Bis- and Tris(difluoramino)alkanes. Beckmann Rearrangement and Fragmentation of α-Difluoraminofluorimines

TRAVIS E. STEVENS

Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807

Received February 11, 1969

α-Substituted α-difluoraminofluorimines and α,α-bis(difluoramino)fluorimines undergo Beckmann fragmentations and rearrangements. Fragmentation in the presence of boron trifluoride produces α-substituted α-difluoramino fluorides; in the presence of difluoramine, 1,1-bis- and 1,1,1-tris(difluoramino)alkanes are formed. Rearrangement, however, is the major reaction path for α,α-bis(difluoramino)fluorimines, and a variety of products, including the expected amides, are produced. Characterization of the Beckmann products and the possible pathways leading to them are discussed in detail.

A variety of methods for preparing polydifluoramino compounds have evolved in the last decade. Among these methods are the addition of tetrafluorohydrazine (N_2F_4) to olefins,[1] the reaction of difluoramine (HNF_2) and carbonyl compounds to give geminal bis(difluoramino)alkanes,[2] the preparation of 1,2,2-tris(difluoramino)alkanes by a combination of the N_2F_4 and HNF_2 reactions,[3] and routes centered on additions to perfluoroguanidines.[4]

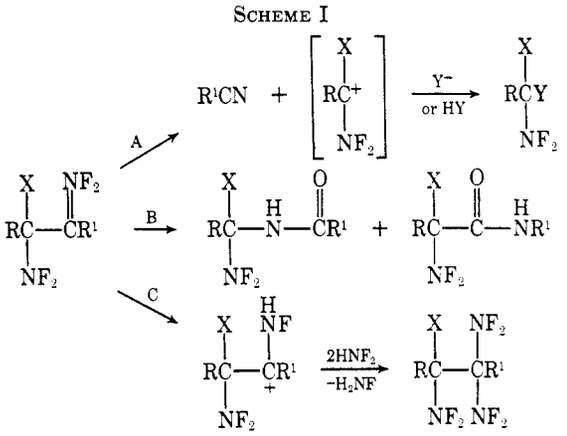
The addition of alcohols to perfluoroguanidine, followed by fluorination of the adduct,[4] provided a great variety of α,α,α-tris(difluoramino) ethers, but no general route to 1,1,1-tris(difluoramino)alkanes or 1-halo-1,1-bis(difluoramino)alkanes has been developed. For the reasons outlined earlier,[2] addition of HNF_2 to acid halides, esters, or ortho esters did not give such difluoramines.

To prepare bis- and tris(difluoramino)alkanes by alkylation of difluoramine, a convenient source of α-difluoramino- and α,α-bis(difluoramino)carbonium ions was necessary. When it was discovered that α-difluoraminofluorimines would cleave under acidic conditions (path A), in a process obviously related to the well-known Beckmann fragmentation,[5] a source of such carbonium ions for alkylation of difluoramine was available.

Other reaction paths are possible when molecules such as α-difluoraminofluorimines are treated with strong acid. The usual Beckmann rearrangement (Scheme I, path B) is shown, as well as one involving protonation on nitrogen (path C). The latter might eventually lead to a tris- or tetrakis(difluoramino)-alkane, but no evidence for path C was found in this work. Loss of fluoride ion from the difluoramino group, accompanied by migration of hydrogen or alkyl group, is also a known reaction of difluoramines.[6,7]

This paper summarizes a study of the Beckmann fragmentation and rearrangement reactions of a variety of α-substituted α-difluoramino- and α,α-bis(difluoramino)fluorimines, and reports a general route to

SCHEME I



geminal bis(difluoramines) and 1,1,1-tris(difluoramino)-alkanes that are not readily accessible by other synthetic routes.

The structures of some of the materials used in this study are summarized in Table I; they provide the key to Tables II–V.

Preparation of Fluorimines.—A tabulation of the unreported fluorimines used in this study is given in Table II. The α-substituted α-difluoraminofluorimines were readily prepared by addition of tetrafluorohydrazine to the appropriate olefin,[1] followed by dehydrofluorination with alcoholic base or an amine. Dehydrofluorination of α,α,β-tris(difluoramino) materials[3] provided the samples of α,α-bis(difluoramino)-fluorimines.

The fluorimine function, when an α C–H bond is available, will undergo a Neber reaction.[8] Thus, it was best to avoid an excess of a strong base such as methoxide when conducting dehydrofluorinations.

All the fluorimines reported in Table II were, according to their ^{19}F nmr spectra, of only one configuration. Presumably the fluorine of the fluorimine function is oriented *trans* to the α-difluoramino group.

Reactions of α-Substituted α-Difluoraminofluorimines.—Admittedly, most of our interest in the chemistry of fluorimines was centered on a synthetic route to the 1,1,1-tris(difluoramino)alkanes. Certain α-substituted α-difluoraminofluorimines were examined, however, not only to gain a better understanding of the reaction but also with the hope that certain fluorimines, such as α-halo materials, would directly produce the tris(difluoramino)alkanes when exposed to

(1) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967).

(2) (a) K. Baum, *J. Amer. Chem. Soc.*, **90**, 7083, 7089 (1968); (b) W. H. Graham and J. P. Freeman, *J. Org. Chem.*, in press.

(3) J. P. Freeman, R. C. Petry, and T. E. Stevens, *J. Amer. Chem. Soc.*, in press.

(4) (a) R. A. Davis, J. L. Koon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967); (b) R. L. Rebertus and P. F. Toren, *ibid.*, **32**, 4045 (1967).

(5) Reviewed by P. A. S. Smith, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1964, pp 483–507.

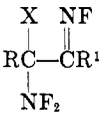
(6) K. Baum and H. M. Nelson, *J. Amer. Chem. Soc.*, **88**, 4459 (1966); T. E. Stevens and W. H. Graham, *ibid.*, **89**, 182 (1967).

(7) T. E. Stevens, *Chem. Commun.*, 1181 (1967).

(8) W. H. Graham and T. E. Stevens, unpublished results.

TABLE I

STRUCTURES OF FLUORAMINES



No.	R	R^1	X
1	CH_3	CH_3	CH_3
2	C_6H_5	CH_3	CH_3
3	CH_3	C_6H_5	CH_3
4	CH_3	CH_3	Cl
5	CH_3	CH_3	Br
6	4-BrC_6H_4	CH_3	Cl
7	CH_3	CH_3	NF_2
8	$-(CH_2)_4-$		CH_3
9	$-(CH_2)_3-$		NF_2
10	$-(CH_2)_4-$		NF_2
11	$-(CH_2)_5-$		NF_2
12	C_6H_5	C_2H_5	NF_2
13	4-ClC_6H_4	CH_3	NF_2
14	4-$CH_3OC_6H_4$	CH_3	NF_2
15	4-BrC_6H_4	CH_3	NF_2
16	C_6H_5	CH_3	Cl
17	C_6H_5	CH_3	Br
18	$-(CH_2)_4-$		Cl
25	C_6H_5	C_6H_5	F
34	CH_3	C_6H_5	NF_2
35	C_6H_5	CH_3	NF_2

No.	R	X
19	C_6H_5	Cl
20	C_6H_5	Br
21	C_6H_5	CH_3
22	$-(CH_2)_4CN$	Cl
23	$-(CH_2)_4CN$	CH_3
24	$-(CH_2)_3CN$	NF_2

No.	R	X
26	CH_3	Cl
27	C_6H_5	Cl
28	C_6H_5	Br
29	C_6H_5	F
30	$-(CH_2)_4CN$	Cl
31	$-(CH_2)_4CN$	CH_3
32	4-BrC_6H_4	Cl
36	C_6H_5	NF_2
37a	4-$CH_3OC_6H_4$	NF_2
37b	4-ClC_6H_4	NF_2
38	$-(CH_2)_3CN$	NF_2
39	$-(CH_2)_4CN$	NF_2
40	$-(CH_2)_5CN$	NF_2

TABLE II

α-DIFLUORAMINOFLUORIMINES

Fluorimine	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	^{19}F nmr spectra[a] $-NF_2$, ϕ[a]	$-NF$, ϕ[a]
1[b]	38.96	5.88	18.18	39.28	6.23	18.43	−27.4	−27.7
2	55.55	5.13	12.96	55.35	5.27	13.45	F_A −30.0	
							F_B −25.0	−28.5
							J_{FF} = 580	
3[c]	55.55	5.13	12.96	55.30	5.38	12.62	−29.5	−38.6
4[d]	27.52	3.47	16.05	28.05	3.72	15.49	F_A −40.9	
							F_B −29.5	−34.6
							J_{FF} = 580	
5	21.93	2.76	12.79	22.13	2.86	12.71	F_A −48.6	
							F_B −32.2	−34.4
							J_{FF} = 568	
6	34.25	2.24	8.80	33.71	2.61	9.26	F_A −46.2	
							F_B −34.8	−36.3
							J_{FF} = 563	
7	25.22	3.17	21.99	25.04	3.19	22.81	−28.2	−40.2
8[e]	46.66	6.15	15.53	46.92	6.47	15.56	F_A −26.3	
							F_B −18.5	−22.3
							J_{FF} = 582	
9	29.56	2.98	20.69	29.94	3.30	20.25	−35.4	−60.2
10	33.18	3.71	19.35	33.65	3.80	19.15	−1840 Hz[f]	
							−1204 Hz	−38.4
							−1156 Hz	
							−536 Hz	
11							−29.1	−37.1
12	44.95	3.77	15.72	44.75	3.87	16.04	−31.7	−42.5
13[g]	37.58	2.45	14.61	37.36	2.66	15.03	−31.0	−48.3
14	42.41	3.56	14.84	41.82	3.09	15.33	−32.2	−49.5
15	32.55	2.13	12.65	32.68	2.33	12.59	−30.9	−48.8

[a] At 40 MHz in CCl_4 or $CDCl_3$ solution. Usually, CCl_3F was the internal standard. ϕ values are parts per million from CCl_3F. J values are given in hertz. [b] F, 37.1 (calcd 37.0); bp 55° (50 mm); $n^{20}D$ 1.3940. [c] Mp 41–43°; F, 26.3 (calcd 26.4). [d] Cl, 26.2 (calcd 26.3). [e] F, 31.9 (calcd 31.6). [f] Appears to be AA'BB' spectrum. [g] Cl, 12.0 (calcd 12.3); F, 33.3 (calcd. 33.0).

TABLE III

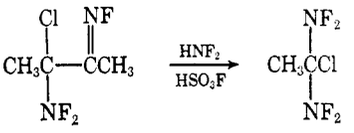
α-DIFLUORAMINO FLUORIDES

Fluorimine	Product	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
16	19	42.99	2.58	7.16	43.28	2.87	7.89
17	20[a]	35.03	2.10	5.84	35.69	2.55	6.40
2	21	54.86	4.60	8.00	54.78	4.80	8.40
18	22	35.92	4.02	13.97	35.72	4.30	14.17
8	23	46.66	6.15	15.55	46.73	6.40	15.80
9	24	29.56	2.98	20.69	30.28	3.20	22.09

[a] *Anal.* Calcd: F, 23.75; Br, 33.3. Found: F, 23.9; Br, 33.1.

expected as a consequence of the added stability of the α-phenylcarbonium ion.[15]

When we turned our attention to the α-halofluorimines **4** and **5**, it became evident that fluorosulfonic acid was a reagent of choice for fluorimine cleavages.



4 **26**

TABLE IV

1,1-BIS(DIFLUORAMINO)-1-HALOALKANES FROM FLUORIMINES AND HNF_2

Fluorimine	Product	Acid used	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % F	Found, % C	Found, % H	Found, % N	Found, % F	^{19}F nmr spectra,[a] ϕ[b]
4	26	HSO_3F	54	14.42	1.81	16.83	45.6	14.12	2.01	16.69	45.4	−34.7
16	27	BF_3 or H_2SO_4	60	36.78	2.20	12.26	33.3	37.38	3.10	13.07	35.8	−37.1
17	28	H_2SO_4	41	30.79	1.85	10.26	29.3	31.41	2.18	10.76	28.1	−44.0
25	29	HSO_3F	59	39.63	2.38	13.21		39.69	2.88	14.22		−23.6[c]
18	30	HSO_3F	23	30.85	3.45	17.99	32.5	31.23	3.80	18.53	32.8	F_A −35.2, F_B −33.9, J_{FF} = 605
8	31	HSO_3F	15	39.44	5.20	19.71		39.53	5.35	20.14		−27.5
6	32	H_2SO_4	72	27.34	1.31	9.11	24.7	28.07	1.61	9.77	25.11	−37.5

[a] At 40 MHz with CCl_3F internal standard. J values are given in hertz. [b] ϕ value are parts per million from CCl_3F. [c] C–F resonance at ϕ +152.4.

difluoramine under acidic conditions.[9,10] Conversion of α-halofluorimines into tris(difluoramino)alkanes was never accomplished.[10]

As part of this study, some of the α-difluoraminofluorimines were exposed to boron trifluoride (without added difluoramine). This Lewis acid, that neither complexes nor destroys HNF_2 at ordinary temperature,[11] appeared to be a particularly promising reagent for Beckmann cleavages of fluorimines. In these experiments without added difluoramine, fluoride ion appeared to be an effective trap for the α-difluoramino carbonium ion.[12,13] Table III summarizes characterization of the α-difluoramino fluorides produced in this way. When difluoramine was present, fluoride ion did not compete effectively with HNF_2 for the carbonium ion.[14]

The preliminary experiments that suggested the synthetic possibilities of fluorimine cleavages in the presence of difluoramine were conducted with fluorimines **1**, **2**, and **3**. Both **1** and **3**, upon treatment with HNF_2 and neat 96 or 100% sulfuric acid, gave 2,2-bis(difluoramino)propane. Fluorimine **2**, however, gave acetophenone (after hydrolysis), indicating that cleavage indeed occurred, but that the intermediate carbonium ion did not readily alkylate HNF_2. In view of the similar results obtained when acetophenone was exposed to HNF_2/H_2SO_4 under similar conditions,[2] this was

(9) 2-Chloro-2-difluoraminopropane, however, was successfully converted into 2,2-bis(difluoramino)propane: Dr. K. Johnson, Rohm and Haas Co., unpublished.

(10) Certain α-phosphato-α-difluoraminofluorimines could be converted into tris(difluoramines) in one step as discussed below.

(11) A. D. Craig, *Inorg. Chem.*, **3**, 1628 (1964).

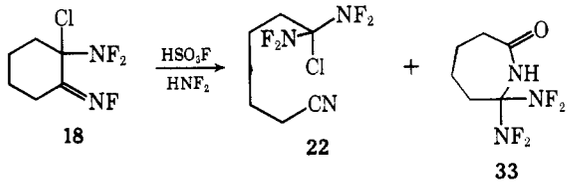
(12) For a preliminary report, see T. E. Stevens, *Tetrahedron Lett.*, 3017 (1967).

(13) For examples of chloride ion functioning in a similar way in Beckmann fragmentation, see A. Hassner and E. G. Nash, *ibid.*, 525 (1965), and M. Ohno and I. Terasawa, *J. Amer. Chem. Soc.*, **88**, 5683 (1966).

(14) The last entry in Table III, **24**, was isolated from a reaction conducted with HNF_2 present.

Fluorimine **4** gave 1-chloro-1,1-bis(difluoramino)ethane (**26**) cleanly. However, only trace amounts of 1-bromo-1,1-bis(difluoramine)ethane could be obtained from α-bromofluorimine **5** and HNF_2 with either fluorosulfonic or sulfuric acid. Bromine was liberated in these experiments. The results of these experiments, as well as related work, are summarized in Table IV.

With the cyclohexylfluorimine **18**, the main product was the chlorobis(difluoramino)nitrile **22** (23%), although a small amount of amide **33** also was isolated.



18 **22** **33**

Intramolecular cyclization of the capronitrile **22** could give rise to **33**, but there was no evidence for the formation of the amide when a sample of **22** was subjected to HSO_3F and HNF_2. In view of the results of rearrangements conducted in the presence of BF_3 (see below) it is more likely that a route such as is sketched leads to **33** (Scheme II).

Amide **33**, mp 70–71°, was characterized by a ^{19}F nmr peak at ϕ −24.7, and ^1H nmr peaks at τ 2.3 (NH) and at 115–155 Hz in a ratio of 1:8; no ^1H signal at τ 6.8, characteristic of the CH_2NH– function of caprolactam, was evident.

The three α-aryl-α-halo-α-difluoraminofluorimines **6**, **16**, and **17** were converted into α,α-bis(difluoramino)-α-halotoluenes. Here, the favorable experimental environment include sulfuric acid as catalyst and methy-

(15) Under more stringent conditions, acetophenone can be converted into 1,1-bis(difluoramino)-1-phenylethane, and a small amount of the bis(difluoramino)ethane could be obtained from **2**, BF_3, and HNF_2.

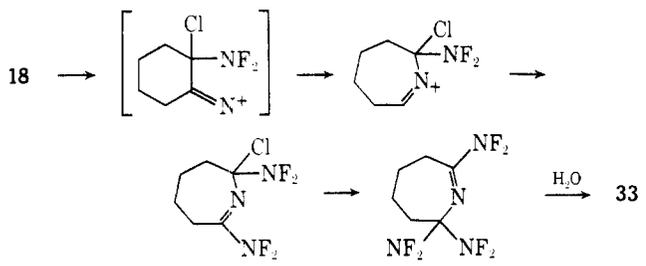
TABLE V

1,1,1-TRIS(DIFLUORAMINO)ALKANES

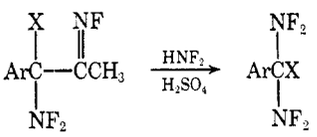
Fluorimine	Tris(difluoramine)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	^{19}F nmr spectra, ϕ^a
34 or **7**	$CH_3C(NF_2)_3$	3							−28.0
12 or **35**	**36**[b]	17	34.29	2.06	17.15	34.67	2.37	17.73	−27.8
14	*p*-$CH_3OC_6H_4C(NF_2)_3$ (**37a**)	12	34.92	2.56	15.27	34.51	2.89	14.58	−26.9
13	*p*-$ClC_6H_4C(NF_2)_3$ (**37b**)	c	30.07	1.44	15.03	30.05	1.69	15.11	−28.0
9	$NC(CH_2)_3C(NF_2)_3$ (**38**)	15	25.43	2.56	23.73	26.56	2.68	24.01	−27.7
10	$NC(CH_2)_4C(NF_2)_3$ (**39**)	11	28.81	3.22	22.40	28.42	3.44	21.87	−27.7
11	$CN(CH_2)_5C(NF_2)_3$	8	31.82	3.82	21.21	31.89	4.05	20.74	−27.5

[a] At 40 MHz in CCl_4 solution. ϕ values are in parts per million from internal CCl_3F. [b] F, 45.8 (calcd 46.5). [c] This material had a high vapor pressure, about 60 mm at 30°, and its isolation by chromatographic and distillation techniques was very inefficient.

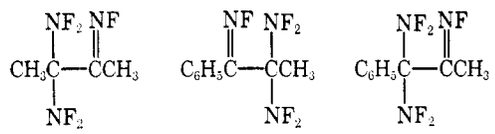
SCHEME II



lene chloride as solvent. Without solvent, the interaction of the fluorimine and sulfuric acid was difficult to control and often gave an exothermic decomposition that resulted in formation of the benzoic acid corresponding to the aryl group. Conversion of **16** into **27** with boron trifluoride was equally effective.



Reaction of α,α-Bis(difluoramino)fluorimines.—Attention then was shifted to α,α-bis(difluoramino)-fluorimines. On the basis of the experiences with α-halofluorimines, the three fluorimines **7**, **34**, and **35** were chosen for further study. The close electronic relationship of **4** and **7** is obvious, while with **34** formation of benzonitrile might be expected to aid the initial carbon–carbon bond cleavage. In **35** the aromatic ring

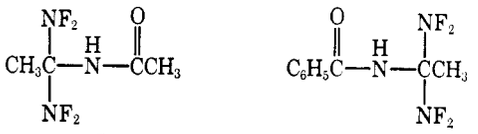


7 **34** **35**

should stabilize the bis(difluoramino)-substituted carbonium ion. The preparation of **34** and **35** was reported recently.[3]

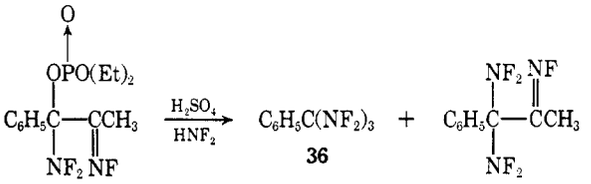
Only very small amounts of 1,1,1-tris(difluoramino)-ethane (from **7** or **34**) and α,α,α-tris(difluoramino)-toluene (from **35**) could be obtained by cleavage and difluoramination using sulfuric or fluorosulfonic acids. The tris(difluoramino)ethane was characterized only by spectral data. Table V summarizes the characterization of the tristoluene and other 1,1,1-tris(difluoramino) compounds.[16,17]

Amides **45** and **46** were obtained in low yield (up to 30%) from **7** and **34**, respectively. In sulfuric acid, fluorimine **35** was converted into benozic acid rather than a difluoraminoamide.[18] Apparently the com-



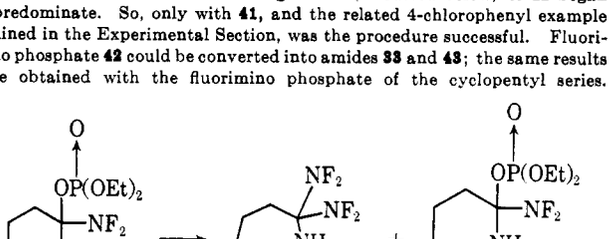
45 **46**

(16) The possibility that α-phosphato-α-difluoraminofluorimines such as **41**, often used as precursors to α,α-bis(difluoramino)fluorimines,[3] could be converted directly into the tris(difluoramino)alkanes was explored in some detail. This would, of course, shorten the sequence considerably. Phosphate **41**, which would give about 50% **35**,[3] was converted directly into **36**



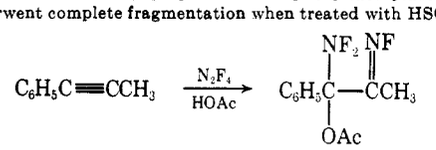
41 **36** **35**

(3% yield) with a longer reaction time. Under the same reaction conditions (30% fuming sulfuric acid), **35** gave **36** (5% yield). With fluorosulfonic acid, Beckmann and related rearrangements (discussed below) of **41** began to predominate. So, only with **41**, and the related 4-chlorophenyl example outlined in the Experimental Section, was the procedure successful. Fluorimino phosphate **42** could be converted into amides **33** and **43**; the same results were obtained with the fluorimino phosphate of the cyclopentyl series.



42 **33** **43**

The fluorimino acetate **44**, prepared from phenylmethylacetylene and N_2F_4,[17] underwent complete fragmentation when treated with HSO_3F/HNF_2.



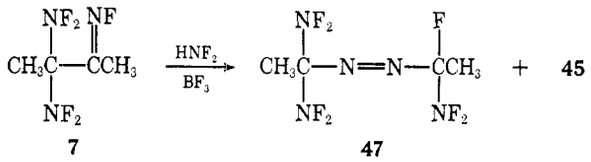
44

(17) W. H. Graham, 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, Abstract S-159.

(18) The α,α,α-tris(difluoramino)toluenes, in particular, were rather sensitive to strong acid, and readily liberated difluoramine. Thus, the same conditions that gave fragmentation of the fluorimine destroyed the desired product. This instability of the tris(difluoramino) was a limitation that was never successfully circumvented; the amount of trisalkane formed and destroyed was never determined.

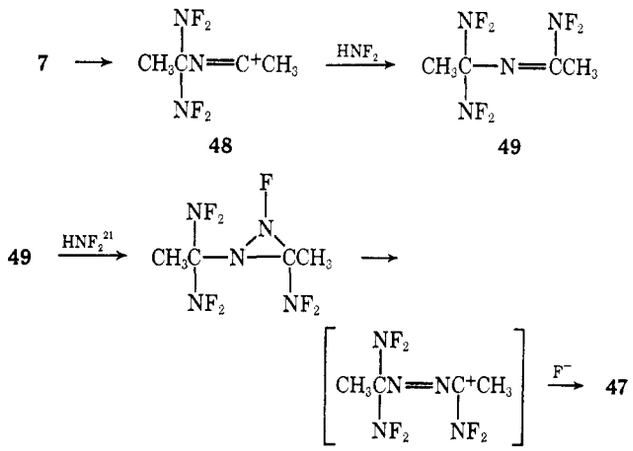
bined electronegativity of the two difluoramino groups hinders the cleavage necessary to produce 1,1-bis(difluoramino)carbonium ions. Instead, an ordinary Beckmann rearrangement with migration of the bis(difluoramino)alkyl fragment predominates.

Rather unexpected rearrangements were encountered when boron trifluoride was used with fluorimines **7** and **35**. No detectable 1,1,1-tris(difluoramino)ethane was isolated from **7**, HNF_2, and BF_3. The major volatile product (about 15% yield) was assigned structure **47** on the basis of the elemental analysis and spectral data



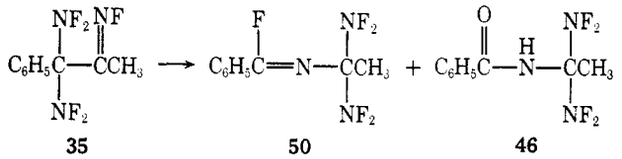
given in the Experimental Section. Amide **45**, 34%, was obtained after hydrolysis of the reaction residue.

Of all the fluorimines examined here, only **7** gave isolable quantities of an azo compound such as **47**. Formation of **47** can be explained, however, in terms of processes familiar to difluoramine chemistry.[19] Presumably, one of the initial products of the interaction of **7** and BF_3 would be a carbonium ion such as **48**.[20] Formation of imine **49**, or a related species,[21] would give an imine that might give an N-fluorodiaziridine. Re-



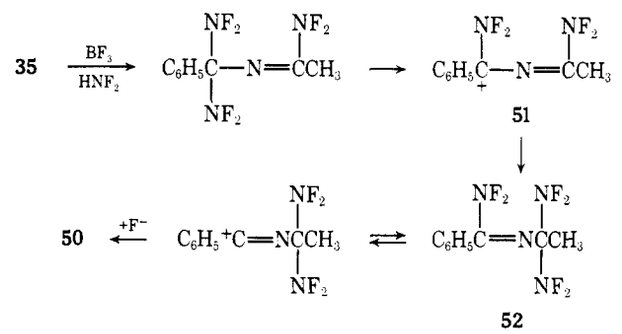
arrangement of this diaziridine in the manner shown, a process analogous to some proposed for reactions of imines and HNF_2,[19] would lead to **47**. Internal return of fluoride ion predominates in such processes.[17,19]

The products obtained from **35**, BF_3, and HNF_2 were the C-fluorimine **50** (56%) and amide **46** (about 15%). The structure of imine **50** was evident from its spectral properties. The infrared spectrum had strong C=N absorption at 5.80 μ; ^{19}F nmr peaks at ϕ −27.5 (4 F)

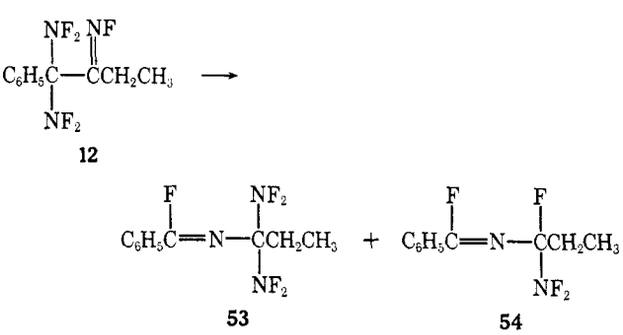


and ϕ +25.4 (1 F) were observed. In the ^1H nmr spectrum, the methyl group next to the geminal difluoramino function was evident; a single peak at τ 8.02 with J_{HF} = 2 Hz was present. The aromatic ring protons were at τ 1.92 (2 H) and 2.44 (3 H). Hydrolysis of **50** produced **46**.

This surprising reorganization of **35** is probably due to an initial Beckmann rearrangement, followed by alkylation of difluoramine by the resulting carbonium ion. Possibly, the added stability of cation **51** contributes to the rearrangement to **52**. Imine **52** may well be the material that hydrolyzes to produce amide **46**. The C-fluorimine **50** may arise when fluoride ion irreversibly traps the carbonium ion formed when **52** ionizes as shown.



No α,α,α-tris(difluoramino)toluene appeared to form from either **35**, BF_3, and HNF_2, or from the closely related fluorimine **12** and the same reagents. Another imine, **54**, as well as expected products **53** and the benzamide derived from **53**, was obtained from **12**. Probably, **54** arises from fluoride ion trapping either the initial carbonium ion or one of the other intermediates that usually leads to **50** or **53**.



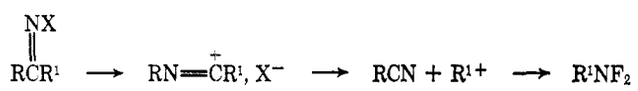
Both the 4-chloro- and 4-methyoxyphenylfluorimines (**13** and **14**, respectively) gave small amounts of the corresponding tris(difluoramino)toluene under the BF_3–HNF_2 reaction conditions. The major products, however, were the C-fluorimines related to **50**. Details of these reactions are given in the Experimental Section. Apparently both the 4-chloro- and the 4-methoxy substituents contribute sufficiently to the stability of the α,α-bis(difluoramino)carbonium ion to allow cleavage to compete with the rearrangement.

(19) W. H. Graham, *J. Amer. Chem. Soc.*, **88**, 4677 (1966).

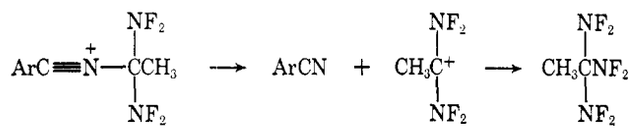
(20) Very likely it is a nitrilium tetrafluoroborate, $CH_3C(NF_2)_2{}^+N{\equiv}CCH_3$, $BF_4{}^-$; see C. A. Grob, H. P. Fischer, W. Rondenbusch, and J. Zergeny, *Helv. Chim. Acta*, **47**, 1003 (1964). Attempts to obtain definitive nmr and infrared spectra of nonvolatile residues from these BF_3 reactions were not successful; solubility was a major problem. Since any C-fluoro- or C-difluoraminoimine such as **49**, possible precursors to amide **45**, would be volatile enough to be removed from the reaction mixture *in vacuo*, some nonvolatile, insoluble salt must remain and give **45** upon hydrolysis.

(21) Variations of this route are equally possible. Fluoride ion, instead of difluoramine, could add to the initial carbonium ion **48**, and difluoramine could be trapped by the α-azocarbonium ion. Addition of HNF_2 to the imine may be a stepwise process, rather than the insertion of NF nitrene pictured.[19]

Since there is evidence that carbonium–nitrilium ions from the Beckmann rearrangement may be formed and then fragment,[20] the possibility that fluorimines **35**, **12**, **13**, and **14** might yield not α,α,α-tris(difluoramino)-toluene, but rather 1,1,1-tris(difluoramino)ethane, was

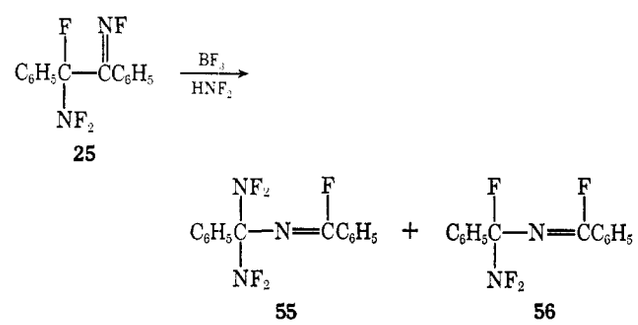


not overlooked. That is, there was no evidence that the α-aryl carbonium ions postulated in the scheme above fragmented as shown. The reaction products



were carefully monitored for the presence of the tris-(difluoramino)ethane; it was never detected.

Although the α,α-bis(difluoramino)-α-fluorotoluene (**29**) reported in Table IV was formed from **25**, HNF_2, and HSO_3F, treatment of **25** with BF_3, with or without



25

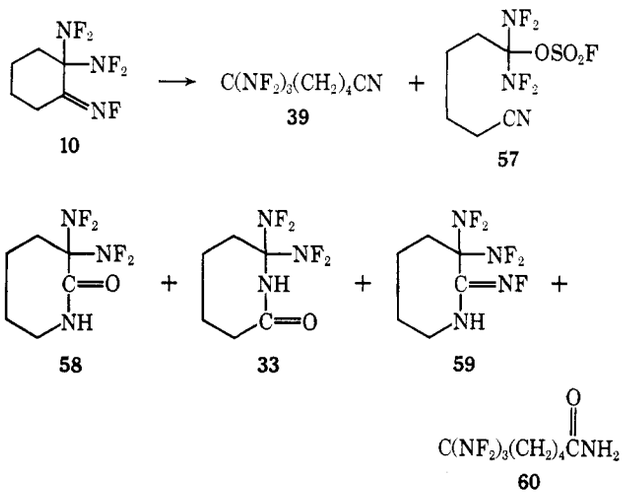
55 **56**

HNF_2 present, gave a mixture of **55** and **56**.[22] Imines **55** and **56** were never completely separated from one another, but variations in the composition of the mixtures allowed the ^{19}F nmr peaks at ϕ −28.1 [multiplet, $-C(NF_2)_2$] and ϕ +15.7 (multiplet, CF) to be assigned to **55**, and the peaks at ϕ −20.7 (NF_2), +29.5 (doublet, J_{FF} = 18 Hz, FC=N), and +124.3 (doublet, J_{FF} = 18 Hz, CF) to be assigned to **56**.

It should be noted, however, that cleavage was the predominant reaction when the α-halofluorimines **16** and **17** were exposed to BF_3. Perhaps a trace of imine **50** was formed from **17**, BF_3, and HNF_2, but the reaction was not of preparative significance.

Also, there was no indication that the C-fluorimines such as **50** would react further with difluoramine to give N-fluorodiaziridines or azo materials such as **47**. The imines were recovered unchanged after treatment with HNF_2–BF_3 or HNF_2–sodium fluoride.

For further study of α,α-bis(difluoramino)fluorimines, the cyclic fluorimines **9**, **10**, and **11** were selected. Of these three, **10** was examined most carefully. Initial experiments conducted with **10**, sulfuric acid, and difluoramine gave no tris(difluoramine); with **10**, BF_3, and HNF_2, C-fluoro products complicated the reaction mixture. Fluorosulfonic acid seemed to lead to appreciable amounts of the product sought—6,6,6-tris(difluoramino)hexanenitrile (**39**)—so the materials formed from the reaction of **10**, HNF_2 and HSO_3F in methylene chloride or 1,1,2-trichlorotrifluoroethane solution were characterized. These products included compounds **33**, **39**, **57**, **58**, **59**, and **60**.[23]



10 **39** **57**

58 **33** **59**

60

Nitrile **39** formed to the extent of 5–12% of theory, while less than 5% of its hydrolysis product, amide **60**, was usually present. Amide **33**, the "expected" Beckmann rearrangement product, and its structural isomer, amide **58**, were usually the major products here (25–40% of theory). Amide **33** usually predominated in the fluorosulfonic acid runs, but in sulfuric acid **58** was the major product. Fluorosulfate **57** was apparently an initial product of the cleavage reaction, and was converted into nitrile **39** under the reaction conditions. Appreciable quantities (5–10%) of **57** were encountered only with limited reaction times.[24] The yield of fluorimine **59**, which appeared to be stable under the reaction conditions, was 5–15%.

Amide **58**, mp 109–110°, had a single ^{19}F nmr peak at ϕ −26.5. The ^1H nmr clearly showed the $-CH_2N-$ peak at τ 6.6. Fluorosulfate **57** had ^{19}F nmr peaks at ϕ −48.3 (SF) and −25.6 (NF). Fluorimine **59** had peaks at ϕ −27.4 and −26.7 due to the geminal difluoramine, and at ϕ +41.2, doublet J_{HF} = 8 Hz, due to C=NF. The addition of trifluoroacetic acid, or heterodecoupling, collapsed the ϕ +41.2 peak to a singlet.

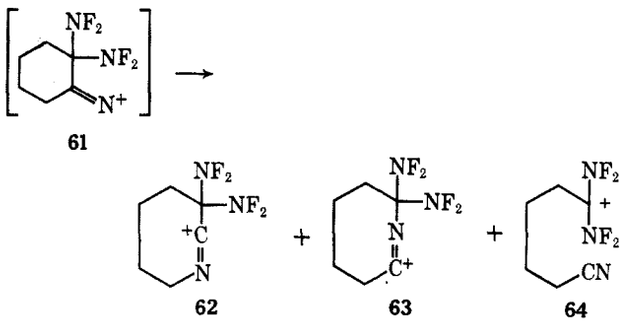
The isolation of appreciable amounts of amide **58** shows a nonstereospecific Beckmann rearrangement occurs. Whether this is due to isomerization of the fluorimine under the reaction conditions, so that *trans* migration of the methylene group led to **58** or whether an intermediate close to immonium cation **61**[25] rearranges and fragments as shown is not known.

(22) The reaction was much cleaner with HNF_2 present; appreciable tarring occurred in its absence.

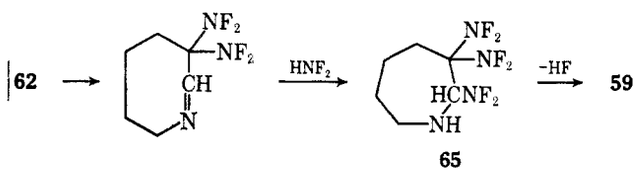
(23) The presence of 1,1-bis(difluoramino)-2-aza-3-fluoro-2-cycloheptene was often indicated by ^{19}F nmr peaks at ϕ −26.6 and +29.2, but this material was never completely characterized. On hydrolysis, however, it gave amide **33**.

(24) This fluorosulfate (**57**) could be converted into **39** by further exposure to HNF_2 and fluorosulfonic acid.

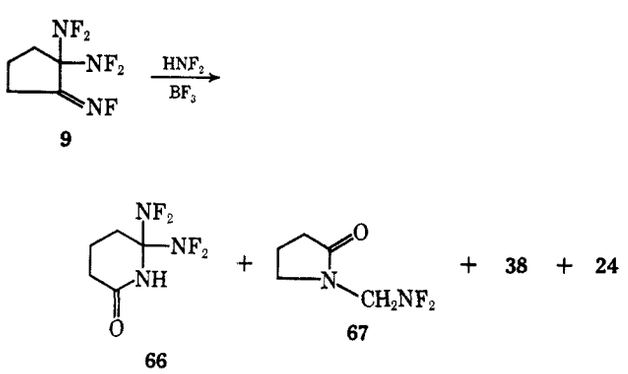
(25) P. T. Lansburg and N. R. Mancuso, *J. Amer. Chem. Soc.*, **88**, 1205 (1966); *Tetrahedron Lett.*, 2245 (1965).



Certainly, cation **62** is the logical precursor of both amide **58** and imine **59**. Reduction of some intermediate is necessary to produce **59**; the material reduced may well be ion **62**.[26] Difluoramine, present in excess, may participate in this reduction, although examples of related reductions (without HNF_2) have been reported.[26] Addition of difluoramine to imine shown gives **65**; loss of HF then produces **59**.

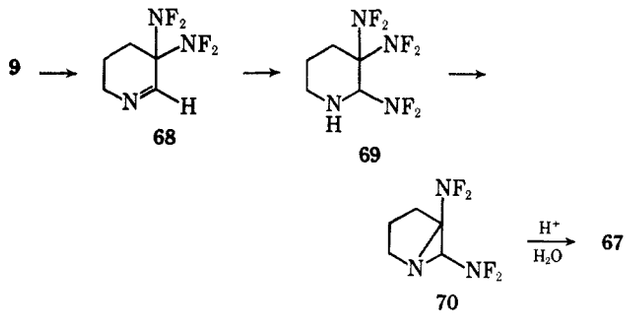


The preparation of the cyclopentylfluorimine **9** was hindered by difficulties reported elsewhere.[3] Limited experiments with **9**, however, indicated that cleavage and difluoramination to give 5,5,5-tris(difluoramino)-pentanenitrile (**38**, Table V) proceeded with the same limited success encountered in the cyclohexyl series. In addition to **38**, 5,5-bis(difluoramino)-5-fluoropentanenitrile (**24**, Table II), a small amount of amide **66**, and another rearrangement product, pyrrolidone **67**, were obtained from **9**, HNF_2, and BF_3.



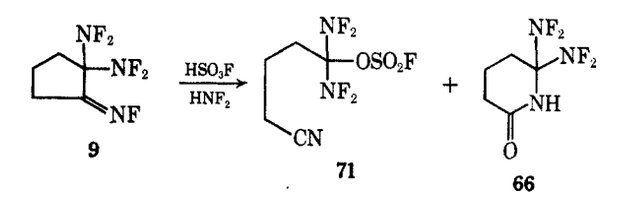
The identity of N-(difluoraminomethyl)pyrrolidone (**67**) was established by an independent synthesis from pyrrolidone and difluoraminomethanol[27] and by the spectral properties that follow. The infrared spectrum of **67** had strong 5.8-μ carbonyl absorption; the ^{19}F nmr spectrum had a peak at ϕ −43.4, triplet, J_{HF} = 24 Hz. In the ^1H nmr spectrum of **67**, the $-CH_2NF$ peak was a triplet, J_{HF} = 24 Hz at τ 5.16, the $-CH_2N-$ peak at τ 6.35 was also a triplet, J_{HH} = 7 cps, and the remaining four ring protons were a multiplet centered at τ 7.64.

The mechanism of formation of **67** is obscure, but the following rationale is proposed. Reduction of the carbonium ion produced by migration of the methylene group would produce imine **68**. A similar reduction

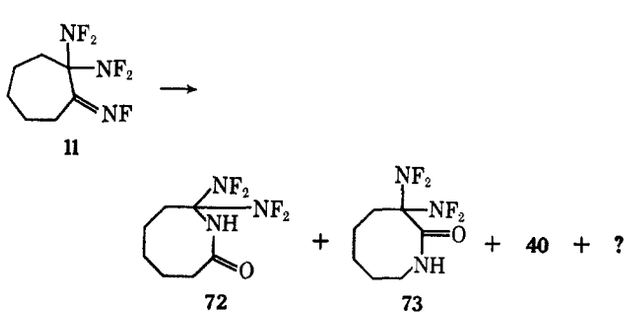


was postulated in the cyclohexyl series just discussed. Here, however, addition of difluoramine to the imine gives an adduct (**69**) that reacts further in a manner different than **65**. Intramolecular loss of HNF_2 from **69** would give bicyclic difluoramine **70**,[28] a possible precursor to **67**.

With fluorosulfonic acid and a limited reaction time, fluorosulfate **71** (17%) and amide **66** (7%) were the major products from **9**. With difluoramine and sulfuric acid, **71** was converted into the tris(difluoramino)-pentane **38**.



The cycloheptylfluorimine **11** gave products expected on the basis of experience with the five- and six-ring systems. Amides **72** (3%), mp 85–87°, and **73** (12%), mp 71–73°, along with 7,7,7-tris(difluoramino)heptanenitrile (**40**, Table IV) and a material of unknown structure were obtained with fluorosulfonic acid and difluoramine. Details are in the Experimental Section.



The geminal and trisdifluoramino compounds reported in this work are considerably more shock sensitive than nitroglycerin; they should be handled with great care.

Experimental Section

Melting points and boiling points are uncorrected. The ^{19}F nmr spectra were run in CCl_4 or $CDCl_3$ at 40 MHz on a Varian 4300B spectrometer; proton nmr spectra were recorded on a Varian A-60 spectrometer.

(26) For examples of reduction during Beckmann rearrangements, see R. T. Conley and M. C. Annis, *J. Org. Chem.*, **27**, 1961 (1962).

(27) A procedure developed by Imperial Chemical Industry: Dr. A. Dinwoodie, personal communication.

(28) For similar reactions of 3-chloropiperidine, 2-(chloromethyl)pyrrolidines, and bicyclic aziridines, see C. F. Hammer and S. R. Heller, *Chem. Commun.*, 919 (1966). For the parent bicyclic aziridine, see P. G. Gassman and A. Fentiman, *J. Org. Chem.*, **32**, 2388 (1967).

The reaction mixtures and products reported below must be considered explosive hazards. Adequate shielding must be employed at all times.

Preparation of 2-Methyl-2-difluoramino-3-(fluorimino)butane (1).—The addition of tetrafluorohydrazine to 2-methyl-2-butene, 7.0 g (0.10 mol), was carried out in 30 ml of methylene chloride at ambient temperature and 85 psi over a period of 90 hr.[1] The methylene chloride solution of the adduct was mixed with 100 ml of absolute ethanol and cooled in an ice bath while 70 ml of 1.43 *N* potassium hydroxide in 90% ethanol was added dropwise. A reaction temperature of 12–15° was maintained during this addition; the reaction mixture was then stirred for 1 hr at 25°. The mixture was diluted with salt water and extracted with methylene chloride. The extract was washed three times with water and dried over magnesium sulfate. Distillation of the extract through a Holtzmann column gave, after removal of the methylene chloride, 2-methyl-2-difluoramino-3-fluoriminobutane (1): 7.85 g, bp 55° (50 mm), n^{20}D 1.3940.

Preparation of 1-Phenyl-1-fluorimino-2-methyl-2-(difluoramino)propane (3).—A solution of 9.1 g (38.6 mmol) of the tetrafluorohydrazine–β,β-dimethylstyrene adduct in 70 ml of ethanol was cooled in an ice bath while 30 ml of 1.30 *N* potassium hydroxide in 90% ethanol was added dropwise. After the mixture had stirred for 1 hr at 25°, it was processed as described above. Distillation gave 6.1 g of product, bp 50° (1 mm). After chromatography on silica gel (elution with pentane–methylene chloride, 3:1) and recrystallization from hexane, the 1-phenyl-1-fluorimino-2-methyl-2-(difluoramino)propane (3) was obtained as white crystals, mp 41–43°.

Preparation of 2-Chloro-2-difluoramino-3-(fluorimino)butane (4).—The product from the reaction of 2-chloro-2-butene (10.0 g) and tetrafluorohydrazine in methylene chloride solution was diluted to 60 ml with methylene chloride. A 10-ml sample of this solution was distilled in the Holtzmann column; 2-chloro-2,3-bis(difluoramino)butane [2.2 g, bp 50° (40 mm)] was obtained.

Anal. Calcd for $C_4H_7ClN_2F_4$: C, 24.69; H, 3.63; N, 14.40. Found: C, 25.60; H, 4.08; N, 14.94.

The remainder of the methylene chloride solution was treated with 62 ml of 1.45 *N* potassium hydroxide in ethanol in the manner described above. The product, 2-chloro-2-difluoramino-3-(fluorimino)butane (4), 7.65 g, was isolated by distillation, bp 48° (52 mm).

Preparation of 2-Bromo-2-difluoramino-3-(fluorimino)butane (5).—The addition of tetrafluorohydrazine to 2-bromo-2-butene (10.0 g) was carried out as usual (80°, 80 psi) in 30 ml of methylene chloride. The solution from the reactor was diluted with 100 ml of ethanol and the mixture was stirred with ice-bath cooling while 54 ml of 1.38 *N* potassium hydroxide in 90% ethanol was added dropwise. When the addition of base was completed the solution was stirred at 25° for 1 hr. Water was added and the organic product was extracted with methylene chloride. The extract was distilled through a Holtzmann column and gave the fluoriminobutane (5), 11.5 g, bp 60° (62 mm).

Dehydrofluorination of 2,2,3-Tris(difluoramino)butane.—A solution of 1.74 g of 2,2,3-tris(difluoramino)butane[3] in 10 ml of methylene chloride and 10 ml of methanol was stirred in an ice bath while 19.5 ml of 0.43 *N* sodium methoxide in methanol was added dropwise. When addition of methoxide was complete, the cooling bath was removed and the solution allowed to warm to 15°. The reaction mixture was poured into water and extracted with methylene chloride. The organic extract was dried over magnesium sulfate and concentrated to about 3 ml by distillation. The residue was fractionated *in vacuo* through 0, −45, and −80 baths. The −45° fraction, 1.0 g, was 2,2-bis(difluoramino)-3-(fluorimino)butane (7). A small amount of methylene chloride and, in some cases, a less volatile material (mostly retained in the 0° trap) contaminated the sample. A sample for analysis was purified by vpc at 75° on a silicone (GE SF-96) column.

Preparation of 1,1-Bis(difluoramino)-2-(fluorimino)cyclohexane (10).—A solution of 2.15 g of 1,1,2-tris(difluoramino)cyclohexane[3] in 20 ml of methylene chloride and 25 ml of methanol was stirred in an ice bath while 6.5 ml of 1.42 *N* sodium methoxide in methanol was added dropwise. The solution was stirred 15 min, then poured into ice water. The organic product was taken up in methylene chloride. The residue obtained upon evaporation of the methylene chloride was transferred with gentle warming into a −25° trap *in vacuo* to give 1,1-bis(difluoramino)-2-(fluorimino)cyclohexane (10), a colorless liquid.

1,1-Bis(difluoramino)-1-*p*-methoxyphenyl-2-(fluorimino)propane (14).—1-(Diethylphosphato)-1-difluoramino-1-*p*-methoxyphenyl-2-(fluorimino)propane was prepared from *p*-methoxypropiophenone in the usual way[3] and was characterized by ^{19}F nmr spectrum. Peaks at −1782, −1208, −1104, and −532 Hz (40 MHz, CClF standard) were observed for the $-NF_2$ quartet, while the C=NF peak was at ϕ −33.6. From 20 g of the phosphate in methylene chloride and difluoramine–sulfuric acid (1 hr, 15°) was obtained 1,1-bis(difluoramino)-1-(*p*-methoxyphenyl)-2-fluoriminopropane (14, 2.6 g) as an oil.

Reactions of 1,1-Bis(difluoramino)-1-*p*-methoxyphenyl-2-(fluorimino)propane, Difluoramine, and Boron Trifluoride.—A mixture of 0.85 g (3 mmol) of the fluorimine 14, 90 ml (STP) of boron trifluoride, 110 ml (STP) of difluoramine, and 2 ml of methylene chloride in a pressure tube[29] was stirred at 0° for 90 min. The tube was vented and the residue was removed with a methylene chloride–water mixture. The organic product, isolated in methylene chloride, was chromatographed on a silica gel column. Elution of the column with pentane–methylene chloride (4:1) gave α,α,α-tris(difluoramino)-*p*-methoxytoluene (37a), 0.102 g, as an oil, ^{19}F nmr single peak at ϕ −26.9.

The next fraction from the column (3:1 pentane–methylene chloride) was 1-fluoro-1-(*p*-methoxyphenyl)-2-aza-3,3-bis(difluoramino)-1-butene, 0.095 g.

Anal. Calcd for $C_{10}H_{10}N_3F_5O$: C, 42.41; H, 3.56; N, 14.84. Found: C, 42.16; H, 3.65; N, 13.97.

The ^{19}F nmr spectrum showed a peak at ϕ −26.9 (geminal NF_2's) and at +27.7 [-(F)C=N].

1,1-Bis(difluoramino)-1-phenyl-2-(fluorimino)butane (12).—The usual procedure was followed to prepare 1-phenyl-1-difluoramino-1-(diethylphosphato)-2-(fluorimino)butane;[3] this phosphate was characterized by ^{19}F nmr. The NF_2 quartet (40 MHz, CCl_3F standard) was at −1776, −1196, −1080 and −504 Hz and the C=NF absorption was at ϕ −28.6.

From 19.2 g of this phosphate, after exposure to difluoramine-sulfuric acid, was obtained 1,1-bis(difluoramino)-1-phenyl-2-fluoriminobutane (12), 6.2 g. The fluorimine was purified by silica gel chromatography.

Reaction of 1,1-Bis(difluoramino)-1-phenyl-2-(fluorimino)-butane, Difluoramine, and Boron Trifluoride.—A mixture of 0.80 g (3 mmol) of the fluorimine 12, 4 mmol of boron trifluoride, 5 mmol of difluoramine, and 3 ml of methylene chloride was stirred overnight at ambient temperature in a Fischer–Porter pressure tube.[29] The tube was vented and the residue was partitioned between water and methylene chloride. The organic residue was chromatographed on silicic acid, but pentane eluted 0.35 g of mixed materials. This fraction was rechromatographed on silica gel. The first fraction eluted was 1-fluoro-1-phenyl-2-aza-3,3-bis(difluoramino)-1-pentene (53), an oil.

Anal. Calcd for $C_{10}H_{10}N_3F_5$: C, 44.95; H, 3.77; N, 15.72; F, 35.6. Found: C, 44.57; H, 3.99; N, 16.15; F, 37.0.

The ^{19}F nmr spectrum showed peaks at ϕ −27.0 and −26.6 (geminal NF_2's) and at +23.8 (-CF=N).

The next fraction eluted was 1,3-difluoro-1-phenyl-2-aza-3-difluoramino-1-pentene (54), also an oil.

Anal. Calcd for $C_{10}H_{10}N_2F_4$: C, 51.28; H, 4.30; N, 11.96; F, 32.45. Found: C, 51.41; H, 4.70; N, 11.34; F, 31.9.

The ^{19}F nmr spectrum showed peaks at ϕ −19.0 ($-NF_2$), +33.6 (doublet J_{FF} = 24 Hz, due to -(F)C=N-, and a multiplet centered at +128.3.

Observing ^{19}F and irradiating ^{1}H, the upfield peak collapses to a doublet. Homodecoupling the upfield peaks was not successful, but they are almost certainly due to F–F coupling. No evidence of H–F coupling was noted observing the ϕ 33.6 peak while irradiating ^{1}H.

Crude samples of N-[1,1-bis(difluoramino)-1-propyl]benzamide were eluted later from the column. The sample characterized was prepared by hydrolysis of the C-fluorimine in aqueous methanolic hydrochloric acid (50°, 1 hr). It was recrystallized from hexane, mp 79–81°.

Anal. Calcd for $C_{10}H_{11}N_3F_4O$: C, 45.28; H, 4.18; N, 15.85; F, 28.7. Found: C, 45.61; H, 4.36; N, 15.42; F, 29.4.

The ^{19}F nmr spectrum showed a single peak at ϕ −24.6.

Reaction of 1-(4-Chlorophenyl)-1-difluoramino-1-(O,O-diethylphosphoryloxy)-2-(fluorimino)propane and Difluoramine.—A 15-g sample of the above fluoriminophosphate in 10 ml of methylene chloride was added to excess difluoramine refluxing over 20 ml of 30% fuming sulfuric acid. After a contact time of 130 min at

(29) Described by R. P. Rhodes, *J. Chem. Educ.*, **40**, 423 (1963).

15–25°, excess methylene chloride was added, the acid layer was separated, and the organic solution was washed with water and aqueous sodium bicarbonate. The residue obtained upon evaporation of the solvent was chromatographed on silica gel. The first fraction eluted from the column (pentane–methylene chloride, 19:1) was α,α,α-tris(difluoramino)-4-chlorotoluene (**37b**), 0.23 g.

The ^{19}F nmr spectrum showed a single peak at ϕ −28.0. The ^{1}H nmr spectrum showed only an aromatic multiplet centered at τ 2.55.

The next fraction eluted (by pentane–methylene chloride, 10:1) was 1,1-bis(difluoramino)-1-(4-chlorophenyl)-2-(fluorimino)propane (**13**), 2.1 g, a clear liquid.

Reaction of Boron Trifluoride and 1,1-Bis(difluoramino)-1-(4-chlorophenyl)-2-(fluorimino)propane.—A mixture of 1.44 g of the fluorimine **13**, 3 ml of methylene chloride, 80 ml (STP) of difluoramine, and 140 ml (STP) of boron trifluoride was stirred in a 15-ml Fischer–Porter pressure tube at 0° (30 min) and at ambient temperature (90 min). The tube was vented and the residue was partitioned between water and methylene chloride. The residue from the organic phase was chromatographed on silica gel. The first fraction from the column, 0.089 g, was α,α,α-tris(difluoramino)-4-chlorotoluene (**37b**). The next fraction eluted from the column was 2-aza-1-fluoro-1-*p*-chlorophenyl-3,3-bis(difluoramino)-1-butene, 0.93 g, a clear liquid.

Anal. Calcd for $C_9H_7ClN_3F_6$: C, 37.58; H, 2.45; N, 14.61; F, 33.0; Cl, 12.3. Found: C, 37.21; H, 2.68; N, 15.31; F, 34.4; Cl, 11.8.

The ^{19}F nmr spectrum showed peaks at ϕ −27.2 [$C(NF_2)_2$] and +27.7 [−(F)C=N−]. The ^{1}H nmr spectrum showed τ 2.28 (aromatic multiplet) and 8.01 ($-CH_3$). The next fraction from the column, 0.057 g, was recovered starting material. Methylene chloride eluted N-[1,1-bis(difluoramino)-ethyl]-*p*-chlorobenzamide, 0.10 g, mp 92–94° (from hexane).

Anal. Calcd for $C_9H_8N_3F_4ClO$: C, 37.84; H, 2.82; N, 14.71; F, 26.6. Found: C, 37.79; H, 2.92; N, 14.38; F, 26.1.

The ^{19}F nmr spectrum showed peaks at ϕ −23.9 and −24.4 (doublet). The ^{1}H nmr spectrum showed τ 2.37 (aromatic multiplet) and 7.73 ($-CH_3$).

Preparation of 6-Chloro-6-difluoramino-6-fluorohexanenitrile (**22**).—A mixture of 0.80 g (4 mmol) of 1-chloro-1-difluoramino-2-fluoriminocyclohexane, 5 ml of methylene chloride, and 90 cc (STP) of boron trifluoride was stirred in a pressure tube at 0° for 30 min and at ambient temperature for 2 hr. The tube was vented, and the residual methylene chloride solution was washed with aqueous sodium bicarbonate and water. This was combined with another run of the same size, and the product was chromatographed on silica gel. Elution of the column with pentane–methylene chloride (1:1) gave 6-difluoramino-6-fluoroheptanenitrile (**23**), 0.28 g.

The ^{19}F nmr spectrum showed peaks at ϕ −19.1 (NF_2) and +142.7 (CF).

Preparation of 6,6-Bis(difluoramino)heptanenitrile (**31**).—A mixture of 3 ml of methylene chloride, 3 ml of fluorosulfonic acid, and 8 mmol of difluoramine in a closed system was stirred at −20° while 0.90 g (5 mmol) of 1-difluoramino-1-methyl-2-(fluorimino)cyclohexane in 2 ml of methylene chloride was added dropwise. The reaction mixture then was stirred at 0° for 30 min and at ambient temperature for 2 hr. The difluoramine was pumped off and the residue poured over ice. The residue obtained after the usual extraction procedure was chromatographed on silica gel. The pentane–methylene chloride (1:1) eluates gave 6,6-bis(difluoramino)heptanenitrile (**31**), 0.16 g.

Preparation of α-Chloro-α-difluoramino-α-fluorotoluene (**19**).—A mixture of 0.71 g (3 mmol) of 1-chloro-1-difluoramino-1-phenyl-2-fluoriminopropane (**16**), 70 cc (STP) of boron trifluoride, and 5 ml of methylene chloride was sealed in a pressure tube at −80°. The mixture was warmed to −10° (10 min) and then 0° (1 hr) before the boron trifluoride was vented. The methylene chloride solution was washed (5% aqueous sodium bicarbonate and water) and dried. The organic phase was concentrated by distillation, then fractionated *in vacuo* through a −45° trap. The −45° trap retained α-difluoramino-α-fluorotoluene (**19**), 0.40 g.

Preparation of α,α-Bis(difluoramino)-α-fluorotoluene (**29**).—A mixture of 5 ml of methylene chloride, 2 ml of fluorosulfonic acid, and 7 mmol of difluoramine was stirred at −10° in a closed system while 1.13 g (4 mmol) of 1-difluoramino-1-fluoro-2-fluorimino-1,2-diphenylethane in 5 ml of methylene chloride was added dropwise. The mixture was then stirred at 0° for 1 hr. The HNF_2 was pumped off *in vacuo* and the residual mixture was poured on ice. The organic product was extracted into methylene chloride; the methylene chloride phase was washed with 5% aqueous sodium bicarbonate and water. When the extract had been concentrated to 1 ml by distillation, the residue was fractionated *in vacuo* through traps cooled to −45 and −80°. The −45° trap contained 0.67 g of benzonitrile (about 25% of total) and the desired product. Chromatography on a 0.25 in. × 5 ft Aerograph Dow 710 silicone on 60/80 Chromosorb B at 115° separated the benzonitrile (10-min retention) from α,α-bis-(difluoramino) α-fluorotoluene (**29**) (4-min retention).

Reaction of Boron Trifluoride, Difluoramine, and 1-Phenyl-1-chloro-1-(difluoramino)-2-(fluorimino)propane.—A mixture of 0.72 g (3 mmol) of fluorimine **16**, 100 cc (STP) of difluoramine, 70 cc (STP) of boron trifluoride, and 2 ml of methylene chloride was stirred for 2 hr at ambient temperature in a Fischer–Porter pressure tube.[29] The tube was opened and the volatile contents were removed *in vacuo*. The residue in the tube was partitioned between water and methylene chloride. Concentration of the methylene chloride solution followed by distillation *in vacuo* through −25 and −80° traps gave, in the −25° trap, α-chloro-α,α-bis(difluoramino)toluene (**27**), 0.4 g, identified by infrared and nmr spectra. Only a trace of nonvolatile material remained in the distillation flask.

Preparation of α,α-Bis(difluoramino)-α-chlorotoluene (**27**).—A mixture of 4 ml of 100% sulfuric acid and 4 ml of methylene chloride was cooled to −115°, and 1.42 g (6 mmol) of 1-phenyl-1-chloro-1-difluoramino-2-(fluorimino)propane was added to the cold mixture. The mixture was degassed and then 150 ml (STP) of difluoramine was condensed into the U tube. The cooling bath was removed and the mixture was allowed to warm until it could be stirred magnetically; at this point an ice bath was placed around the U tube. After stirring for 35 min, the mixture was distilled *in vacuo* through −25, −80, and −115° traps. The −25° trap retained α,α-bis(difluoramino)-α-chlorotoluene (**27**), 0.86 g.

Preparation of 1-Chloro-1,1-bis(difluoramino)ethane (**26**).—Fluorosulfonic acid, 6 ml, was frozen, and 1.04 g (6 mmol) of 2-chloro-2-difluoramino-3-fluoriminobutane (**4**) was added to the solid acid. The mixture was degassed *in vacuo* and then 220 ml (STP) of difluoramine was condensed into the 300-ml reaction bulb. The cooling bath was removed, and the reaction mixture was allowed to come to ambient temperature. After the acid solution had been stirred for 90 min the mixture was pumped *in vacuo* through −80, −96, and −127° baths. 1-Chloro-1,1-bis(difluoramino)ethane (**26**), 0.54 g, was retained in the −80° trap.

Preparation of α,α-Bis(difluoramino)-α-bromotoluene (**28**).—A mixture of 4 ml of 100% H_2SO_4, 4 ml of methylene chloride, 1.68 g (6 mmol) of 1-phenyl-1-bromo-1-difluoramino-2-(fluorimino)-propane (**17**), and 230 ml (STP) of difluoramine was allowed to interact in the fashion described above. The reaction mixture was stirred 30 min at ice-bath temperature; then the excess difluoramine was removed *in vacuo*. The residual solution was poured over ice and the organic products were taken up in methylene chloride. The residue remaining (1.3 g) after evaporation of the methylene chloride was distilled *in vacuo* to give α,α-bis(difluoramino)-α-bromotoluene (**28**), 0.64 g. The residue from the distillation was starting material (nmr).

Reaction of 2-Chloro-2-difluoramino-1-(fluorimino)cyclohexane and Difluoramine.—Fluorosulfonic acid, 10 ml, was frozen and 2.12 g (10 mmol) of the fluorimine **18** was added to the frozen acid. The mixture was degassed, and difluoramine, 365 cc (STP), was condensed into the reaction flask. The mixture was allowed to warm to ambient temperature and was stirred for 45 min. After the volatiles had been pumped off *in vacuo*, the acid residue was poured over ice and the organic products were isolated by extraction with methylene chloride. The residue was chromatographed on a silica gel column packed in pentane–methylene chloride. Elution of the column with the same solvent gave 6-chloro-6,6-bis(difluoramino)hexanenitrile (**30**), 0.52 g, as a liquid.

A solid was eluted from the column by methylene chloride–ethyl acetate (10:1); 0.09 g, mp 70–71° (from hexane), of 2-aza-3,3-bis(difluoramino)cycloheptanone (**33**) was obtained.

Anal. Calcd for $C_6H_9N_3F_4O$: C, 33.49; H, 4.22; N, 19.53; F, 35.3. Found: C, 33.42; H, 4.43; N, 18.80; F, 37.7.

Reaction of Boron Trifluoride, Difluoramine, and 2,2-Bis(difluoramino)-3-(fluorimino)butane.—A mixture of 0.60 g (3 mmol) of the fluorimine **7**, 40 cc (STP) of difluoramine, and 80 cc (STP) of boron trifluoride was stirred 20 hr at ambient tempera-

ture in a Fischer–Porter pressure tube. The reaction tube was cooled to −80°, opened, and pumped *in vacuo* through traps cooled to −45, −80, and −110°. The −45° trap retained 3,4-diaza-2,2,5-tris(difluoramino)-5-fluorohexane (**47**), 0.12 g, a pale yellow liquid. The analytical sample was purified by vpc on a GE silicon SF-96 column at 70°. The infrared spectrum exhibited no absorption in the 3.5–6.6-μ region; strong, broad peaks at 8.1, 8.4, 10, 10.7, 10.9, 112, and 12.6 μ were present.

Anal. Calcd for $C_4H_6N_8F_7$: C, 18.68; H, 2.35; N, 27.24. Found: C, 18.60; H, 2.33; N, 27.48.

The ^{19}F nmr spectrum showed peaks at ϕ −26.0, −19.5, and +132.2; ratio 4:2:1. The ^1H nmr showed $CH_3(NF_2)_2C-$, a quintet centered at τ 8.20, and $CH_3(NF_2)FC-$, at τ 8.15, doublet, J_{HF} = 18 Hz. Each member of the doublet was further split (*ca.* 2 Hz) by coupling to the NF_2 group.

About 0.5 ml of methylene chloride was added to the nonvolatile residue in the reaction tube; insoluble material remained. The predominant peak in the ^{19}F nmr of this solution was at ϕ −24.5. The entire residue was then partitioned between methylene chloride and water. A solid remained when the methylene chloride was evaporated; this solid was recrystallized from hexane and gave N-[1,1-bis(difluoramino)ethyl]acetamide (**45**), 0.21 g, mp 98–100°.

Anal. Calcd for $C_4H_7N_8F_4O$: C, 25.40; H, 3.73; N, 22.22; F, 40.2. Found: C, 25.71; H, 4.01; N, 21.26; F, 39.5.

The ^{19}F nmr spectrum showed a peak at ϕ −24.5. The ^1H nmr spectrum showed τ 7.83, sharp singlet of $CH_3C{=}O$ superimposed on quintuplet (about one-cycle coupling) of $CH_3C(NF_2)_2$ and broad absorption at τ 3.18 (–NH–).

Preparation of α,α-Bis(difluoramino)-α-chloro-4-bromotoluene (32).—A solution of 10 g of 1-(4-bromophenyl)-1-chloro-1-difluoramino-2-(fluorimino)propane (**6**) in 22 ml of methylene chloride was added to 15 ml of 30% fuming sulfuric acid over which 125 mmol of difluoramine was refluxing from a −80° condenser. After 2 hr at 10–25°, the excess difluoramine was vented in a nitrogen stream, and the residual solution, diluted with methylene chloride, was poured over ice. The organic layer was washed with water and aqueous sodium bicarbonate solution. The residue obtained upon evaporation of the methylene chloride was chromatographed on a silica gel column packed in pentane. Elution of the column with methylene chloride–pentane (1:19) gave **32**, 7.2 g, a colorless liquid.

Reaction of Difluoramine, Boron Trifluoride, and 1-Phenyl-1,1-bis(difluoramino)-2-(fluorimino)propane (35).—A mixture of 4 ml of methylene chloride, 1.00 g (4 mmol) of fluorimine **35**, 200 cc (STP) of difluoramine, and 120 cc (STP) of boron trifluoride in a Fischer–Porter pressure tube was stirred 30 min at ice-bath temperature and at ambient temperature for 1 hr. The tube was opened and the volatile materials were pumped off. The residue was partitioned between methylene chloride and water. The methylene chloride layer was separated, washed, and dried. The organic product was chromatographed on silica gel column packed in pentane–methylene chloride (50:1). Elution of the column with pentane–methylene chloride (15:1) gave a colorless liquid, 0.56 g, presumably 2-aza-1-fluoro-1-phenyl-3,3-bis(difluoramino)-1-butene [ϕ, $-CF{=}NC(NF_2)_2CH_3$], **50**.

Anal. Calcd for $C_9H_8N_8F_5$: C, 42.69; H, 3.18; N, 16.60; F, 37.5. Found: C, 42.49; H, 3.40; N, 17.33; F, 38.0.

The next fraction, 0.15 g, eluted from the column with methylene chloride, was N-[1,1-bis(difluoramino)ethyl]benzamide (**46**), mp 92–93° (from hexane).

Anal. Calcd for $C_9H_9N_8F_4O$: C, 43.03; H, 3.61; N, 16.73; F, 30.26. Found: C, 43.13; H, 3.91; N, 16.18; F, 29.4.

The ^{19}F nmr spectrum showed a doublet at ϕ −25.2, −24.8. The ^1H nmr spectrum showed τ 7.74 ($-CH_3$) and aromatic proton multiplets at τ 2.45 and 2.16.

The nmr spectrum of the residue before chromatography indicated that there was no change in product composition during chromatography.

Hydrolysis of 2-Aza-1-fluoro-1-phenyl-3,3-bis(difluoramino)-1-butene (50).—A solution of 136 mg of the azabutene **50** in 10 ml of methanol–water (1:1) was stirred at ambient temperature while 0.52 *N* sodium methoxide in methanol was added until the reaction mixture remained basic to pH paper for 10 min. Water was added to the methanolic solution, and the organic product was extracted into methylene chloride. Evaporation of the methylene chloride left a solid residue. One recrystallization of this residue from hexane gave N-[1,1-bis(difluoramino)ethyl]-benzamide (**46**), 82 mg, mp 91–92.5°. The infrared spectrum was identical with that of a sample isolated from the boron trifluoride reaction (above).

Hydrolysis of N-[1,1-Bis(difluoramino)ethyl]benzamide.—A mixture of 72 mg of the benzamide **46**, 2 ml of water, 2 ml of methanol, and 4 ml of 0.52 *N* sodium methoxide in methanol was refluxed 105 min. The solution was cooled, acidified, and poured into water. Extraction of the aqueous phase was carried out with methylene chloride. Benzoic acid, 26 mg, was obtained upon evaporation of the methylene chloride and was identified by infrared spectrum and mp 121–122° (from hexane). The aqueous washes contained 21 mg of fluoride ion; theoretical value for destruction of starting material is 22 mg.

Preparation of α,α,α-Tris(difluoramino)toluene (36).—1-Phenyl-1,1-bis(difluoramino)-2-(fluorimino)propane (**35**, 6 g), in 10 ml of methylene chloride was added to 12 ml of 30% fuming acid containing an excess of refluxing difluoramine. The mixture was stirred at 15–25° for 3 hr. Methylene chloride (100 ml) was added, and the acid layer was separated. The methylene chloride was washed with 10% aqueous sodium bicarbonate solution and water. A total of 1.69 g of benzoic acid was recovered from the acid layer and the aqueous washes. The residue remaining after the methylene chloride had distilled was fractionated *in vacuo* through −25 and −80° traps. The −25° trap retained α,α,α-tris(difluoramino)toluene (**36**), 0.3 g, a colorless liquid. The ^{19}F nmr spectrum showed single peak at ϕ −27.8. The ^1H nmr spectrum showed only an aromatic multiplet at τ 2.0–2.5.

The tristoluene **36** was also prepared as follows. A mixture of 4 ml of methylene chloride, 2 ml of fluorosulfonic acid, and 140 cc (STP) of difluoramine was stirred at −10° in a 200 ml, three-necked flask attached to a manometer. A solution of 1.0 g (3.1 mol) of 1,1-bis(difluoramino)-1-phenyl-2-(fluorimino)butane (**12**) in 4 ml of methylene chloride was added dropwise at −10°. The mixture was allowed to warm to 20° and was stirred for 1 hr. The excess difluoramine was quickly condensed off, methylene chloride was added to the residue, and ice water was added. The organic layer was separated as usual and concentrated to 2 ml by distillation. Distillation *in vacuo* through traps cooled to −45 and −80° gave, in the 45° fraction, α,α,α-tris(difluoramino)toluene, 0.14 g.

Reaction of 1,1-Bis(difluoramino)-2-(fluorimino)cyclohexane and Difluoramine.—A 5.3-g sample of the fluorimine **10** in 30 ml of 1,1,2-trichlorotrifluoroethane (Freon 113) was added to about 200 mmol of HNF_2 refluxing over 20 ml of fluorosulfonic acid. The temperature was at 5–11° during the addition, then was maintained at 14–16° for 150 min. The HNF_2 was vented and the residual solution was dumped on ice. The organic product was extracted with methylene chloride, the organic phase was washed with water, 5% aqueous sodium bicarbonate and again with water. The methylene chloride was removed at reduced pressure to leave 4.6 g of residue. This residue was chromatographed on a silica gel column packed in pentane–methylene chloride (20/1). The first material eluted, 0.32 g, had no ^{19}F nmr peak and was discarded. The second fraction, 0.12 g, had ^{19}F nmr peaks at ϕ −23.4 and +26.3, but was not examined further. The third fraction, eluted by 1:1 pentane–methylene chloride, 0.32 g, was 6,6,6-tris(difluoramino)hexanenitrile. The next fraction, eluted by methylene chloride, was 1-aza-2-fluorimino-3,3-bis(difluoramino)cycloheptane (**59**), 0.837 g. A sample was recrystallized from hexane, mp 75–77°.

Anal. Calcd for $C_6H_9N_4F_5$: C, 31.04; H, 3.91; N, 24.13; F, 40.9. Found: C, 30.98; H, 4.04; N, 23.10; F, 41.7.

The ^{19}F nmr spectrum showed peaks at ϕ −27.4 and −26.7 and ϕ +41.1 and +41.3 in CCl_4 solution. Addition of trifluoroacetic acid collapsed the upfield doublet to a singlet at ϕ +45.7. Heterodecoupling the ^{19}F peak at ϕ +41.2 also collapsed it to a singlet.

The next fraction from the column (2% ethyl acetate in methylene chloride) was amide **33**, 0.72 g, mp 70–71°.

This was followed by amide **58**, 0.56 g, mp 109–110°, eluted by 10% ethyl acetate in methylene chloride.

Anal. Calcd for $C_6H_9N_3F_4O$: C, 33.49; H, 4.22; N, 19.53; F, 35.3. Found: C, 33.61; H, 4.30; N, 19.26; F, 35.3.

The ^{19}F nmr spectrum showed a single peak at ϕ −26.5.

The last fraction was eluted by 10% methanol in methylene chloride and was 0.34 g of an oil. This was chromatographed on silicic acid and eluted with methylene chloride–acetone (9:1). The white solid was recrystallized from hexane to give 6,6,6-tris(difluoramino)hexanamide (**60**), mp 72–74°.

Anal. Calcd for $C_6H_{10}N_4F_6O$: C, 26.87; H, 3.76; N, 20.89; F, 42.5. Found: C, 26.75; H, 3.97; N, 20.79; F, 42.6.

The ^{19}F nmr spectrum showed a single peak at ϕ −27.7.

When a reaction was conducted as above, but in methylene chloride solution with a reaction time of 2 hr at −80 to 0°, the main nitrile cut was 6,6-bis(difluoramino)6-fluorosulfatohexanenitrile (**57**). It was purified by chromatography on silica gel; elution was successful with pentane–methylene chloride, 1:1.

Anal. Calcd for $C_6H_8N_3F_5SO_3$: C, 24.24; H, 2.71; N, 14.14. Found: C, 24.89; H, 3.50; N, 14.39.

The ^{19}F nmr spectrum showed single peaks at ϕ −48.3 and −25.6; ratio 1:4.

When a reaction with 5.0 g of fluorimine in 30 ml of methylene chloride (instead of Freon 113) as described above, the products isolated after silica gel chromatography were nitrile **39** (11%), amide **60** (5%), a mixture of amides **33** and **58** (total of 38%) and fluorimine **59** (5%).

Reaction of 1,1-Bis(difluoramino)-2-(fluorimino)cyclopentane and Difluoramine. A. With Fluorosulfonic Acid.—A solution of 2.5 g of the fluorimine **9** in 7 ml of methylene chloride was added to 400 mmol of difluoramine refluxing over 5 ml of methylene chloride and 3 ml of fluorosulfonic acid at −10°. The mixture was stirred at −5° for 1 hr. Excess difluoramine was vented and the residue was poured on ice and methylene chloride. The organic layer was washed with water, 5% aqueous sodium bicarbonate, and water. The methylene chloride was removed at reduced pressure, and after spectral samples had been removed, the residue was chromatographed on silica gel. Elution with 10:1 pentane–methylene chlorides gave 0.16 g of recovered **9**. Elution with the same solvents, 1:1, gave 5,5-bis(difluoramino)-5-fluorosulfatopentanenitrile (**71**), 0.59 g.

Anal. Calcd for $C_5H_6N_3F_5O_3S$: C, 21.21; H, 2.12; N, 14.84; F, 35.5. Found: C, 21.95; H, 2.42; N, 16.58; F, 34.4.

The ^{19}F nmr spectrum showed sharp peaks at ϕ −48.3 and −25.7; ratio 1:4. Continued elution of the column with methylene chloride gave 3,3-bis(difluoramino)-2-azacyclohexanone (**66**), 0.26 g, mp 140–142° (hexane).

Anal. Calcd for $C_5H_7N_3F_4O$: C, 29.85; H, 3.51; N, 20.89. Found: C, 29.86; H, 3.74; N, 20.85.

The ^{19}F nmr spectrum showed a peak at ϕ −23.9.

B. With Boron Trifluoride.—A mixture of 0.60 g of fluorimine **9**, 120 cc (STP) of difluoramine, 180 cc (STP) of boron trifluoride, and 2 ml of methylene chloride was stirred in a pressure tube at 0° for 30 min and at 20° for 90 min. The tube was vented *in vacuo*, and the residue portioned between methylene chloride and water. Evaporation of the methylene chloride left 0.45 g of residue. Chromatography of this residue over silica gel as usual gave, in the pentane–methylene chloride (2:1 and 1:1) eluates, a mixture of nitriles **24** and **38**, 0.10 g. A clean separation of these two nitriles could be obtained by vpc on a 5-ft Dow 710 silicon column at 125°. The fluorobis(difluoramino)nitrile **24** was eluted first (8-min retention time). The ^{19}F nmr spectrum showed peaks at ϕ −21.0 (NF_2) and +142.0 (CF); ratio 4:1. The tris(difluoramino)nitrile **38** had a retention time of 14 min.

Elution with methylene chloride gave amide **66**, 0.075 g. Elution with methylene chloride containing ethyl acetate (5–10%) gave N-(difluoramino)pyrrolidone (**67**), 0.120 g, a liquid.

Anal. Calcd for $C_5H_8N_2F_2O$: C, 40.00; H, 5.37; N, 18.66; F, 25.3. Found: C, 38.23; H, 5.76; N, 18.86; F, 24.3.

Spectral properties of **67** are reported in the Discussion.

Reaction of Paraformaldehyde, Difluoramine, and 2-Pyrrolidone.—Paraformaldehyde, 0.48 g, and difluoramine, 360 cc (STP), were allowed to interact overnight. The difluoramino methanol was then collected by distillation *in vacuo* into a −80° trap, and transferred to a U tube containing 1.7 g of 2-pyrrolidone, 12 ml of concentrated sulfuric acid, and 12 ml of 30% fuming sulfuric acid at −80°. The mixture was allowed to warm to ambient temperature and was stirred 1 hr. The mixture then was poured over ice, and partitioned between methylene chloride and water. Evaporation of the methylene chlorides gave a residue that had infrared, ^{19}F, and ^1H nmr spectra identical with those of **67**.

Reaction of 1,1-Bis(difluoramino)-2-(fluorimino)cycloheptane and Difluoramine.—To a refluxing mixture of 220 mmol of HNF_2 in 20 ml of fluorosulfonic acid and 10 ml of Freon 113 was added dropwise a solution of 5.0 g (0.0216 mol) of 1,1-bis(difluoramino)-2-(fluorimino)cycloheptane (**11**) in 20 ml Freon 113. The contents were allowed to stir for about 15 min at 16°. The contents were poured onto ice and extracted with 50 ml of Freon 113. The organic layer was washed with 5% $NaHCO_3$ solution, then water, and dried over $CaCl_2$. The Freon was removed on a rotary evaporator; the residue weighed 3.2 g. Another similar run was made except the time of the reaction was increased to 100 min. The yield of crude product was 2.80 g. The products were combined after inspection of their ^{19}F resonance spectra revealed the similarity of the two product mixtures.

The purification of the products was effected by chromatography through silica gel. The isolated fractions, in the order in which they were eluted, were 1.95 g of recovered 1,1-bis(difluoramino)-2-fluoriminocycloheptane and 1,1,2-tris(difluoramino)cycloheptane, 0.44 g of unknown compound, 0.89 g of tris(difluoramino)nitrile **40**, 0.19 g of amide **72**, and 0.78 g of amide **73**. These products were rechromatographed to obtain samples for elemental analyses.

Anal. for unknown compound (infrared peaks at 4.56 and 5.95 μ). Found: C, 31.42; H, 4.65; N, 19.83; F, 41.09.

The ^{19}F nmr spectrum showed peaks at ϕ −30.0 and −46.3; ratio 2:1. The ^1H nmr spectrum showed peaks centered at 255, 158, and 112 Hz downfield from TMS at 60 MHz, ratio 2:2:6.

Anal. Calcd for amide **72** (mp 85–87°), $C_7H_{11}N_3F_4O$: C, 36.70; H, 4.80; N, 18.35; F, 33.2. Found: C, 36.43; H, 4.95; N, 17.84; F, 32.17.

The ^{19}F nmr spectrum showed a peak at ϕ −29.7. The ^1H nmr spectrum showed τ 3.13 (NH), 6.42 ($-CH_2N$), 7.50 [$-CH_2C(NF_2)_2$] and 8.27 (ring CH_2); ratio 1:2:2:6.

Anal. Calcd for amide **73** (mp 71–73°), $C_7H_{11}N_3F_4O$: C, 36.70; H, 4.80; N, 18.35; F, 33.2. Found: C, 36.47; H, 4.97; N, 18.31; F, 33.19.

The ^{19}F nmr spectrum showed a peak at ϕ −24.0. The ^1H nmr spectrum showed two broad peaks, τ 7.30 and 8.32; ratio 2:3. The NH appeared to be at τ 2.85.

Registry No.—**1**, 20122-67-2; **2**, 16704-36-2; **3**, 20122-69-4; **4**, 20122-70-7; **5**, 20122-71-8; **6**, 20122-72-9; **7**, 20122-73-0; **8**, 20122-74-1; **9**, 20122-75-2; **10**, 20122-76-3; **11**, 20122-77-4; **12**, 20122-78-5; **13**, 20122-79-6; **14**, 20122-80-9; **15**, 20122-81-0; **23**, 20122-82-1; **26**, 19955-15-8; **27**, 20122-84-3; **28**, 19955-23-8; **29**, 20122-86-5; **30**, 20122-87-6; **31**, 20122-88-7; **32**, 20122-89-8; **33**, 20122-90-1; **36**, 20122-91-2; **37a**, 20122-92-3; **37b**, 20122-93-4; **38**, 20122-94-5; **39**, 201222-95-6; **45**, 20122-96-7; **46**, 20122-97-8; **47**, 20116-42-1; **53**, 20116-43-2; **54**, 20116-44-3; **57**, 20116-45-4; **58**, 20116-46-5; **59**, 20116-47-6; **60**, 20116-48-7; **66**, 20116-49-8; **67**, 20116-50-1; **71**, 20116-51-2; **72**, 20116-52-3; **73**, 20116-53-4; $CH_3C(NF_2)_3$, 20116-54-5; $CN(CH_2)_5C(NF_2)_3$, 20116-55-6; 1-fluoro-1-(*p*-methoxyphenyl)-2-aza-3,3-bis(difluoramino)-1-butene, 20116-56-7; N-[1,1-bis(difluoramino)-1-propyl]benzamide, 20116-57-8; N-[1,1-bis(difluoramino)ethyl]-*p*-chlorobenzamide, 20116-58-9; 2-chloro-2,3-bis(difluoramino)butane, 20116-40-9; 2-aza-1-fluoro-1-*p*-chlorophenyl-3,3-bis(difluoramino)-1-butene, 20116-41-0.

Acknowledgment.—This research was carried out during 1963–1965 for the Advanced Research Projects Agency under U. S. Army Missile Command, Contract DA-01-021-11909. The encouragement and contributions of Dr. J. P. Freeman aided greatly.