Condensation of Diindeno[1,2-*c*:2′,1′-*e*]pyridazine-11,12-dione (34) with Hydrazine. Diindeno[1,2-*c*:2′,1′-*e*]pyridazine-11,12-dihydrazone (32). A mixture of 0.13 g (0.0045 mol) of **34** and 0.15 g (0.16 ml, 0.0045 mol) of 95% hydrazine in 30 ml of a 10:1 mixture of monoglyme and ethanol was stirred for 48 hr at room temperature and for 3 hr on a steam bath. The solution turned from dark green to orange. The reaction mixture was cooled and the solid was collected by filtration to give 0.040 g (30%) of **32**. The infrared spectrum was identical with the product **32** isolated from the condensation of **31** with hydrazine.

Diindeno[1,2-*c*:2′,1′-*e*]pyridazine-11,12-dione (34). A suspension of 0.20 g (0.00064 mol) of **32** in 100 ml of concentrated hydrochloric acid was heated on a steam bath for 2 hr. The solid remaining was removed by filtration while the solution was still hot and the filtrate was allowed to cool to give 0.050 g (27%) of a hydrochloride salt (**33**) of **34**. Recrystallization from chloroform removed the hydrogen chloride from the molecule and gave diketone **34**, mp 306–308°, as needle-like crystals. The hydrochloride salt (**33**) was also decomposed by heating a dry sample of it to about 200°. This was carried out in a capillary tube, and the hydrogen chloride was observed with wet litmus paper. The solid turned from a dark green to a light tan at 200° and continued heating gave mp 306–308°, that of the free diketone (**34**).

Anal. Calcd for $C_{18}H_8N_2O_2$: C, 76.06; H, 2.82; N, 9.86. Found: C, 75.76; H, 3.03; N, 10.20.

The infrared spectrum of **34** showed no >C=N– or –NH_2 absorption and did show a strong >C=O band at 1740 cm^{-1}.

Diindeno[1,2-*c*:2′,1′-*e*]pyridazine (36). I. Preparation from 32. A mixture of 4.0 g (0.013 mol) of **32** and 5.0 g (5.1 ml, 0.15 mol) of 95% hydrazine in 100 ml of ethylene glycol was heated at 170° overnight. The solution was filtered while hot, and the product was collected and washed several times with absolute ethanol to give 3.0 g (92%) of a dark purple, highly crystalline compound, mp 285° dec.

Anal. Calcd for $C_{18}H_{12}N_2$: C, 84.37; H, 4.68; N, 10.93. Found: C, 84.58; H, 4.53; N, 11.06.

The infrared spectrum showed no bands for >C=O, –NH_2, or –N=N– functions.

II. Preparation from 34. A mixture of 0.075 g (0.0021 mol) of **34** and 0.67 g (0.71 ml, 0.021 mol) of 95% hydrazine in 20 ml of ethylene glycol was heated at 150° for 2 days. The solution was allowed to cool, and the solid was collected by filtration to give 0.020 g (37%) of product, mp 285° dec.

The infrared spectrum was identical with that for the product when **32** was heated in hydrazine.

III. Preparation from 31. A mixture of 2.0 g (0.0070 mol) of **31** and 2.2 g (2.3 ml, 0.070 mol) of 95% hydrazine was heated at 80° for 6 hr, and the dihydrazone **32** precipitated as a copper colored crystalline solid. The solution was then heated at 150° overnight and **32** went into a solution to give a dark brown solution. The solution was allowed to cool and the product was isolated by filtration as a brown solid in a quantitative yield, mp 285° dec.

The infrared spectrum was identical with that for the product when **32** was heated in hydrazine.

The condensation of 2-cyclopentene-1,4-dione (**30**),[18] 1,3-cyclopentanedione (**26**),[19] β-tropolone (**37**),[20,21] or 1,3-cycloheptanedione (**38**)[22] with hydrazine under the normal reaction conditions afforded no identifiable products.

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(19) C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **81**, 4920 (1959).

(20) J. Allan and R. Robinson, *J. Chem. Soc.*, 376 (1926).

(21) A. J. Birch, private communication, May 20, 1966.

(22) B. Eistert, F. Haupter, and K. Schank, *Ann.*, **665**, 55 (1963).

Reactions of Carbonyl Compounds with Difluoramine[1]

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Abstract: Ketones and aldehydes were found to react with difluoramine in sulfuric acid or oleum with replacement of carbonyl groups by two difluoramino groups. Carbonium ion precursors in the γ position cyclized to give α-(difluoramino)tetrahydrofurans. One such derivative, 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran was treated further under more forcing conditions, to yield 2,2,5,5-tetrakis(difluoramino)hexane. Acetol gave 2,5-bis(difluoramino)-2,5-dimethyl-1,4-dioxane. Michael addition of difluoramine took place with α,β-unsaturated carbonyl compounds.

Difluoramine has been shown to react as a nucleophile in the presence of acids,[2,3] undergoing alkylation by carbonium ions. In the absence of catalysts, difluoramine was added reversibly to aldehydes and ketones to form α-difluoraminocarbinols.[4] Inasmuch as the difluoramino group is capable of supporting positive charge on neighboring atoms,[3] it appeared possible to prepare geminal bisdifluoramino compounds from carbonyl compounds in the presence of strong acids, with difluoraminocarbinols and difluoraminocarbonium ions as intermediates.

This result was achieved with the ketones shown in Table I. Simple ketones reacted readily with a mixture of concentrated sulfuric acid and refluxing difluoramine (bp −23°), although no reaction took place with sulfuric acid of less than 92% concentration. Electron-withdrawing substituents required more forcing conditions, such as a more acidic medium (oleum) or a higher reaction temperature (attained by using a closed reactor). The sequence leading to bis(difluoramino)alkanes was shown to be reversible; 2-octanone was recovered when 2,2-bis(difluoramino)octane was shaken with sulfuric acid for 1 hr at room temperature. Yields of bis(difluoramino)alkanes are therefore affected by any variables involved in the rates of the individual steps in the equilibria (Scheme I). In general, a high concentration of difluoramine, a solvent with a strong affinity for water, and a low solubility for the product are favor-

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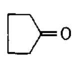
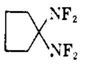
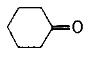
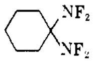
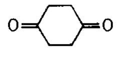
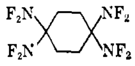
(1) This work was supported by the Office of Naval Research and the Advanced Projects Research Agency.

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

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

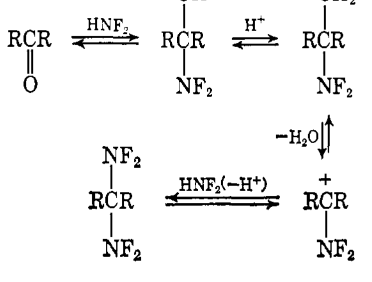
(4) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Am. Chem. Soc.*, **90**, 121 (1968).

Table I. *gem*-Bis(difluoramino) Derivatives of Ketones

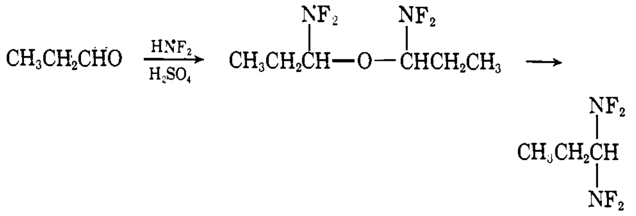
Starting material	Product	Bp, °C (or mp)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_3$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}CH_3$	73
$C_2H_5\underset{\underset{O}{\Vert}}{C}C_2H_5$	$C_2H_5\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}C_2H_5$	40–41 (30 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}(CH_2)_5CH_3$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}(CH_2)_5CH_3$	38 (0.6 mm)
		36 (20 mm)
		44 (7 mm)
		(103)
$ClCH_2\underset{\underset{O}{\Vert}}{C}CH_3$	$ClCH_2\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}CH_3$	41 (60 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}(CH_2)_3CO_2C_2H_5$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}(CH_2)_3CO_2C_2H_5$	93 (2 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}(CH_2)_3NO_2$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}(CH_2)_3NO_2$	65 (0.25 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2\underset{\underset{NO_2}{\vert}}{\overset{\overset{NO_2}{\vert}}{C}}CH_3$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}CH_2CH_2\underset{\underset{NO_2}{\vert}}{\overset{\overset{NO_2}{\vert}}{C}}CH_3$	(47)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2C(NO_2)_3$	$CH_3\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}CH_2CH_2C(NO_2)_3$	(42)

able factors. The importance of reaction conditions in the case of 5,5,5-trinitro-2-pentanone is illustrative. No reaction took place with refluxing difluoramine and concentrated sulfuric acid in 4 hr. Using 100% sulfuric acid, 4 ml/mmol of ketone, and an eightfold excess of difluoramine at room temperature gave a 53% conversion in 40 hr, and starting material was recovered. Using 20% fuming sulfuric acid, only 0.7 ml/mmol of ketone, and a threefold excess of difluoramine at its reflux temperature gave a 99.5% yield in only 2 hr.

Scheme I



Aldehydes were also converted to bis(difluoramino)-alkanes, but more forcing conditions were required than for simple ketones. *n*-Propionaldehyde gave 1,1-bis(difluoramino)propane, and α,α′-bis(difluoramino)-propyl ether was isolated as an intermediate. Trioxane similarly was converted to bis(difluoramino)methane, which was characterized by nitrogen analysis and infrared spectra. Further characterization of bis-(difluoramino)methane was restricted by its extreme sensitivity; explosions occurred during vacuum line manipulations. The synthesis of bis(difluoraminomethyl) ether from difluoraminomethanol and sulfuric acid has been reported.[4]

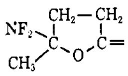
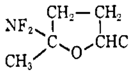
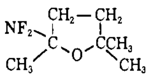
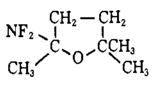
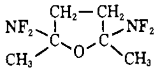
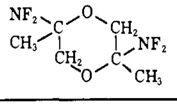


$$CH_3CH_2CHO \xrightarrow[H_2SO_4]{HNF_2} CH_3CH_2\overset{\overset{NF_2}{\vert}}{C}H{-}O{-}\overset{\overset{NF_2}{\vert}}{C}HCH_2CH_3 \longrightarrow CH_3CH_2\underset{\underset{NF_2}{\vert}}{\overset{\overset{NF_2}{\vert}}{C}}H$$

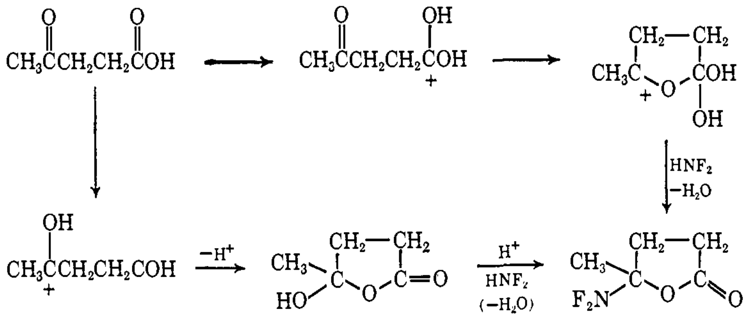
$$(CH_2O)_3 \longrightarrow CH_2(NF_2)_2$$

Carbonyl compounds with carbonium ion precursors in suitable positions gave difluoramino-substituted lactones, tetrahydrofurans, and dioxanes. The reactions listed in Table II were carried out in the presence of refluxing difluoramine, using concentrated sulfuric acid as the solvent. These reactions can be rationalized as difluoramine alkylations by the carbonium ions which result from intramolecular alkylation of carbonyl groups. In the case of levulinic acid, the same product

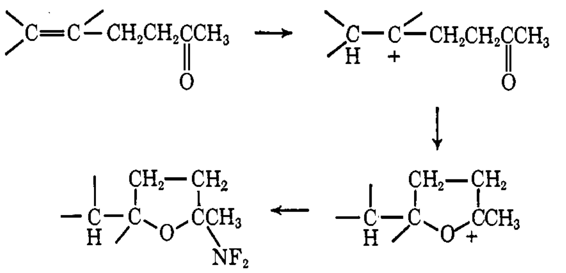
Table II. Cyclization Reactions

Starting material	Product	Bp, °C (or mp)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2COOH$		55–56 (0.5 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2CH{=}CH_2$		34 (8 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2\underset{\underset{NO_2}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}CH_3$		50–51 (19 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$		50–51 (19 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2CH_2\underset{\underset{O}{\Vert}}{C}CH_3$		35 (2.7 mm)
$CH_3\underset{\underset{O}{\Vert}}{C}CH_2OH$		(70)

Scheme II

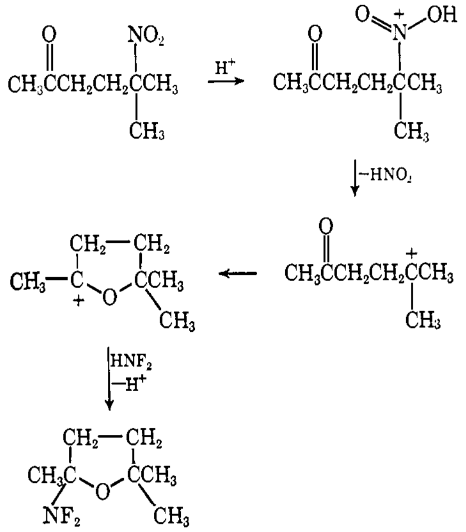


would be formed by the protonation of either the carboxyl or keto carbonyl groups (Scheme II). For the olefinic starting materials in Table II, the observed products can arise only by protonation of the olefinic bonds; initial attack on the carbonyls would give carbocyclic products.

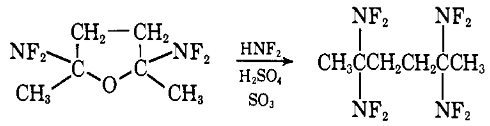


Some similar acid-catalyzed cyclization and addition reactions have been reported for reagents other than difluoramine. For example, the acetylation of levulinic acid was reported to give 4-acetoxy-4-methylbutyrolactone.[5] Tetrahydrofuran derivatives were formed by the acid-catalyzed ring closure of both 4-hydroxy olefins, and 5-hydroxy olefins.[6] Also, γ-hydroxyaldehydes[7] have been reported to give 2-alkoxytetrahydrofurans on reaction with alcohols. The reaction of acetol with alcohols gave 2,5-dialkoxy-2,5-dimethyl-1,4-dioxanes.[8]

The reaction of 5-methyl-5-nitro-2-hexanone is explainable on the basis of protonation of an oxygen atom of the nitro group followed by loss of nitrous acid and intramolecular alkylation of the carbonyl oxygen. This function of a nitro group as a leaving group in an alkylation reaction is novel. Primary and secondary nitroalkanes have been reported to react with acetic anhydride and Lewis acids to give alkyl acetates, but evidence was reported for an SNi mechanism involving an O-acyl intermediate.[9] Recent nmr studies[10] have shown that primary nitroalkanes are protonated reversibly in strong acids, whereas *t*-nitrobutane gives the *t*-butyl cation.

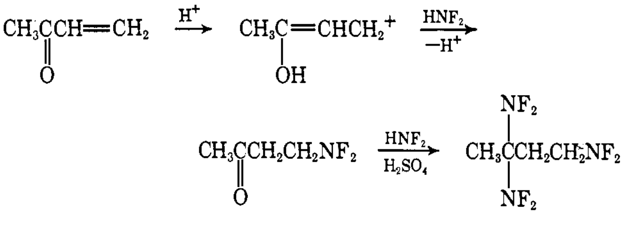


In a prolonged reaction of acetonylacetone with difluoramine in fuming sulfuric acid at room temperature, ring opening of the initially formed tetrahydrofuran derivative took place, and 2,2,5,5-tetrakis(difluoroamino)hexane was prepared. In this experiment, some acetonylacetone was recovered, although none was found when the tetrahydrofuran derivative was prepared under milder conditions.



Methyl vinyl ketone underwent an initial Michael addition of difluoramine with subsequent replacement of the carbonyl to give 1,3,3-tris(difluoramino)butane. Relatively few examples of the Michael reaction under acidic conditions have been reported[11] (Scheme III).

Scheme III



A high-boiling by-product of this reaction was identified as 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydrofuran, which could be formed by dimerization of methyl vinyl ketone and reactions of the double bond and carbonyl with difluoramine. The steps, of course, need not take place in this order (Scheme IV). Other examples of the Michael reaction

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(5) J. Bredt, *Ann.*, **256**, 314 (1890); for a review of other cyclizations of levulinic acid, see R. H. Leonard, *Ind. Eng. Chem.*, **48**, 1331 (1956).

(6) R. Paul and H. Normant, *Compt. Rend.*, **216**, 689 (1943); H. Normant, *ibid.*, **226**, 733 (1948); O. Riobe, *Ann. Chim.*, [12] **4**, 593 (1949).

(7) B. Helferich, *et al.*, *Ber.*, **52**, 1126 (1919).

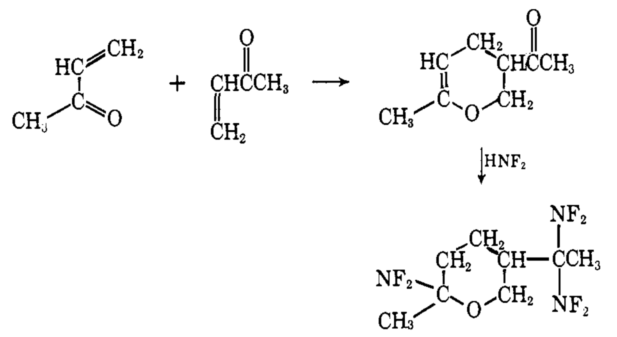
(8) M. Bergmann and A. Miekeley, *ibid.*, **64**, 802 (1931); M. Bergmann and S. Ludewig, *Ann.*, **436**, 1973 (1924).

(9) P. K. Bhattacharyya, A. C. Ghosh, V. M. Sathe, N. L. Dutta, and M. Ram, "Nitro Compounds," T. Urbanski, Ed., The Macmillan Co., New York, N. Y., 1964, p 275.

(10) H. Hogeveen, *Rec. Trav. Chim.*, **86**, 1320 (1967); N. C. Deno, R. W. Gangler, and T. Schuetze, *J. Org. Chem.*, 31, 1968 (1966).

(11) E. D. Bergmann, *Org. Reactions*, 10, 264 (1959).

Scheme VI



of difluoramine were demonstrated using acrylic acid and methyl acrylate; β-(difluoramino)propionic acid and methyl β-(difluoramino)propionate, respectively, were isolated. Acrylonitrile, however, did not react under these conditions.

Since simple primary, secondary, and tertiary alkyldifluoramines rearrange rapidly in sulfuric acid to give fluorimmonium ions,[8,12] the question arises as to why the products observed here survived reaction times of up to several days under essentially the same conditions. Protonation of oxygen-containing products would inhibit the formation of another cationic center by rearrangement. The inductive affect of difluoramino groups[13] of *gem*-bis(difluoramino)alkanes would likewise give a lower electron density on the adjacent carbon than for the simple derivatives.

Nmr and ir data for the compounds reported here is given in the Experimental Section.

Experimental Section

Apparatus and General Procedure. The previously described[3] general procedure for difluoramine reactions was used. Explosion shields or barricades adequate to contain a detonation of the quantity of difluoramine used are essential. For the addition of liquid carbonyl compounds to mixtures of sulfuric acid and refluxing difluoramine, careful control of the addition rate was necessary to control the solution temperature. A convenient method was to inject the reagents by syringe through small diameter "spaghetti" fluorocarbon tubing, connected to the glass apparatus with tapered polyethylene tubing. Material remaining in the tubing was removed by injecting a syringe of nitrogen.

When reaction temperatures higher than the reflux temperature of difluoramine were required, a reactor constructed of heavy-wall Pyrex tubing was used, fitted with three Fischer & Porter 1.25-mm glass and Teflon needle valves. One valve was at the bottom of the reactor for removing the product, the second was in line with the −80° reflux condenser for introducing reagents, and the third was used for pressure equilibration during the addition. The low-pressure end of the third valve was connected to the incoming line and to the low pressure end of the second valve by tubing angled so that the third valve was kept free of liquid. A magnetic stirring bar was sealed in the reactor, and was rotated slowly in a vertical plane by means of a rotating external magnet. Reagents were injected above the second valve and washed into the reactor by the refluxing difluoramine. After the reagents were added, the reactor was cooled externally to condense the difluoramine, and the valves were closed. After the reaction period, the reactor was again cooled, and the upper valves were opened before the product was worked up. A simpler reactor using similar valves has been reported previously.[14] Extensive attempts were not made to optimize yields in the following preparations. Explosion shields and remote manipulation devices were used for handling the neat products.

2,2-Bis(difluoroamino)propane. Acetone (1.5 g, 0.026 mol) was added dropwise with stirring to 9 g of difluoramine and 16 ml of concentrated sulfuric acid. After 4 hr, the product was vacuum transferred to a −80° trap (200 mm). Distillation gave 3.2 g (85% yield) of 2,2-bis(difluoramino)propane, bp 73°.

Anal. Calcd for $C_3H_6N_2F_4$: C, 24.66; H, 4.11; N, 19.18. Found: C, 24.33; H, 3.96; N, 19.28.

The infrared spectrum was as follows: 3.4 (w), 6.88 (m), 7.22 (m), 7.30 (m), 8.01 (w), 8.37 (m), 10.00 (m), 10.27 (s), 11.20 (s), 11.46 (s), and 12.34 μ (w).

The proton nmr spectrum consisted of a quintet at δ 1.52, J = 2 cps. The fluorine spectrum showed a broadened singlet at ϕ^* −27.9.

3,3-Bis(difluoramino)pentane. 3-Pentanone (1.0 g, 0.0116 mol) was added dropwise with stirring to 4.5 g of difluoramine and 15 ml of concentrated sulfuric acid. After 3.5 hr, 5 ml of pentane was added, and the lower layer was discarded. Excess difluoramine was removed with a stream of nitrogen and the solution was distilled to give 1.0 g (0.00575 mol, 49.5% yield) of 3,3-bis(difluoramino)pentane, bp 54° (52 mm).

Anal. Calcd for $C_5H_{10}N_2F_4$: C, 34.48; H, 5.75; N, 16.10. Found: C, 34.39; H, 6.05; N, 16.10.

The proton nmr spectrum showed a triplet for the methyls at δ 1.13, J = 8 cps, and a quartet for the methylenes at δ 2.12, J = 8 cps, with additional quintet splitting (1 cps) for each member.

Infrared peaks in the NF region appeared at 9.97 (m), 10.20 (s), 10.61 (m), 11.30 (vs), and 11.6 μ (sh).

2,2-Bis(difluoramino)octane. 2-Octanone (30.0 g, 0.234 mol) was added slowly with stirring to 150 ml of 100% sulfuric acid and 36 g of difluoramine in a pressure reactor, and the mixture was kept at the reflux temperature of difluoramine for 1 hr. The reactor was closed and kept at ambient temperature for 3.5 hr. Difluoramine was removed and the product (upper layer) was taken up in 150 ml of methylene chloride, dried over sodium sulfate, and distilled to give 30.3 g (60% yield) of 2,2-bis(difluoramino)octane, bp 38° (0.6 mm).

Anal. Calcd for $C_8H_{16}N_2F_4$: C, 44.44; H, 7.40; N, 12.96; F, 35.2. Found: C, 44.80; H, 7.71; N, 13.00; F, 34.3.

Infrared bands in the NF region were 10.10 (s), 10.32 (s), 11.2 (s), and 11.5 μ (sh). The proton nmr spectrum showed a quintet (J = 2 cps) at δ 1.55 for the methyl adjacent to the difluoramino groups, an irregular triplet at δ 0.90 for the other methyl, and multiplets for the methylenes. The fluorine spectrum showed a singlet at ϕ^* −26.69.

1,1-Bis(difluoramino)cyclopentane. Cyclopentanone (2.1 g, 0.025 mol) was added dropwise to 9 g of difluoramine refluxing over 10 ml of concentrated sulfuric acid. After 3.5 hr, the excess difluoramine was removed and the product was vacuum transferred into a −80° trap (8 mm). Distillation gave 1.7 g (0.010 mol, 40% yield) of 1,1-bis(difluoramino)cyclopentane, bp 35.5–36° (20 mm).

Anal. Calcd for $C_5H_8N_2F_4$: C, 34.88; H, 4.65; N, 16.28. Found: C, 34.91; H, 4.65; N, 16.76.

The NF region of the infrared spectrum was as follows: 9.77 (w), 10.0 (m), 10.3 (m), 10.42 (m), 10.61 (s), 10.77 (s), and 11.2–11.6 μ (vs).

1,1-Bis(difluoramino)cyclohexane. Cyclohexanone (2.45 g, 0.025 mol) was added dropwise with stirring to 9 g of difluoramine and 16 ml of concentrated sulfuric acid. After 3 hr, the excess difluoramine was removed and the product was vacuum transferred (1 mm) into a −80° trap. Distillation gave 1.45 g (0.0077 mol, 31% yield) of 1,1-bis(difluoramino)cyclohexane, bp 44° (7 mm).

Anal. Calcd for $C_6H_{10}N_2F_4$: C, 38.72; H, 5.38; N, 15.05. Found: C, 38.60; H, 5.58; N, 14.99.

The proton nmr spectrum consisted of multiplets at δ 2.06 and 1.72 with area ratio 2:3. The fluorine spectrum contained a single broadened signal at ϕ^* −22.79.

The infrared peaks in the NF region were 9.97 (m), 10.29 (m), 11.34 (vs) with shoulders at 11.07, 10.83, 10.70, 11.55, and 11.90 μ.

1,1,4,4-Tetrakis(difluoramino)cyclohexane. 1,4-Cyclohexanedione (1.40 g, 0.0125 mol) was dissolved in 15 ml of cold concentrated sulfuric acid and 9 g of difluoramine was refluxed over this solution for 4.5 hr. The mixture was added to 150 ml of ice. A white solid separated, and was filtered, washed with 50 ml of water, and air dried to give 2.7 g (0.0094 mol, 75% yield) of 1,1,4,4-tetrakis(difluoramino)cyclohexane, mp 103° with a crystalline phase change at 80°. Sublimation onto a −80° coldfinger (0.1 mm) did not change the melting point.

Anal. Calcd for $C_6H_8N_4F_8$: C, 25.00; H, 2.78; N, 19.43. Found: C, 24.62; H, 3.13; N, 19.70.

The proton nmr spectrum showed a broadened singlet at δ 2.41, and the fluorine spectrum showed a broadened singlet at ϕ^* −25.22.

The infrared spectrum of a carbon tetrachloride solution consisted of peaks at 6.88 (m), 9.69 (m), 9.90 (m), 10.29 (m), 10.58 (m), 10.74 (m), 11.10 (s), 11.40 (sh), and 13.9 μ (m).

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1-Chloro-2,2-bis(difluoramino)propane. Chloroacetone (2.3 g, 0.025 mol) was added dropwise with stirring to 9 g of difluoramine and 16 ml of concentrated sulfuric acid. After 4 hr, the excess difluoramine was vented, and the product was vacuum transferred to a −80° trap (5 mm). Distillation of the condensate gave 2.3 g (0.016 mol, 70% yield) of 1-chloro-2,2-bis(difluoramino)-propane, bp 41° (60 mm).

Anal. Calcd for $C_3H_5N_2F_4Cl$: C, 19.95; H, 2.77; N, 15.51. Found: C, 19.71; H, 2.85; N, 14.94.

The infrared spectrum consisted of peaks at 3.4 (w), 6.92 (m), 7.27 (m), 7.70 (w), 8.20 (w), 8.85 (w), 10.01 (s), 10.20 (s), 10.49 (m), 10.72 (m), 11.14 (vs), 11.45 (sh), 12.2–12.3 (w), 12.90 (w), 13.6 μ (w).

The proton nmr spectrum consisted of a broad singlet at δ 4.03 for the methylene and a quintet (J = 2.2 cps) at δ 1.76 for the methyl. The fluorine spectrum showed a broadened band at ϕ^* −27.8.

Ethyl 5,5-Bis(difluoramino)hexanoate. Ethyl 5-ketohexanoate (9.3 g, 0.059 mol) was added slowly to 50 ml of 20% fuming sulfuric acid and 27 g of difluoramine in a pressure reactor. After a 20-hr reaction period, excess difluoramine was vented, and the reaction mixture was added to 1 l. of ice. The product was extracted with methylene chloride, dried, and distilled to give 12.0 g (83% yield) of ethyl 5,5-bis(difluoramino)hexanoate contaminated by 4% ethyl 5-ketohexanoate, bp 90–93° (1.9–2 mm) (mixture analyzed by capillary gas chromatography).

Anal. Calcd for $C_8H_{14}N_2F_4O_2$ + 4% $C_8H_{14}O_3$: C, 39.88; H, 5.85; N, 10.92; F, 30.43. Found: C, 39.72; H, 5.68; N, 10.81; F, 31.5.

The proton nmr spectrum of ethyl 5,5-bis(difluoramino)hexanoate showed a quintet (J = 2.1 cps) at δ 1.64 for $CH_3C(NF_2)_2$, a triplet at 1.24 for the ethoxy methyl, and a complex multiplet at 2.37 and a broad band at 2.03 for the methylenes. The fluorine spectrum showed a symmetrical band at ϕ^* −28.4.

2,2-Bis(difluoramino)-5-nitropentane. 5-Nitro-2-pentanone[15] (5.0 g, 0.038 mol) was added dropwise, with stirring to 27 g of difluoramine and 17 ml of 20% fuming sulfuric acid. After 2.5 hr, the product was quenched with ice, extracted with methylene chloride, dried, and distilled through a 25-cm Holzmann column to give 4.8 g (58% yield) of 2,2-bis(difluoramino)-5-nitropentane, bp 65° (0.25 mm).

Anal. Calcd for $C_5H_9N_3F_4O_2$: C, 27.41; H, 4.11; N, 19.18; F, 34.7. Found: C, 27.68; H, 4.30; N, 18.61; F, 34.9.

Infrared bands in the NF region were 10.02 (s), 10.23 (s), 11.05 (s), and 11.58 μ (s). The proton nmr spectrum consisted of a quintet at δ 1.63 (J = 2 cps) for the methyl, an irregular triplet at 4.37 for the methylene adjacent to the nitro, and a complex multiplet with maximum intensity at 2.2 ppm for the other methylenes. The fluorine spectrum consisted of a slightly broadened signal at ϕ^* −26.94.

2,2-Bis(difluoramino)-5,5-dinitrohexane. To a solution of 1.90 g (0.010 mol) of 5,5-dinitro-2-hexanone[16] in 40 ml of 100% sulfuric acid in a glass pressure reactor, 9 g of difluoramine was added. After the mixture was allowed to stand at ambient temperature for 20 hr, the excess difluoramine was vented. A white solid separated and was washed with water and dried to give 0.50 g (18% conversion, 34% yield), mp 47°. An analytical sample (same melting point) was obtained by subliming the material at 100° (0.1 mm).

Anal. Calcd for $C_6H_{10}N_4F_4O_4$: C, 25.90; H, 3.60; N, 20.14; F, 27.3. Found: C, 26.00; H, 3.47; N, 19.81; F, 26.7.

Quenching the sulfuric acid layer gave 0.90 g (47% recovery) of 5,5-dinitro-2-hexanone.

The NF region of the infrared spectrum of the product showed bands at 9.97 (m), 10.27 (ms), 10.57 (w), 10.85 (sh), 11.07 (s), 11.38 (m), and 11.82 (m).

The proton nmr spectrum (CCl_4 solution) showed a singlet at δ 2.07 for the methyl adjacent to the nitro groups, and a quintet at 1.63 for the methyl adjacent to the difluoramino groups. The methylenes gave complex multiplets.

2,2-Bis(difluoramino)-5,5,5-trinitropentane. 5,5,5-Trinitro-2-pentanone[17] (15.0 g, 0.068 mol) was dissolved in 50 ml of partially frozen 20% fuming sulfuric acid, and the solution was immediately cooled to −80°. The cooling bath was removed after 27 g of difluoramine was introduced. The reflux temperature was maintained for 2 hr, the difluoramine was removed, and the solid product was taken up in 100 ml of methylene chloride. The methylene chloride solution was shaken with sodium sulfate and stripped to give 20.9 g (99.5% yield) of 2,2-bis(difluoramino)-5,5,5-trinitropentane, mp 42°.

Anal. Calcd for $C_5H_7N_5O_6F_4$: C, 19.43; H, 2.27; N, 22.68; F, 24.6. Found: C, 19.51; H, 2.32; N, 22.60; F, 24.8.

Infrared bands (all m) in the NF region were 10.0, 10.21, 10.64, 10.85, 11.08, 11.38, 11.70, and 11.99 μ. The proton nmr spectrum (CCl_4 solution) consisted of a quintet (J = 2 cps) at δ 1.71 for the methyl and signals at 3.16 and 2.54 with A_2X_2 splitting for the methylenes. The latter multiplet showed additional splitting and therefore probably represents the methylene adjacent to the difluoramino groups.

The reaction conditions described above for 2,2-bis(difluoramino)-5,5-dinitrohexane gave 2,2-bis(difluoramino)-5,5,5-trinitropentane in 53% yield, and some starting material was recovered.

1,1-Bis(difluoramino)propane. Propionaldehyde (1.0 g, 0.0172 mol) was added dropwise with stirring to a mixture of 9 g of difluoramine and 10 ml of 20% fuming sulfuric acid. After 4 hr, the excess difluoramine was removed and the product was collected in a −80° trap (20 mm). Distillation of the condensate gave 1.63 g (0.0112 mol, 65% yield) of 1,1-bis(difluoramino)propane, bp 63°.

Anal. Calcd for $C_3H_6N_2F_4$: C, 24.66; H, 4.11; N, 19.18. Found: C, 24.91; H, 4.19; N, 18.90.

The proton nmr consisted of a triplet at δ 1.1 (J = 8 cps) for the methyl, a quintet at 2.0 (J = 7 cps) for the methylene, and a quintet (J = 19 cps) of triplets (J = 6.5 cps) at 4.6 for the methine. The fluorine nmr spectrum consisted of a doublet (J = 20 cps) at ϕ^* −36.3.

Infrared bands in the NF region were 9.84 (m), 10.0 (m), 10.40 (m), 11.4–11.6 (vs), and 12.1 μ (s).

When concentrated sulfuric acid was used instead of fuming sulfuric acid, a mixture of 1,1-bis(difluoramino)propane and α,α'-bis(difluoramino)propyl ether, bp 25° (17 mm), was isolated.

Anal. Calcd for $C_6H_{12}N_2F_3O$: C, 35.24; H, 5.88; N, 13.73. Found: C, 34.90; H, 5.95; N, 14.09.

The infrared spectrum contained an ether band at 8.9 μ and NF bands at 9.80 (m), 9.90 (m), 10.9 (s), 11.2–11.7 (s), and 12.15 μ (s).

Bis(difluoramino)methane. When a mixture of 1.0 g of trioxane, 15 ml of 20% fuming sulfuric acid, and 9 g of difluoramine was allowed to reflux for 4 hr, a liquid slightly less dense than the solvent separated. Vacuum transferred into a −80° trap gave 3 ml of liquid.

Anal. Calcd for $CH_2N_2F_4$: N, 23.73. Found: N, 24.13.

The infrared spectrum was characterized by bands at 7.07 (m), 7.60 (w), 7.78 (w), 9.28 (m), 9.70 (s), 10.40 (s), 10.25 (sh), 11.15 (vs), 11.80 (vs), 13.92 (m), and 14.7 μ (w).

Further characterization of bis(difluoramino)methane was restricted by its extreme sensitivity; explosions occurred during vacuum line manipulation.

2-Difluoramino-2,5-dimethyltetrahydrofuran. 5-Hexen-2-one (2.45 g, 0.025 mol) was added dropwise with stirring to 9 g of refluxing difluoramine, and then 15 ml of concentrated sulfuric acid was added dropwise. After 4.5 hr, unreacted difluoramine was removed, and the sulfuric acid solution was drained onto 150 ml of crushed ice. The product was extracted with four 50-ml portions of methylene chloride. The combined methylene chloride solutions were dried over sodium sulfate and distilled to give 2.6 g (69% yield) of 2-difluoramino-2,5-dimethyltetrahydrofuran, bp 34° (8 mm).

Anal. Calcd for $C_6H_{11}NF_2O$: C, 47.70; H, 7.29; N, 9.28. Found: C, 47.60; H, 7.17; N, 9.61.

The compound had infrared peaks at 3.45 (m), 3.55 (sh), 7.0 (m), 7.33 (m), 7.71 (w), 8.00 (w), 8.20 (w), 8.30 (sh), 8.65 (m), 8.81 (s), 9.39 (m), 9.69 (m), 10.35 (s), 10.4 (sh), 10.6 (sh), 11.2 (s), 11.7 (s), and 12.45 μ (w).

The proton nmr spectrum displayed a sextet (J = 6 cps) of δ 4.31 for the methine, a superposition of multiplets at 1.5 to 2.6 ppm for the methylenes, two triplets (J = 2 cps) with almost the same chemical shift (1.45) representing methyls adjacent to the NF_2 groups, and two almost superimposed doublets (J = 6 cps) at 1.25 for methyls on methine carbons. The fluorine nmr spectrum consisted of an AB quartet centered at ϕ^* −23.66 (with the central members separated by 228 cps and J_{FF} = 574 cps) and a singlet at ϕ^* −24.09. The data indicate a mixture of *cis* and *trans* isomers. The F^{19} AB quartet would result from asymmetry of the center at which the NF_2 is attached[18] in one isomer; the singlet would indicate accidental equivalence of the fluorines in the other isomer.

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2-Difluoramino-2,5,5-trimethyltetrahydrofuran. A. **From 5-Methyl-5-nitro-2-hexanone.** Concentrated sulfuric acid (15 ml) was added dropwise with stirring to a solution of 4.77 g (0.030 mol) of 5-methyl-5-nitro-2-hexanone[15] in 9 g of refluxing difluoramine. External cooling was required to keep the reaction temperature below $-10°$ during the addition. The difluoramine was allowed to reflux for an additional 3 hr. Unreacted difluoramine was removed, and the solution was added to 200 ml of crushed ice. The product was extracted with four 50-ml portions of methylene chloride. The methylene chloride solution was dried and distilled to give 3.3 g of colorless liquid, bp 50° (20 mm). Gas chromatography showed that the sample consisted of two components in the ratio 9:1. The major component was identified as 2-difluoramino-2,5,5-trimethyltetrahydrofuran (60% corrected yield).

Anal. Calcd for $C_7H_{13}NF_2O$: C, 50.91; H, 7.89; N, 8.48. Found: C, 50.80; H, 7.85; N, 8.57.

The infrared spectrum was as follows: 3.35 (m), 6.86 (m), 7.27 (m), 7.60 (m), 7.9–8.0 (m), 8.20 (m), 8.70 (s), 9.31 (w), 9.81 (m), 10.14 (s), 10.25 (sh), 10.40 (sh), 11.18 (s), 11.40 (sh), 11.62 (s), and 13.0 μ (w).

The proton nmr spectrum (carbon tetrachloride solution) consisted of a broad complex multiplet centered at δ 2.1 for the methylenes, a triplet (J = 2.5 cps) at 1.45 for the methyl adjacent to the difluoramino group, and singlets at 1.24 and 1.33 for the other methyls (nonequivalent because of *cis–trans* geometry with respect to the difluoramino group). The fluorine spectrum consisted of an AB quartet centered at ϕ^* -23.6, J_{FF} = 498 cps. The separation of the central peaks was 187 cps.

B. **From Methallylacetone.** Methallylacetone (1.43 g, 0.0125 mol) was added dropwise with stirring over a 20-min period to 7.5 ml of concentrated sulfuric acid and 4.5 g of difluoramine. After 15 min the mixture was drained onto 100 ml of ice. The product was extracted with three 25-ml portions of methylene chloride, and the solution was dried over sodium sulfate. Distillation, using a 25-cm Holzmann column, gave 1.20 g (57% corrected yield) of liquid, bp 50° (20 mm), identical with that above.

4-Difluoramino-4-methylbutyrolactone. Levulinic acid (1.46 g, 0.0125 mol) was added dropwise with stirring to a mixture of 4.5 g of difluoramine and 7.5 ml of concentrated sulfuric acid. After 1.5 hr, the reaction mixture was drained onto 75 ml of crushed ice. The product was extracted with two 30-ml portions of methylene chloride. The methylene chloride solutions were combined, dried over sodium sulfate, and distilled to give 1.75 g (92.6% yield) of colorless liquid, bp 55–56° (0.5 mm).

Anal. Calcd for $C_5H_7NF_2O_2$: C, 39.74; H, 4.63; N, 9.28. Found: C, 39.90; H, 4.77; N, 9.28.

The infrared spectrum showed bands at 3.30–3.40 (w), 6.50–6.60 (s), 6.90 (m), 7.05 (m), 7.21 (m), 7.91 (s), 8.08 (s), 8.28 (m), 8.65 (s), 8.90 (s), 9.05 (sh), 9.82 (m), 9.97 (s), 10.20 (s), 10.38 (s), 11.10 (s), 11.40 (s), 11.80 (s), 12.40 (m), 12.70 (w), 13.60 (w), and 14.70 μ (w).

The proton nmr spectrum of a sample diluted with carbon tetrachloride consisted of a triplet (J = 3 cps) at δ 1.65 for the methyl group and a complex multiplet for the methylenes centered at 2.4. The area ratio was 3:4. The 56.4-Mc fluorine spectrum consisted of an AB quartet centered at ϕ^* -23.6, J_{FF} = 593 cps. The central elements were separated by 47 cps.

2,5-Bis(difluoramino)-2,5-dimethyl-1,4-dioxane. Concentrated sulfuric acid (15 ml) was added dropwise with stirring to a solution of 1.85 g (0.025 mol) of acetol in 9 g of refluxing difluoramine. The reaction temperature was kept below 0°; intermittent external cooling was necessary during the early part of the addition. The reaction was kept at the reflux temperature of difluoramine for 3 hr after the addition was completed and then the excess difluoramine was vented. A white solid separated. The mixture was extracted with 100 ml of methylene chloride. Removal of solvent from the organic phase gave 2.0 g (73% yield) of crude 2,5-bis(difluoramino)-2,5-dimethyl-1,4-dioxane, a white solid, mp 62–64°. This solid was sublimed at room temperature (0.3 mm) onto a $-80°$ coldfinger to give 1.15 g (42% yield), mp 70°.

Anal. Calcd for $C_6H_{10}N_2F_4O_2$: C, 33.03; H, 4.58; N, 12.85. Found: C, 33.39; H, 4.86; N, 13.00.

The infrared spectrum consisted of peaks at 3.40 (w), 3.46 (w), 6.92 (m), 7.28 (m), 7.75 (m), 8.10 (w), 8.31 (s), 8.73 (w), 9.21 (s), 9.90 (w), 10.25 (s), 11.0 (m), 11.25 (s), 13.9 (w), and 14.33 (m).

The proton nmr spectrum of a carbon tetrachloride solution consisted of a triplet for the methyl groups at δ 1.40 (J_{HF} = 2 cps) and an irregular multiplet approximating an AB quartet at 4.00, representing the methylenes. The fluorine spectrum consisted of an AB quartet (J_{FF} = 600 cps) with chemical shifts of ϕ^* -9.58 and -21.85.

2,5-Bis(difluoramino)-2,5-dimethyltetrahydrofuran. Acetonylacetone (1.0 g, 0.0088 mol) was added dropwise with stirring to a mixture of 9 g of difluoramine and 15 ml of concentrated sulfuric acid. Stirring was continued for 30 min after the addition was completed. The mixture was then drained onto 200 ml of crushed ice, and the product was extracted with two 50-ml portions of methylene chloride. The methylene chloride solution was washed with three 50-ml portions of water, dried over sodium sulfate, and distilled to give 1.2 g (68% yield) of 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran, bp 43° (4 mm).

Anal. Calcd for $C_6H_{10}N_2F_2O$: C, 35.65; H, 4.95; N, 13.88. Found: C, 35.33; H, 5.05; N, 13.55.

The infrared spectrum consisted of the following peaks: 3.30 (w), 6.83 (m), 7.2 (m), 7.51 (m), 7.86 (m), 8.07 (m), 8.31 (m), 8.65 (s), 9.30 (m), 10.0–10.2 (s), 10.7 (sh), 10.9 (s), 11.2–11.6 (s), 12.1 (w), and 12.6 μ (w).

The proton nmr spectrum consisted of a triplet for the methyls at δ 1.60, J_{HF} = 2.9 cps, and a multiplet at 2.30 for the methylenes. The ^{19}F spectrum consisted of an AB quartet at ϕ^* -23.79, J_{FF} = 590 cps, with central elements separated by 31.5 cps.

2,2,5,5-Tetrakis(difluoramino)hexane. Acetonylacetone (2.32 g, 0.020 mol) was added dropwise with stirring to 9 g of difluoramine, 35 ml of 20% fuming sulfuric acid, and 15 ml of concentrated sulfuric acid in a pressure reactor. After a 40-hr reaction period at room temperature, the excess difluoramine was vented and the mixture was drained onto 600 ml of ice. The product was extracted with five 50-ml portions of methylene chloride, and the solution was dried over sodium sulfate and distilled to give 2.03 g of liquid, bp 70° (4 mm).

Gas chromatography (2.5-m column of 5% diethylene glycol succinate on Fluoropak 80, 85°, 60 cc of He/min) showed four components with the following retention times (minutes) and relative areas: 7, 13%; 11, 13.1%; 21, 59.9%; 39, 13.9%. The first component was identical with the 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran described above. The ir spectrum of the second component was different from that of the first one slightly, with reduced absorption at 8.7 μ. Nitrogen analysis indicated that it was an isomer, but not enough material was available for complete characterization.

Anal. Calcd for $C_6H_{10}N_2F_4O$: N, 13.88. Found: N, 14.30.

The third component was 2,2,5,5-tetrakis(difluoramino)hexane.

Anal. Calcd for $C_6H_{10}N_4F_8$: C, 24.83; H, 3.45; N, 19.32. Found: C, 25.29; H, 3.75; N, 19.51.

The NF portion of the ir spectrum showed bands at 10.0 (s), 10.25 (s), 10.5 (sh), 11.05 (s), 11.35 (s), and 11.77 μ (sh). The proton nmr spectrum (CCl_4 solution) consisted of a quintet at δ 1.63 (J = 2 cps) for the methyls and a poorly resolved quintet at 2.28 for the methylenes. The fluorine spectrum consisted of a single peak at ϕ^* -26.6.

The last gas chromatography component was identified as acetonylacetone by comparing its retention time and ir spectrum with an authentic sample.

Methyl β-(Difluoramino)propionate. Methyl acrylate (2.92 g, 0.034 mol) was added to 9 g of difluoramine and 17 ml of concentrated sulfuric acid. After 3.5 hr, the mixture was added to 150 ml of ice, and the product was extracted with four 50-ml portions of methylene chloride and dried over sodium sulfate. Distillation gave 3.50 g (74% yield) of methyl β-difluoraminopropionate, bp 47° (20 mm).

Anal. Calcd for $C_4H_7NF_2O_2$: C, 34.53; H, 5.04; N, 10.07. Found: C, 34.25; H, 5.22; N, 10.20.

Infrared bands in the NF region appeared at 9.80 (s), 10.07 (m), 10.51 (s), 10.8 (s), and 11.8–12 μ (s).

The proton nmr spectrum showed a triplet of triplets at δ 3.80 (J_{HF} = 29 cps, J_{HH} = 9 cps) for the β-methylene, a triplet at 2.72 (J = 9 cps) for the α-methylene, and a singlet at 3.71 for the methyl. The fluorine spectrum consisted of a triplet at ϕ^* -53.64.

β-(Difluoramino)propionic Acid. Acrylic acid (4.0 g, 0.055 mol) was added dropwise to 9 g of difluoramine and 15 ml of concentrated sulfuric acid. After 2 hr, the reaction mixture was quenched with ice, and the product was extracted with methylene chloride and dried over sodium sulfate. Distillation gave 4.6 g (67% yield) of β-(difluoramino)propionic acid, bp 60° (1 mm).

Anal. Calcd for $C_3H_5NF_2O_2$: C, 28.80; H, 4.00; N, 11.20. Found: C, 28.90; H, 4.28; N, 11.20.

The infrared spectrum showed bands at 3–4 (s), 5.85 (s), 7.0 (s), 7.88 (s), 8.19 (s), 9.20 (w), 9.77 (m), 10.50 (s), 11.30 (sh), 11.9 (s), and 12.5 μ (s).

The proton nmr spectrum showed a singlet at δ 11.6 for the OH, a triplet of triplets (J_{HF} = 29 cps, J_{HH} = 8 cps) at 3.70 for the β-methylene, and a triplet (J = 8 cps) at 2.80 for the α-methylene. The fluorine spectrum exhibited a triplet at ϕ^* −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 ($J_{\rm HF}$ = 2.2 cps) at δ 1.67 for the methyl, a distorted triplet ($J_{\rm HH}$ = 7.5 cps) at 2.47 for the methylene adjacent to the bis(difluoramino) methylene group, and a triplet of triplets ($J_{\rm HF}$ = 28.5 cps, $J_{\rm HH}$ = 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 $>C(NF_2)CH_3$, a quintet (J = 2 cps) for the other methyl, a broadened doublet at 4.61 for $>CHCH_2O-$, 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 ϕ^* −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.

Acknowledgment. The author is grateful to Dr. H. M. Nelson and Mr. L. A. Maucieri for nmr analysis, Mr. K. Inouye for elemental analysis, Mr. F. J. Gerhart, Mr. O. S. Schaeffler, and Mr. M. A. Sims for assistance in the synthesis work, and Mr. J. R. Fischer for guidance and encouragement.

Reaction of Acetylenes with Difluoramine[1]

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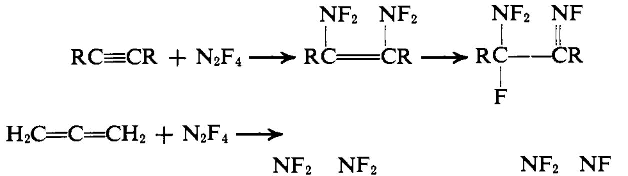
Abstract: The reaction of 3-hexyne with difluoramine, catalyzed by the boron trifluoride complex of phosphoric acid gave 3-hexanone, 3,3-bis(difluoramino)hexane, 3-difluoramino-3-fluorohexane, and N-(α-difluoraminopropyl)-propropionamide. Under the same conditions 1-hexyne gave 2-hexanone, 2,2-bis(difluoramino)hexane, 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



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

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

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.

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