methylene, and a triplet ($J = 8$ cps) at 2.80 for the α-methylene. The fluorine spectrum exhibited a triplet at $\phi^* -53.15$, $J = 28.4$ cps.

1,3,3-Tris(difluoramino)butane. Freshly distilled methyl vinyl ketone (5.0 g, 0.084 mol) was added slowly to 75 ml of 100% sulfuric acid and 27 g of difluoramine. After 3 hr, 75 ml of pentane was added and difluoramine was removed. Distillation of the pentane solution through a 25-cm Holzman column gave 10.65 g (60% yield) of 1,3,3-tris(difluoramino)butane, bp 50° (30 mm).

Anal. Calcd for $C_4H_7N_3F_6$: C, 22.74; H, 3.31; N, 19.90. Found: C, 23.09; H, 3.51; N, 19.90.

The infrared spectrum showed bands at 3.3–3.4 (w), 6.90 (m), 7.20 (m), 10.21 (s), 10.5 (sh), 11.1 (vs), 11.73 (s), and 12.03 μ (s).

The proton nmr spectrum consisted of a quintet ($J_{HF} = 2.2$ cps) at δ 1.67 for the methyl, a distorted triplet ($J_{HH} = 7.5$ cps) at 2.47 for the methylene adjacent to the bis(difluoramino) methylene group, and a triplet of triplets ($J_{HF} = 28.5$ cps, $J_{HH} = 7.5$ cps) at 3.80 for the other methylene.

2-Methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran. Methyl vinyl ketone (3.0 g, 0.043 mol) was added dropwise to 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. After 3 hr, 50 ml of pentane was added and difluoramine was removed. The lower layer was drained onto 50 g of ice, and extracted with three 30-ml portions of methylene chloride. The methylene chloride solution was dried and stripped. Molecular distillation of the residue gave 0.70 g (5.8% yield) of 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran.

Anal. Calcd for $C_8H_{13}N_3F_6O$: C, 34.17; H, 4.66; N, 14.95; F, 40.5. Found: C, 34.20; H, 4.48; N, 15.19; F, 41.1.

The infrared spectrum showed bands at 3.33 (m), 6.87 (m), 7.20 (m), 7.79, (w), 8.03 (s), 8.70 (m), 9.10 (m), 9.40 (s), 10.0 (s), 10.2 (sh), 11.1 (vs), and 11.9 μ (w).

The proton nmr spectrum showed a triplet ($J = 2$ cps) at δ 1.44 assigned to the $>C(NF_2)\mathit{CH}_3$, a quintet ($J = 2$ cps) for the other methyl, a broadened doublet at 4.61 for $>CH\mathit{CH_2O}-$, and a complex multiplet (maximum intensity at 108 cps) for the remaining ring protons. The fluorine spectrum showed an AB quartet (ϕ^* -11.35 and -17.39, $J = 593$ cps) for the single difluoramino group and a singlet at $\phi^* -27.80$ for $>C(NF_2)_2$.

Distillation of the original pentane layer gave 3.4 g (37.5% yield) of 1,3,3-tris(difluoramino)butane.

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Reaction of Acetylenes with Difluoramine[1]

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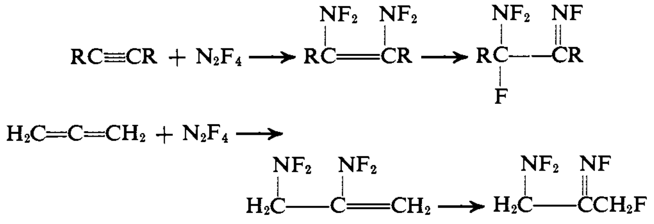
Abstract: The reaction of 3-hexyne with difluoramine, catalyzed by the boron trifluoride complex of phosphoric acid gave 3-hexanone, 3,3-bis(difluoramino)hexane, 3-difluoramino-3-fluorohexane, and N-(α-difluoraminopropyl)-propropionamide. Under the same conditions 1-hexyne gave 2-hexanone, 2,2-bis(difluoramino)hexane, 2-difluoramino-2-fluorohexane, and N-(difluoraminomethyl)valeramide. When sulfuric acid was used as the catalyst, 3-hexyne, 1-hexyne, and propargyl chloride were found to react with difluoramine to give 3,3-bis(difluoramino)-hexane, 2,2-bis(difluoramino)hexane, and 1-chloro-2,2-bis(difluoramino)propane, respectively. Possible mechanisms are discussed.

The addition of tetrafluorohydrazine to acetylenes has been reported to take place with the formation of vicinal bis(difluoramino)ethylenes, with subsequent pseudoallylic fluorine migration.[2,3] It was possible to isolate the unrearranged adduct only in the case of perfluoroalkyl acetylenes.[3] The reaction of tetrafluorohydrazine with allene proceeded with similar rearrangement[3] (Scheme I). The rearrangement of acetylene adducts of tetrafluorohydrazine was recently reported to proceed under solvolytic conditions through a mesomeric cation which could be trapped by nucleophiles other than fluoride.[4]

Scheme I



$$RC{\equiv}CR + N_2F_4 \longrightarrow R\overset{NF_2}{\overset{|}{C}}{=}\overset{NF_2}{\overset{|}{C}}R \longrightarrow R\overset{NF_2}{\overset{|}{\underset{F}{\underset{|}{C}}}}{-}\overset{NF}{\overset{\|}{C}}R$$

$$H_2C{=}C{=}CH_2 + N_2F_4 \longrightarrow H_2\overset{NF_2}{\overset{|}{C}}{-}\overset{NF_2}{\overset{|}{C}}{=}CH_2 \longrightarrow H_2\overset{NF_2}{\overset{|}{C}}{-}\overset{NF}{\overset{\|}{C}}CH_2F$$

The reaction of difluoramine with an acetylene would be expected to give a vinyldifluoramine as the initial adduct under mild conditions, and the ultimate products would reflect the chemical properties of this moiety. This reaction has now been studied using the boron trifluoride complex of phosphoric acid or sulfuric acid as catalyst. Sulfuric acid has been reported to promote the addition of difluoramine to olefins,[5] but the products rearrange rapidly to fluorimonium ions under the same conditions.[6] This problem was not encountered with the boron trifluoride complex of phosphoric acid, which also catalyzed the additions.[5,7]

Difluoramine reacted at its reflux temperature (−23°) with 3-hexyne in the presence of the boron trifluoride complex of phosphoric acid. The volatile products, separated by gas chromatography, were identified as 3-hexanone (Ia), 3,3-bis(difluoramino)hexane (IIa), and

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(1) This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.

(2) R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, *J. Org. Chem.*, 32, 1534 (1967).

(3) G. N. Sausen and A. L. Logothetis, *ibid.*, 32, 2261 (1967).

(4) W. H. Graham, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(5) W. H. Graham and J. P. Freeman, *J. Am. Chem. Soc.*, **89**, 716 (1967).

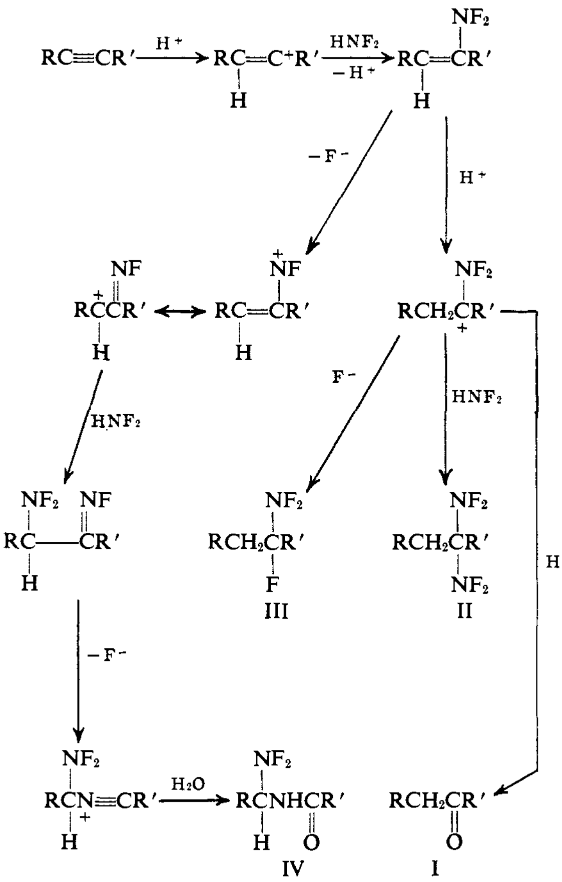
(6) K. Baum and H. M. Nelson, *ibid.*, **88**, 4459 (1966).

(7) K. Baum, *J. Org. Chem.*, 32, 3648 (1967).

3-difluoramino-3-fluorohexane (IIIa). When the nonvolatile residue containing the catalyst was quenched with water, a solid (mp 50–51.5°) was obtained identified as N-(α-difluoraminopropyl)propionamide (IVa). The analogous products, 2-hexanone (Ib), 2,2-bis(difluoramino)hexane (IIb), 2-difluoramino-2-fluorohexane (IIIb), and N-(difluoraminomethyl)valeramide (IVb), were obtained from 1-hexyne. The latter product was an uncrystallizable oil and was purified by molecular distillation.

Ketones have been shown to react with difluoramine in sulfuric acid to give *gem*-bis(difluoramino)alkanes.[8] The fact that ketones I were isolated in the above reactions raises the question as to whether ketones were intermediates in the formation of II. However, a control experiment using 3-hexanone under the same conditions did not give IIa. The observed products can be rationalized as shown in the equations in Scheme II.

Scheme II



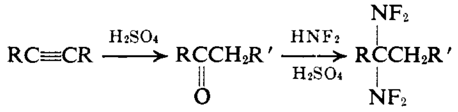
a, R = R′ = C_2H_5
b, R = H; R′ = C_4H_9

Protonation of the acetylene followed by alkylation of difluoramine would give the vinyldifluoramine. Further protonation would give the difluoraminocarbonium ion, which could alkylate difluoramine to give II or fluoride to give III.[9] The ketone could result from hydration of the original acetylene or of the difluoraminocarbonium ion; α-difluoraminocarbinols have been shown to dissociate readily to ketones and difluoramine.[10]

The loss of fluoride ions from the vinyldifluoramine would give a mesomeric cation, capable of alkylating difluoramine. Beckmann rearrangement of the resulting fluorimine would then give IV.

The fact that no vicinal bis(difluoramino)alkanes were isolated is evidence of the ability of the difluoramino group, as a pseudohalogen, to stabilize a carbonium ion center.

Acetylenes also reacted with difluoramine in the presence of concentrated sulfuric acid, but the only products isolated were *gem*-bis(difluoramino)alkanes. Thus, 1-hexyne, 3-hexyne, and propargyl chloride gave 2,2-bis(difluoramino)hexane, 3,3-bis(difluoramino)hexane, and 1-chloro-2,2-bis(difluoramino)propane, respectively. When 3-hexyne was treated with sulfuric acid under the same conditions in the absence of difluoramine, a 50% yield of 3-hexanone was isolated. Since ketones are converted to *gem*-bis(difluoramino)alkanes under these conditions,[8] it appears probable that the reaction proceeded *via* acetylene hydration.



$$RC\equiv CR \xrightarrow{H_2SO_4} R\underset{\underset{O}{\|}}{C}CH_2R' \xrightarrow[H_2SO_4]{HNF_2} R\overset{NF_2}{\underset{NF_2}{C}}CH_2R'$$

a, R = R′ = C_2H_5
b, R = C_4H_9; R′ = H
c, R = CH_2Cl; R′ = H

Infrared and nmr spectra of the products are described in the Experimental Section. It is noteworthy that the nmr spectra of the *gem*-(difluoramino)fluoroalkanes, IIIa and IIIb, showed no coupling between C–F and NF_2. Lack of resolvable coupling between geminal fluorine and difluoramino groups has also been reported for tris(difluoramino)fluoromethane.[11]

Experimental Section

General. The previously described[7,8] difluoramine generation train was used. Explosion shields or barricades adequate to contain a detonation of the quantity of difluoramine used are essential. Neat difluoramino compounds were manipulated behind safety shields with remote handling devices.

Reaction of 3-Hexyne with Difluoramine. To a mixture of 1 ml of boron trifluoride complex of phosphoric acid[12] and 9 g of refluxing difluoramine, 2.0 g (0.024 mol) of 3-hexyne was added dropwise, with stirring. After 30 min, the excess difluoramine was flushed from the system, and the product was vacuum transferred into a −80° trap to yield 1.5 g of colorless liquid, bp 56–65° (39 mm). Gas chromatography (0.25 in. × 25 ft column of L45 silicone oil on Fluoropak 80, 60 cc/min of helium, 45°) gave peaks with retention times of 62, 69, and 133 min with relative areas of 37:22:36. The third component was identified as 3,3-bis(difluoramino)hexane by comparison with an authentic sample. The first two peaks overlapped so that pure samples could not be isolated using this column. The trapped mixture of the two components was resolved using a 0.25 in. × 6 ft column of dioctyl phthalate on Fluoropak 80. The second component was identified as 3-hexanone by comparison with an authentic sample. The first component was identified as 3-difluoramino-3-fluorohexane.

Anal. Calcd for $C_6H_{12}NF_3$: C, 46.45; H, 7.75; N, 9.05. Found: C, 45.92; H, 7.67; N, 9.05.

The proton nmr spectrum consisted of overlapping triplets at δ 1.03 for the methyls and a multiplet with maximum intensity at 1.65 for the methylenes. The fluorine spectrum consisted of a broadened singlet at ϕ^* −16.7 for the difluoramino group and a quintet (J = 18 cps) at 145.3 for the C–F. The infrared spectrum

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(8) K. Baum, *J. Am. Chem. Soc.*, **90**, 7083 (1968).

(9) An alternative path for the formation III is the addition of difluoramine to the fluoro olefin resulting from the addition of HF to the original acetylene.

(10) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Am. Chem. Soc.*, **90**, 121 (1968).

(11) R. J. Koshar, D. R. Husted, and D. C. Wright, *J. Org. Chem.*, **32**, 3859 (1967).

(12) A. V. Topchiev, *et al.*, "Boron Trifluoride and Its Compounds as Catalysts in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 125.

showed peaks in the CF region at 8.32 (s), 8.57 (s), and 8.68 μ (s), and in the NF region at 9.7 (m), 9.89 (m), 10.21 (s), 10.78 (m), and 10.20 μ (s).

When the catalyst layer was diluted with 5 ml of ice water, gas evolved for several minutes and an oil separated. Extraction with two 10-ml portions of methylene chloride and distillation gave 0.95 g (24% yield) of N-(α-difluoraminopropyl)propionamide, bp 74° (0.2 mm). Low-temperature crystallization from ether–pentane gave a white solid, mp 50–51.5°.

Anal. Calcd for $C_6H_{12}N_2F_2O$: C, 43.37; H, 7.23; N, 16.88; F, 22.9. Found: C, 43.40; H, 7.65; N, 16.70; F, 22.1.

The fluorine nmr spectrum consisted of an AB quartet[13] centered at ϕ^* −30.5, with each member showing doublet splitting by the adjacent tertiary hydrogen (J_{FF} = 584 cps, J_{F_AH} = 16.3 cps, J_{F_BH} = 24.5 cps). The proton nmr spectrum showed a doublet at δ 8.06 for NH, a multiplet at 5.1 for the tertiary hydrogen, superimposed triplets at 1.14 for the methyls, and a multiplet due to overlapping methylene signals centered at 2.24. The infrared spectrum showed NH at 3.0 (s), carbonyl at 6.0 (s) and 6.5 (s), and bands in the NF region at 9.9 (w), 10.1 (w), 10.35 (w), 10.6 (w), 10.75 (m), 11.05 (m), 11.3 (s), 11.5 (s), 12.0 (s), 12.2 (m), and 12.5 μ (w).

Reaction of 1-Hexyne with Difluoramine. The above procedure using 1-hexyne gave 0.66 g of volatile product with gas chromatogram peaks (area per cent) at 60 min (37), 71 min (22), and 132 min (36). The first two components were resolved for isolation using the above dioctyl phthalate column. The second and third components were shown to be 2-hexanone and 2,2-bis(difluoramino)hexane, respectively by comparison with authentic samples. The first component was identified as 2-difluoramino-2-fluorohexane.

Anal. Calcd for $C_6H_{12}NF_3$: C, 46.45; H, 7.75; N, 9.05. Found: C, 45.74; H, 8.24; N, 8.73.

The proton nmr spectrum contained an irregular triplet at δ 0.95 for the methyl of the *n*-butyl group, a doublet (J_{HF} = 19 cps) of triplets (J_{H-NF_2} = 2 cps) at 1.87 for the other methyl, superimposed over a broad multiplet assigned to the methylenes. The fluorine spectrum consisted of a broadened singlet at ϕ^* −19.1 for the NF_2 and a sextet (J_{HF} = 18 cps) at 145.7 for the CF. Infrared bands in the NF region were 10.10 (s), 10.50 (m), 10.71 (w), 11.25 (s), 11.60 (m), and 11.92 μ (w).

Quenching of the acid layer gave 1.40 g (35% yield) of N-(difluoraminomethyl)valeramide, isolated by molecular distillation (bp 60–70° (0.025 mm)). The center fraction was used for analysis; the material could not be crystallized.

Anal. Calcd for $C_6H_{12}N_2F_2O$: C, 43.37; H, 7.23; N, 16.88; F, 22.9. Found: C, 43.99; H, 7.51; N, 15.46; F, 21.9.

The infrared spectrum showed NH at 3.0 (s), carbonyl at 5.98 (s) and 6.5 (s), and NF at 9.9 (w), 11.1 (m), 11.70 (w), and 12.30 μ (m). The proton nmr spectrum showed a broadened triplet (*J* = 16 cps) at δ 8.30 for the NH, a triplet (J_{HF} = 24.6 cps), of doublets (J_{HH} = 6 cps) at 4.74 for NF_2CH_2NH, an irregular triplet (*J* = 7 cps) at 2.30 for $O{=}CCH_2$, an irregular triplet (*J* = 7 cps) at 0.93 for the methyl, and a multiplet centered at 1.5 for the other methylenes. The fluorine spectrum consisted of a triplet (J_{HF} = 24.9 cps) at ϕ^* −40.82.

3,3-Bis(difluoramino)hexane. To a mixture of 3.3 g of refluxing difluoramine and 8 ml of sulfuric acid, 0.50 g (0.0061 mol) of 3-hexyne was added dropwise with stirring. After 2 hr, the excess difluoramine was vented and the mixture was extracted with 20 ml of pentane. No product was isolated by quenching the sulfuric acid layer. The pentane layer was treated with sodium sulfate and distilled to give 0.26 g (23% yield) of 3,3-bis(difluoramino)hexane, bp 34° (4.5 mm).

Anal. Calcd for $C_6H_{12}N_2F_4$: C, 38.26; H, 6.44; N, 14.88; F, 40.4. Found: C, 38.22; H, 6.57; N, 14.83; F, 39.7.

Infrared bands in the NF region were 9.83 (sh), 10.12 (m), 10.50 (w), 10.9 (sh), 11.21 (s), and 11.4 μ (sh). The proton nmr spectrum showed two methyl triplets (*J* = 7.5 cps) at δ 1.02 and 1.13, superimposed triplets (*J* = ~7 cps) at 2.07 with further multiplet splitting for the methylenes adjacent to $C(NF_2)_2$, and a complex multiplet at 1.67 for the other methylene. The fluorine spectrum consisted of a broadened singlet at ϕ^* −28.5.

2,2-Bis(difluoramino)hexane. 1-Hexyne (1.08 g, 0.013 mol) was added dropwise with stirring to a mixture of 9 g of refluxing difluoramine and 8 ml of concentrated sulfuric acid. After 2.5 hr, the excess difluoramine was removed, and the product was vacuum transferred into a −80° trap (1.5 mm) to give 0.80 g (33% yield) of 2,2-bis(difluoramino)hexane.

Anal. Calcd for $C_6H_{12}N_2F_4$: C, 38.26; H, 6.44; N, 14.88. Found: C, 38.20; H, 6.44; N, 14.43.

Infrared bands in the NF region were 10.07 (s), 10.29 (s), 10.70 (m), 11.20 (s), 11.42 μ (sh). The proton nmr spectrum consisted of a quintet (J_{HF} = 2.1 cps) at δ 1.55 for $CH_3C(NF_2)_2$–, a distorted triplet (*J* = 5.3 cps) at 0.97 for the other methyl, a multiplet at 1.97 for $-CH_2C(NF_2)_2$–, and a multiplet at 1.5 for the other methylenes. The ^{19}F spectrum consisted of a broadened singlet at ϕ^* −27.6.

1-Chloro-2,2-bis(difluoramino)propane. Propargyl chloride (1.87 g, 0.025 mol) was added dropwise with stirring to 15 ml of sulfuric acid and 9 g of difluoramine. After 3 hr, the excess difluoramine was removed, and the product was vacuum transferred to a −80° trap (90 mm) to give 0.33 g (14% yield) of 1-chloro-2,2-bis(difluoramino)propane. The infrared spectrum was identical with that of an authentic sample.[8]

Acknowledgment. The author is indebted to Mr. F. J. Gerhart for assistance in the synthesis work, to Dr. H. M. Nelson and Mr. L. A. Maucieri for nmr analysis, and to Mr. K. Inouye for elemental analysis.

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(13) For a discussion of the nonequivalence of fluorines of difluoramino groups sttached to asymmetric centers see F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, 32, 466 (1967).