CH_2FN_2^+$ (100); 75, $CH_2FN_3^+$ (1); 113, $CH_2F_3N_3^+$ (16.5), parent peak (no peaks at higher mass). *Anal.* Calcd for $CH_2F_3N_3$ (113.05): C, 10.6; F, 50.4; N, 37.2. Found: C, 10.9; F, 50.0; N, 35.9.

Treatment of **3** with aqueous NaOH liberates 1 mol of N_2 per mol of compound, as observed in the reaction of **1** and base.[13] Fluorination of **3** yields **1**.

Fluorination of 2. Preparation of Tetrakis(difluoramino)methane (4) without Solvent.—The adduct **2** (approximately 2.9 mmol), prepared as above and free of most of the solvent, was fluorinated in the glass reactor with approximately sixfold molar excess of 3% F_2 (97% N_2) at −30° over a period of about 5 hr. The effluent gases were passed through a tube filled with NaF at 25° and into two borosilicate glass traps (containing glass beads) connected in series and cooled with liquid oxygen. The products were separated by glpc (Table IV) on a 0.5 in. × 18 ft column (33% KF-8126 on Celite) at 25°. The products isolated (area %) included $C(NF_2)_4$ **4** (20), **5** (16), **1** (14), **7** (<5), **6**(<5), and $(F_2N)_3CNFH$ **9** (<5), isolated in the backflush (see below for analysis of **9**). All except **4**[3] and **9** are known compounds.[2,4]

TABLE IV

GAS CHROMATOGRAPHY DATA (AT 25°) FOR $C(NF_2)_4$

Column	Dimensions, in. × ft	T_R[a]
33% KF-8126 on Celite	0.5 × 5	153
33% KF-8126 on Celite	0.5 × 18	160
20% FS-1265 on firebrick	0.5 × 20	111
33% FC-45 on Celite	0.5 × 24	468

[a] Relative to $CFCl_3$ = 100; $T_R = (T_{compound} - T_{air})/(T_{ref} - T_{air}) \times 100$

(13) R. L. Rebertus and B. W. Nippoldt, *J. Org. Chem.* **32**, 4044 (1967).

In Trifluoroethanol.—The adduct **2** described above was dissolved in dry trifluoroethanol and fluorinated with 2 to 20% F_2 (N_2 diluent) at about −30°. The gaseous products were again separated by glpc to afford about a 20% yield of **4** (based on NH_3 used to prepare **2**).

Most of the properties of $C(NF_2)_4$ are presented in Table I. Additional data (glpc, ir, and mass spectrum) are given below.

The infrared spectrum (gas) of **4** contains the following absorptions: 8.94 (m), 9.47 (w), 10.19 (vs) NF, 10.51 (vs) NF, 10.96 (vs) NF, 14.76 μ (w).

The mass spectrum of **4**, reported in Table V, was run on a Consolidated Electrodynamics Corp. Model 21-1030 mass spectrometer. An ionization potential of 70 eV and an ionization temperature of 250° were employed.

TABLE V

MASS SPECTRUM OF $C(NF_2)_4$

m/e[a]	Ion	Rel intensity	*m/e*[a]	Ion	Rel intensity
14	N	5.33	40	CN_2	7.78
19	F	1.92	45	CNF	5.51
26	CN	7.52	47	N_2F	2.33
28	N_2	3.77	50	CF_2	16.91
31	CF	56.94	52	NF_2	64.15
33	NF	41.05	54	CN_3	1.00
59	CN_2F	7.94	97	CN_2F_3	100.0
64	CNF_2	79.77	98	Isotope	1.82
65	Isotope	1.16	116	CN_2F_4	0.81
78	CN_2F_2	11.99	168	CN_3F_6	38.27
83	CNF_3	1.11			

[a] I_m = 0.258 A and 0.538 (*m/e* 64, 168).

Fluorination of 2, Bis(difluoramino)bis(fluoramino)methane (8), and Tris(difluoramino)fluoraminomethane (9).—In a 20-ml capacity poly(chlorotrifluoroethylene) reactor containing a ptfe-coated magnetic stirring bar were condensed 3 ml of CH_3OCH_3 and 1.2 g (8 mmol) of **1** at −110°. To this stirred solution was transferred over several minutes under vacuum a gaseous mixture of NH_3 (5 mmol) and CH_3OCH_3 (from 2 ml of liquid). After stirring for 10 min at −110°, the reactor was warmed to −63° and most of the CH_3OCH_3 was removed under vacuum to a vapor pressure of 25 mm. CH_3CN (2 ml) was added and the reaction mixture was fluorinated at −37° by means of a tube placed beneath the liquid through which a stream of 3% F_2 (97% N_2) was introduced at a rate of 50–100 cc/min. The reaction mixture was monitored by glpc (approximately 0.01-ml samples) on a 0.25 in. × 6 ft SF-96 column on Anakrom ABS at 50°. The principal peaks are shown in Table VI.

TABLE VI

FLUORINATION OF $H_2NC(NF_2)_2NFH$ (2)

			Glpc peaks and areas			
		Time, min	1.58	3.50	9.50	11.25
Time, hr	F_2, mmol	T_R Identity	100 CH_3CN	258 **9**	758 **8**	904 **3**[a]
1.5	3.2		31	*b*	2.5	4.9
2.0	5.3		22	*b*	2.3	2.6
2.75	8.5		32	0.3	5.7	1.6
3.75	12.7		35	7.3	5.3	1.8
4.5	16		66	10.1	3.8	0.5

[a] Represents adduct **2**, since **2** converts to **3** on heating. [b] Trace.

Compounds **8** and **9** were isolated by glpc using the same column described above except that the dimensions were 0.375 in. × 14 ft. Compound **8**, $(F_2N)_2C(NFH)_2$, is a colorless liquid with vapor pressure about 20 mm at 22°: ^{19}F nmr ($CFCl_3$) ϕ −23.6 (s, 2, NF_2), 135.0 (d, 1, NFH); ir 3.01 (m) NH, 7.01 (m), 9.84 (m), 10.66–11.79 μ (s) NF; mass spectrum *m/e* (ion) 28

(N_2^+, largest peak), 45 (CFN^+), 46 ($CHFN^+$), 59 (CFN_2^+), 61 ($CH_2FN_2^+$), 64 (CF_2N^+), 79 ($CHF_2N_2^+$), 80 ($CH_2F_2N_2^+$), 113 ($CH_2F_3N_3^+$), 132 ($CH_2F_4N_3^+$, parent minus NF_2 group); mol wt (theory), 184; found (by mass spectral effusion rates on *m/e* 64 peak), 192.

Compound **9** [$(F_2N)_3CNFH$] is a colorless liquid: ^{19}F nmr ϕ −26.4 (s, 6, NF_2), 136.1 (d, J = 5 Hz, 1, NFH); ir 3.03 (w) NH, 10.07 (s) NF, 10.48 (s) NF, 11.07 (vs) NF, 11.89 μ (s) NF; mass spectrum *m/e*, ion (rel intensity), 31, CF^+ (100); 34, NHF^+ (51); 52, NF_2^+ (41); 64, CF_2N^+ (27); 79, $CHF_2N_2^+$ (35); 97, $CF_3N_2^+$ (23); 150, $CHF_5N_3^+$ (16); the latter peak is the parent minus NF_2.

Treatment of **9** with NaF caused loss of HNF_2 and formation of **1**.

Preparation of *N*-Bis(difluoramino)fluoraminomethyl-*N'*-isopropylidine Hydrazine (20), Bis(difluoramino)fluoromethylamine (23), and Difluoraminofluoraminodifluoromethane (24).—In a 1.5-ml capacity glass nmr tube was placed 18.7 mg (0.26 mmol) of acetone hydrazone; then 0.1 ml of dimethyl ether, 0.03 ml of $CFCl_3$, and 0.45 g (0.30 mmol) of **1** were transferred in under vacuum using a −110° bath. The tube was sealed with a flame and the reagents were mixed at −110° to give a yellow solution. The ^{19}F nmr was run at −95 to −85°. The principal peaks were at ϕ −20.4 (s, 4, NF_2) and 138.2 (d m, 1, NFH), consistent for the adduct **20** [$(CH_3)_2C{=}NNHC(NF_2)_2$-NFH]. **20** decomposed on warming to room temperature.

The reaction was repeated on a 20 times larger scale, and the reaction mixture was allowed to warm to room temperature while it was pumped through 0, −78, and −196° traps connected in series. A dark, oxidizing oil remained in the reactor; the 0° trap was empty, the −78° trap contained a pale yellow liquid, and the −196° trap contained only dimethyl ether. The contents of the −78° trap were separated by glpc on a 0.5 in. × 14 ft column (25% SF-96 on Anakrom ABS) at 25°. The main components were dimethyl ether and HNF_2 (74 total area %) eluting at 1.8–2.5 min. The peak eluting at 5.9 min (T_R = 85, $CFCl_3$ = 100), 4.7%, was identified as a mixture of F_2NCF_2-NFH (**24**) and N_2O. The 23.4-min peak (3.9%) was found to be $FC(NF_2)_2NH_2$ (**23**).

Properties of 23 follow: bp 68° (extrapolated from vapor pressure data); ^{19}F nmr ($CFCl_3$) ϕ −21.4 (s, 4, NF_2), 113.6 (s, 1, CF); ir (gas) 2.86 and 2.93 (w), NH_2, 6.20 (m), 7.63 (m), 8.84 (w), 9.21 (w), 9.84 (w), 10.60 (s), and 11.26 μ (m), NF_2; mass spectrum *m/e*, ion (rel intensity), 16, NH_2^+ (7.7); 28, CH_2N^+ (24.6); 31, CF^+ (37); 33 NF^+ (27); 41, CHN_2^+ (39); 46, $CHFN^+$ (100); 47, CH_2FN^+ (22); 60, $CHFN_2^+$ (51); 66, $CH_2F_2N^+$ (17); 99, $CH_2F_3N_2^+$ (22). *Anal.* Calcd for $CH_2F_5N_3$ (151): C, 8.0; F, 62.9. Found: C, 8.1; F, 61.0.

Properties of 24 (further purified by glpc)[6] follow: bp 17.7° (from vapor pressure data); nmr ($CFCl_3$) ϕ −17.0 (s, 2, NF_2), 104.4 (d, $J_{CF_2/NH}$ = 12.7 Hz, d, $J_{CF_2/NF}$ = 27.5 Hz, 2, CF_2), 132.3 (d, J_{FH} = 56 Hz, t, J_{F/CF_2} = 27.5 Hz, 1, NFH); $\tau \sim 0$ (d, J = 56 Hz, NFH); ir (gas) 3.0 (w) NH, 7.0 (m), 7.6 (s), 8.1 (s), 8.4 (m), 8.7 (m), 9.7 (m), 10.1 (m), 10.75 (vs), and 11.7 μ (s) NF_2; mass spectrum *m/e*, ion (rel intensity), 31, CF^+ (18); 46, $CHFN^+$ (30); 50, CF_2^+ (13); 52, NF_2^+ (10); 64, CF_2N^+ (100); 65, CHF_2N^+ (30); 69, CF_3^+ (50); 84, CHF_3N^+ (99); 98, $CHF_3N_2^+$ (7); 116, CF_4N_2 (2); mol wt, theory for CHF_5N_2, 136; found (from mass spectral effusion rates), 133. **24** slowly loses HF to yield **7**.

Preparation of Chlorodifluoraminodiazirine (25).[14]—Semicarbazide hydrochloride (0.10 g, 1 mmol) was treated with 0.15 g (1 mmol) of **1** by condensing the latter into a glass reactor at −110° and allowing the mixture to warm slowly to room temperature while stirring by means of a ptfe-coated magnetic stirring bar. The gas phase was sampled periodically and studied by glpc on a 0.25 in. × 24 ft column (Kel-F tetramer on Celite) at 25°. A peak with a T_R of 46 ($CFCl_3$ = 100) was observed to reach maximum concentration after 6 hr. This product was trapped out and fully characterized as chlorodifluoraminodiazirine (**25**). Properties and analytical data have been reported.[7] Other products identified (glpc, nmr, ir) in this reaction include **26**,[8] **27**,[9] and **7**.[2]

Preparation of 1,1-Dimethyl-2,3,3-trifluoroguanidine (31).[14]—A glass nmr tube was charged with 0.135 g (0.30 mmol) of $(CH_3)_2NH$, 0.060 g (0.40 mmol) of **1**, 0.1 g of CH_3OCH_3, and 0.035 g of $CFCl_3$. The tube was sealed and allowed to warm to −78° and the ^{19}F nmr spectrum was obtained at this temperature. Complete conversion to $(CH_3)_2NC(NF_2){=}NF$ (**31**) had taken place with no evidence for the intermediate adduct $(CH_3)_2$-$NC(NF_2)_2NFH$. ^{19}F nmr peaks for **31** were at ϕ −40.8 (s, 2, NF_2) and 61.7 (s, 1, =NF). **31** was purified by glpc on a 0.375 in. × 15 ft column (SF-96 on Anakrom ABS) at 80°. The peak eluting at about 12 min was trapped for analysis: mass spectrum *m/e*, ion (rel intensity), 15, CH_3^+ (100); 28, CH_2N^+ (92); 33, NF^+ (24); 42, $C_2H_4N^+$ (72); 69, $C_3H_5N_2^+$ (82); 70, $C_3H_6N_2^+$ (86); 89, $C_3H_6FN_2^+$ (59); 141, $C_3H_6F_3N_3^+$ (26, parent ion). *Anal.* Calcd for $C_3H_6F_3N_3$ (141.1): C, 25.5; F, 40.4. Found: C, 25.5; F, 40.4.

The nonbasicity of **31** was demonstrated by the absence of a shift in the ^{19}F nmr peaks after addition of anhydrous HCl.

Preparation of *N,N*-Dimethyl-*N'*-hexafluorisopropylidine Hydrazine (33).[11b]—A mixture of 0.35 g (3 mmol) of **29**, $(CF_3)_2$-C=NF, 0.11 g (2.5 mmol) of $HN(CH_3)_2$, and 0.4 g of $CFCl_3$ was allowed to react at room temperature in a sealed tube for 18 hr. ^{19}F nmr revealed no **29** remaining. Separation of the reaction mixture by glpc on a 0.375 in. × 12 ft column (FS-1265, 25%, on Chromosorb P) at 100° afforded a colorless liquid, T_R 638 (CCl_4 = 100), having a vapor pressure of about 2 mm at 25°, and identified as $(CF_3)_2C{=}NN(CH_3)_2$ (**33**): nmr ϕ 63.7 (quartet, J_{F-F} = 8.5 Hz, anti CF_3), 52.0 (quartet, J_{F-F} = 8.5 Hz, septet, J_{F-H} = 2.7 Hz, syn CF_3); τ 6.75 (multiplet, CH_3); ir 6.25 μ (C=N); mass spectral analysis gave a large parent peak at *m/e* 208, and lower molecular weight fragments. *Anal.* Calcd for $C_5H_6F_6N_2$ (208.1): C, 28.85; H, 2.9; F, 54.8; N, 13.5. Found: C, 29.7; H, 3.3; F, 54.0; N, 13.6. Compound **33** was also synthesized by the reaction of hexafluoroacetone and *N,N*-dimethylhydrazine followed by dehydration of the intermediate adduct (see equation in text). This was the method used to prepare an analogous compound, $(CF_3)_2C{=}NNH_2$.[10a]

Dimerization of 33. Preparation of 1,1,3,3-Tetramethyl-2,2-4,4-tetrakis(trifluoromethyl)-1,3-diazetidine (34).—In the initial preparation of **33** (from **29** and dimethylamine), some of the chromatographed product was allowed to remain in the borosilicate glass trap for several days, during which time it appeared to partially crystallize. Vaporizing the liquid portion (**33**) under vacuum and analysis of the solid residue, mp 112–113°, revealed that a cyclization–dimerization had apparently occurred to yield the diazetidine **34**. Treatment of **33** with concentrated H_2SO_4 also induced cyclization to **34**, but uv irradiation was without effect. The dimer **34** was analyzed by nmr, ir, and mass spectrum: nmr ($CFCl_3$) ϕ 69.6 (s, CF_3), τ 7.29 (s, CH_3); ir showed no peaks due to unsaturation between 3.5 and 6.8 μ; mass spectrum *m/e*, ion (rel intensity), 15, CH_3^+ (30.4); 28, N_2^+ or CH_2N^+ (17.4); 42, $CH_2N_2^+$ or $C_2H_4N^+$ (53.5); 43, $CH_3N_2^+$ or $C_2H_5N^+$ (100); 69, CF_3^+ (8.6); 139, $C_4H_6N_2F_4$ (42.3); 189, $C_5H_6F_5N_2^+$ (8.7); 207, $C_5H_5F_6N_2^+$ (2.8); 208, $C_5H_6F_6N_2^+$ (2.7, 50% parent peak); 265, $C_7H_{11}F_6N_4^+$ (1.6); 416, $C_{10}H_{12}F_{12}N_4^+$ (11.6, parent peak). *Anal.* Calcd for $C_{10}H_{12}F_{12}N_4$ (416.24): C, 28.85; H, 2.9; F, 54.8; N, 13.5. Found: C, 29.5; H, 2.9; F, 55.0; N, 14.0.

Registry No.—**1,** 10051-06-6; **2,** 35404-98-9; **3,** 37950-72-4; **4,** 17125-65-4; **7,** 14362-70-0; **8,** 37931-22-9; **9,** 37931-23-0; **11,** 37931-24-1; **12,** 37931-25-2; **13,** 37931-26-3; **14,** 37931-27-4; **15,** 37931-28-5; **16,** 37931-29-6; **17,** 37931-30-9; **18,** 37931-31-0; **19,** 37931-32-1; **20,** 37931-33-2; **21,** 37931-34-3; **22,** 37931-35-4; **23,** 37931-36-5; **24,** 37931-37-6; **28,** 758-35-0; **29,** 2802-70-2; **30,** 37931-40-1; **31,** 37931-11-6; **32,** 1619-94-9; **33,** 34224-15-2; **34,** 37931-14-9; **35,** 37931-15-0; NH_3, 7664-41-7; *p*-$CF_3C_6H_4NH_2$, 455-14-1; *p*-$NCC_6H_4NH_2$, 873-74-5; *n*-$C_4H_9NH_2$, 109-73-9; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3CNH_2$, 75-64-9; $HClO_4 \cdot H_2NNH_2$, 27978-54-7; $(CH_3)_2C{=}NNH_2$, 5281-20-9; $CF_3CONHNH_2$, 1538-08-5; $COCH_2CH_2CONH$, 123-56-8.

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The Addition of Isocyanic Acid to Pentafluoroguanidine. Bis(difluoramino)fluoraminomethyl Isocyanate and Tris(difluoramino)methyl Isocyanate

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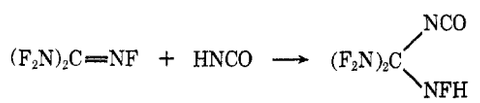
Isocyanic acid and pentafluoroguanidine reacted in the presence of a catalyst to form a 1:1 adduct, bis(difluoramino)fluoraminomethyl isocyanate (**1**), and a 2:1 adduct (**2**). The products obtained from the reactions of **1** with ethyl alchol, water, isocyanic acid, and 100% sulfuric acid are described. Fluorination of **1** gave tris(difluoramino)methyl isocyanate (**3**) and tetrakis(difluoramino)methane.

In connection with a program on the synthesis of compounds with a high content of N–F bonds, the addition of isocyanic acid to pentafluoroguanidine[2,3] was investigated. The addition was successful,[4,5]



1

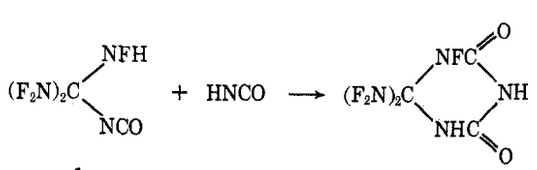
and the adduct proved to be a useful intermediate for the synthesis of a variety of new N–F compounds.

The low nucleophilicity of isocyanic acid and its rapid polymerization at room temperature operate against the desired addition to pentafluoroguanidine. Because of the low nucleophilicity of isocyanic acid, a basic catalyst, in this case urea, was added. When the catalyst was not used, erratic results were obtained. In order to minimize the polymerization reaction, a temperature of about −30° was used during the initial phase of the reaction. At this temperature isocyanic acid is quite stable, while at 0° it polymerizes readily.

The liquid 1:1 adduct (**1**) was separated from unchanged pentafluoroguanidine, isocyanic acid, and solid by-products by fractionation in a vacuum line.

The 1:1 adduct was assigned structure **1** on the basis of its infrared spectrum, proton and fluorine nmr spectra, and chemical reactions. Infrared absorptions at 3340 and 1410 cm^{-1} caused by the NH group in conjunction with a doublet of multiplets in the ^{19}F nmr spectrum at 125.0 ppm (J = 53 Hz) and a doublet at τ 1.59 (J = 53 Hz) in the ^{1}H nmr spectrum[6] establish the presence of an –NFH group. A broad, strong peak at −26.8 ppm was assigned to the difluoramino groups. Characteristic infrared absorptions at 2300 and 1480 cm^{-1} showed the presence of an isocyanate group.[8] The infrared spectrum is shown in Figure 1. Several reactions of **1** have established the presence of a carbon tetranitrogen skeleton and thus eliminated the possibility of a cyanate structure.

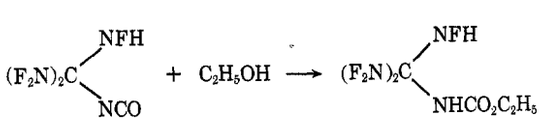
A 2:1 adduct (**2**) was extracted from the solid by-products formed during the preparation of **1**. It can also be prepared by the reaction of **1** with isocyanic



1 **2**

acid. The formulation of **2** as a cyclic compound is based upon the facts that the infrared and nmr spectra, respectively, show that the isocyanic acid has reacted with both the isocyanate and fluoramino groups, while its volatility (sufficient to allow vacuum sublimation at 50°) indicates that the compound is not a polymer. The question of whether the reaction occurs by initial reaction of the isocyanate or fluoramino group with isocyanic acid is not resolved.

The expected carbamate formed when **1** was treated with anhydrous ethyl alcohol.



The reaction of **1** with water was followed using fluorine nmr analysis. The results indicated that the amine which formed initially was unstable and lost difluoramine to form 1,1,2-trifluoroguanidine. Tri-

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, with monitoring by the Bureau of Naval Weapons, RMMP, under Contract NOrd 18728, and by the Bureau of Naval Weapons under Contract NOw 65-0277-c.

(2) R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967); R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967); R. J. Koshar and D. R. Husted, U. S. Patent 3,461,162 (1969).

(3) The pentafluoroguanidine was prepared by S. Frank, M. D. Meyers, and A. J. Fanelli, of these laboratories. An aqueous fluorination of guanidine hydrofluoride was used.

(4) A related addition of isocyanic acid to hexafluoroisopropylidenimine has been reported: W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

(5) Other adducts of pentafluoroguanidine have also been prepared: J. L. Zollinger, C. D. Wright, J. J. McBrady, D. H. Dybvig, F. A. Fleming, G. A. Kurhajec, R. A. Mitsch, and E. W. Neuvar, *ibid.*, **38**, 1065 (1973); C. D. Wright and J. L. Zollinger, *ibid.*, **38**, 1075 (1973).

(6) Fluorine and proton nmr spectra are reported in parts per million from trichlorofluoromethane and in τ values,[7] respectively.

(7) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(8) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).