10^{-3} *M; cf.* Table I. It is thus useful for determination of pK's approximately in the range of 3–10. No doubt its range could be extended at the weak acid limit by using an aliphatic mercaptan instead of thiophenol. In water, alkanethiols have pK_a's about four units greater than thiophenol.[11b] However, in that case it might be necessary to determine the pK of the thiol in methanol by reaction with ArF in a buffered solution (*e.g.*, acetate buffer) rather than in a solution of PTS or sulfuric acid.

The odor of thiophenol or another thiol might be thought a severe disadvantage. In our experience, odor problems can virtually be eliminated if most transfers are made in the fume hood, if transfers are made neatly, and particularly if all thiol-containing residues and rinsings are first poured into a jar containing water and an oxidizing agent (*e.g.*, $KMnO_4$) rather than directly into the laboratory sink.

Other Solvents.—Although our determinations were all made in methanol, this method should be applicable with equal ease and rigor to other waterlike solvents including especially mixtures of water with organic cosolvents. The indicator method, which is perhaps the chief rival of this kinetic method in regard to convenience of application, suffers from the disadvantage in a new solvent that first the pK_a of the indicators be used must be determined. Conventionally, that would imply conductimetric or potentiometric measurements preceding the actual photometric work with the indicator. With this kinetic method, the same general type of technique, photometric kinetics, is used throughout.

Experimental Section

For the most part, materials and methods were as described in an accompanying paper.[12] Pyridine (Aldrich reagent) was refluxed over sodium for 2 hr and distilled over sodium; bp 115°. Pyridine–pyridinium chloride buffer was prepared by mixing a standard solution of hydrogen chloride in methanol (titrated after László[21]) with twice its molar amount of a standard solution of pyridine in methanol. The ampoule technique was used for the runs of Table I and direct observation of reacting solutions in a Gilford spectrophotometer for those of Tables II and III.

Registry No.—Methanol, 67-56-1; 2,4-dinitrofluorobenzene, 70-34-8; thiophenoxide ion, 13133-62-5; thiophenol, 108-98-5.

(21) N. László, *Gyógyszerészet*, 215 (1966).

Reactions of Chloro Olefins with Difluoramine[1]

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The reaction of 2-chloro-2-penten-4-one with difluoramine and fuming sulfuric acid gave 2,2,4,4-tetrakis(difluoramino)pentane, 2-chloro-2,4,4-tris(difluoramino)pentane, and 2-chloro-3,4,4-tris(difluoramino)pentane. *cis*-3-Chlorocrotonic acid gave 3-chloro-3-(difluoramino)butyric acid but ethyl 3-chlorocrotonate did not react. 1,1-Dichloro-1-buten-3-one gave 1,1-dichloro-3,3-bis(difluoramino)-1-butene when a very large excess of difluoramine was used and N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide with less difluoramine. A possible mechanism for the formation of the latter compound is presented. The reaction of 1,1-dichloroethylene with difluoramine and fuming sulfuric acid gave 1,1-dichloro-1-(difluoramino)ethane and 1-chloro-1,1-bis(difluoramino)ethane.

In a previous paper[2] it was demonstrated that *gem*-bis(difluoramino)alkanes can be prepared in a reversible reaction of ketones and aldehydes with difluoramine in the presence of sulfuric acid. Acrylic acid and its esters underwent Michael addition of difluoramine under these conditions, whereas methyl vinyl ketone underwent Michael addition and subsequent replacement of the carbonyl group. This investigation has been extended to chlorinated substrates with the prospect of exploring chemical similarities between chlorine and difluoramino groups. Halogenlike electronic effects of difluoramino groups have been discussed previously.[3] The reversibility of the *gem*-bis(difluoramino)alkane formation shows that difluoramino groups as well as halogens can act as leaving groups in sulfuric acid. Graham, Freeman, and Johnson[4] have also obtained a low yield of 2,2-bis(difluoramino)propane from 2-chloro-2-(difluoramino)propane and difluoramine in sulfuric acid.

2-Chloro-2-penten-4-one was found to react with difluoramine and fuming sulfuric acid to give three products which could not be separated by distillation (Scheme I). The components, comprising 90, 5, and 5% of the sample (15, 0.9, and 0.9% yields), were separated by gas chromatography and were identified by elemental analysis and ir and nmr spectra as 2,2,4,4-tetrakis(difluoramino)pentane, 2-chloro-2,4,4-tris(difluoramino)pentane, and 2-chloro-3,4,4-tris(difluoramino)pentane, respectively. The expected product of Michael addition of difluoramine to 2-chloro-2-penten-4-one is 2-chloro-2-difluoramino-4-pentanone, and replacement of the carbonyl group with two difluoramino groups would give 2-chloro-2,4,4-tris(difluoramino)pentane. Ionization of chloride ion from this product and alkylation of difluoramine by the resulting carbonium ion would give 2,2,4,4-tetrakis(difluoramino)pentane. The formation of 2-chloro-3,4,4-tris(difluoramino)pentane can be rationalized on the basis of a 1,2-hydride shift in a chlorocarbonium ion followed by alkylation of difluoramine by the resulting secondary carbonium ion.

The reaction of *cis*-3-chlorocrotonic acid with refluxing difluoramine (bp −23°) in the presence of fuming sulfuric acid gave the Michael adduct, 3-chloro-3-

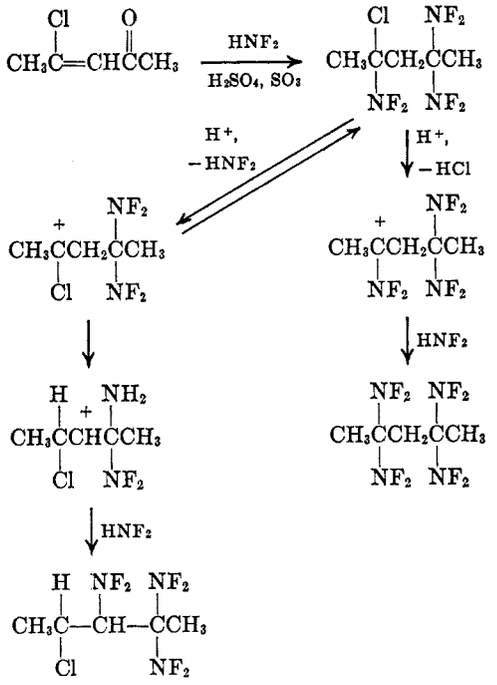
(1) This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.

(2) K. Baum, *J. Amer. Chem. Soc.*, **90**, 7083 (1968).

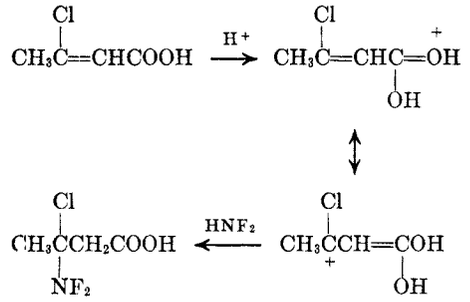
(3) K. Baum, *J. Org. Chem.*, **32**, 3648 (1967).

(4) W. H. Graham, J. P. Freeman, and K. E. Johnson, private communication.

SCHEME I

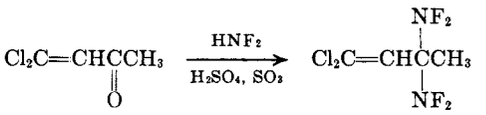


SCHEME II



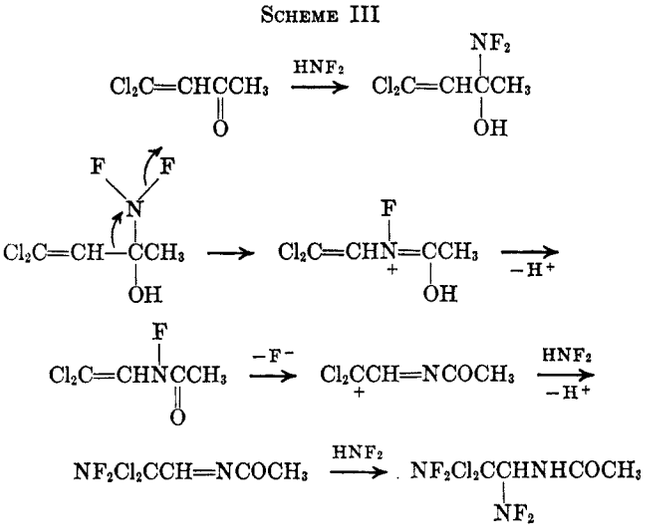
(difluoramino)butyric acid, in 59% yield (Scheme II). Ethyl 3-chlorocrotonate, on the other hand, did not react under these conditions, and the starting material was recovered. The stability of 3-chloro-3-(difluoramino)butyric acid in sulfuric acid, and the failure of chlorine to leave, is attributed to protonation of the carboxy group; subsequent chloride ionization would give a doubly charged cation. Failure of ethyl 3-chlorocrotonate even to add difluoramine is probably due to the greater stability of the protonated starting material, rendering the carbonium-ion center unreactive.

The reaction of 1,1-dichloro-1-buten-3-one with difluoramine took two entirely different courses, depending upon the conditions. In the presence of fuming sulfuric acid and such a large excess of liquid difluoramine that the latter was essentially the solvent (weight ratio of substrate/difluoramine/acid, 1:9:6.3), 1,1-dichloro-3,3-bis(difluoramino)-1-butene was isolated in 57% yield.



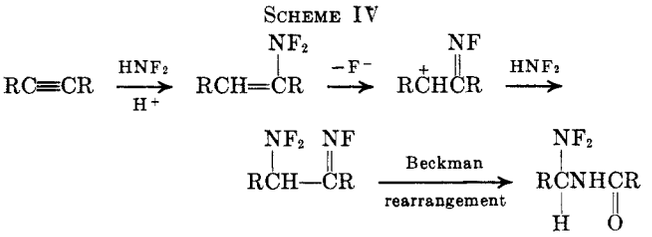
When this reagent ratio was changed to 1:1.3:6.2, no 1,1-dichloro-3,3-bis(difluoramino)-1-butene was obtained, but a product identified as N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide was isolated in 24% yield. This product could be formed from the difluoraminocarbinol resulting from addition of difluoramine to the carbonyl group. Loss of fluoride and migration of the vinyl group would give a fluorimonium ion, which is also a protonated N-fluoroamide. Ionization of the "allylic" fluorine of the latter and the alkylation of difluoramine by the resulting carbonium ion center would give 1,1-dichloro-1-difluoramino-2-N-acetyliminoethane. The addition of difluoramine would then give N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]-acetamide (Scheme III).

SCHEME III



Difluoraminocarbinols have been prepared by the uncatalyzed addition of difluoramine to carbonyl compounds[5] and are assumed to be intermediates in the formation of *gem*-bis(difluoramino)alkanes in the presence of sulfuric acid.[2] Alkyldifluoramines rearrange to fluorimonium ions under the same conditions,[3,6] and in this example the high mobility of vinyl groups in nucleophilic rearrangements[7] serves to make rearrangement competitive with hydroxyl removal. The ionization of the "allylic" fluorine of the resulting N-fluoroamide is similar to that of vinyldifluoramines formed by the addition of tetrafluorohydrazine[8-10] or difluoramine[11] to acetylenes. In the latter reaction a product of difluoramine alkylation by the resulting fluoriminocarbonium ion was isolated (Scheme IV).

SCHEME IV



(5) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Amer. Chem. Soc.*, **90**, 121 (1968).
(6) K. Baum and H. M. Nelson, *ibid.*, **88**, 4459 (1966).
(7) P. A. S. Smith, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 574.
(8) R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, *J. Org. Chem.*, **32**, 1534 (1967).
(9) G. N. Sausen and A. L. Logothetis, *ibid.*, **32**, 2261 (1967).
(10) W. H. Graham, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.
(11) K. Baum, *J. Amer. Chem. Soc.*, **90**, 7089 (1968).

In the presence of a high concentration of difluoramine, removal of the hydroxyl group of the difluoraminocarbinol and alkylation of difluoramine to give the geminal derivative is favored over fluorimonium-ion formation. The failure of 1,1-dichloro-1-buten-3-one to undergo simple 1,4 addition of difluoramine is in accord with reports of the resistance of conjugated ω-dichlorovinyl compounds to acid-catalyzed additions.[12,13] The reactivity of the double bond of 1,1-dichloro-3,3-bis(difluoramino)-1-butene is reduced by the steric and inductive effects of the two adjacent difluoramino groups.

The ability of a dichlorovinyl group to undergo difluoramine addition and of the adduct to undergo substitution of chlorine was demonstrated using a simpler substrate. The reaction of difluoramine and fuming sulfuric acid with 1,1-dichloroethylene at the reflux temperature of difluoramine gave an 8% yield of 1,1-dichloro-1-(difluoramino)ethane. When the reaction was conducted in a closed reactor at ambient temperature for a prolonged period, a mixture of 1,1-dichloro-1-(difluoramino)ethane (7.2% yield) and 1-chloro-1,1-bis(difluoramino)ethane (3.3% yield) was obtained. The compounds had little difference in boiling point, but were separated by gas chromatography. Further extension of the reaction time, however, did not result in replacement of the remaining chlorine.

$$CH_2{=}CCl_2 \longrightarrow CH_3CCl_2NF_2 \longrightarrow CH_3CCl(NF_2)_2$$

These results can be related to the fact that the difluoramino group is more electronegative than chlorine,[14] yet can provide mesomeric stabilization of adjacent positive charge.[3] Since both chlorine and difluoramino groups were shown to function as leaving groups in sulfuric acid, one would expect the chlorine of 1-chloro-1,1-bis(difluoramino)ethane to undergo substitution in the presence of a large excess of difluoramine. Molecular models indicate, however, that in the bis(difluoramino)carbonium ion both difluoramino groups cannot be in the same plane, as required for mesomeric stabilization. The additivity of the inductive effect of two difluoramino groups but not the mesomeric effect serve to favor the alternative reverse reaction to give the unstrained difluoraminochlorocarbonium ion.

Extensive attempts were not made to optimize yields in this work. It is apparent that experimental conditions have a profound effect not only on yields but on the type of products formed. The tendency toward rearrangement at lower difluoramine concentrations, as observed for the 1,1-dichloro-1-buten-3-one reactions, may have more general synthetic utility in difluoramine reactions.

Experimental Section

Difluoramine.—The previously described procedure for the generation of difluoramine was used.[2,3] *Explosion shielding adequate to withstand detonation of the quantity of difluoramine used is essential.* Manipulations were conducted remotely. Similar care is required in handling the potentially explosive products.

2,2,4,4-Tetrakis(difluoramino)pentane, 2-Chloro-2,4,4-tris(difluoramino)pentane and 2-Chloro-3,4,4-tris(difluoramino)pentane.—2-Chloro-2-pentan-4-one[15] (3.0 g, 0.028 mol) was treated with 18 g of difluoramine and 10 ml of 20% fuming sulfuric acid for 4 hr at ambient temperature with stirring in a 200-ml reactor fitted with needle valves.[2] Difluoramine was vented and the product, insoluble in the acid, was taken up in 50 ml of pentane and treated with sodium sulfate. Distillation through a 25-cm Holzmann column gave 1.30 g of colorless liquid, bp 30° (1 mm). Gas chromatography (8 ft × 1/4 in. column, 10% dioctyl phthalate on Fluoropak 80, 95°, 75 ml/min He) gave three components with retention times of 56, 66, and 81 min, comprising 90, 5, and 5% of the sample. The components were characterized as 2,2,4,4-tetrakis(difluoramino)pentane (15% yield), 2-chloro-2,-4,4-tris(difluoramino)pentane (0.9% yield), and 2-chloro-3,4,4-tris(difluoramino)pentane (0.9% yield).

The proton nmr spectrum of 2,2,4,4-tetrakis(difluoramino)-pentane consisted of a quintet (J = 3 cps) at δ 1.77 for the methyls and a broadened singlet at 2.90 for the methylene. The fluorine spectrum consisted of a singlet at ϕ^* −28.24. The infrared spectrum showed strong NF bands at (μ) 10.0 and 11.1.

Anal. Calcd for $C_5H_8N_4F_8$: C, 21.74; H, 2.90; N, 20.3. Found: C, 21.80; H, 3.20; N, 20.0.

The proton nmr spectrum of 2-chloro-2,4,4-tris(difluoramino)-pentane consisted of a quintet (J = 2.5 cps) at δ 1.79 for $CH_3C(NF_2)_2$, a triplet (J = 2 cps) at 1.97 for $CH_2C(NF_2)Cl$, and a broadened singlet at 2.93 for the methylene. Infrared bands in the NF region were at (μ) 10.0 (s), 11.13 (s), and 11.45 (m).

Anal. Calcd for $C_5H_8ClN_3F_6$: C, 23.13; H, 3.09; N, 16.2; F, 44.0. Found: C, 23.50; H, 3.34; N, 15.9; F, 42.9.

The proton nmr spectrum of 2-chloro-3,4,4-tris(difluoramino)-pentane consisted of a quintet (J = 2.5 cps) at δ 1.91 for $CH_3C(NF_2)_2$, two doublets (J = 6.3 cps) at 1.58 and 1.62 attributable to CH_3CHCl in two diastereomers, a poorly resolved multiplet at 4.55 for CH_3CHCl, and a broad multiplet at 4.13 for $CH(NF_2)$. Infrared bands in the NF region were at (μ) 10.06 (s), 10.30 (s), 10.85 (sh), 11.1 (s), and 11.50 (s).

Anal. Calcd for $C_5H_8ClN_3F_6$: C, 23.13; H, 3.09; N, 16.2; F, 44.0. Found: C, 23.59; H, 3.28; N, 15.7; F, 43.7.

3-Chloro-3-(difluoramino)butyric Acid.—*cis*-3-Chlorocrotonic acid (2.4 g, 0.020 mol) was added dropwise to 27 g of refluxing difluoramine and 10 ml of 20% fuming sulfuric acid. After 4.5 hr, the excess difluoramine was removed and the solution was quenched with 50 ml of ice. The product was extracted with three 20-ml portions of methylene chloride, dried, and distilled to give 2.05 g (59% yield) of colorless liquid which solidified in the receiver: mp 29–30°, bp 68° (0.2 mm).

Anal. Calcd for $C_4H_6NF_2ClO_2$: C, 27.68; H, 3.49; N, 8.09; F, 21.9. Found: C, 27.50; H, 3.24; N, 8.02; F, 20.1.

The proton nmr spectrum consisted of a triplet (J = 2 cps) at δ 2.07 for the methyl, a broadened singlet at 3.16 for the methylene, and a singlet at 11.74 for the OH. The fluorine spectrum consisted of an AB quartet (J_{FF} = 563 cps) with ϕ^*_A −32.63 and ϕ^*_B −36.16.

When ethyl 3-chlorocrotonate was treated as above, it was recovered unchanged in 70% yield.

1,1-Dichloro-3,3-bis(difluoramino)-1-butene.—1,1-Dichloro-1-buten-3-one[12] (3.0 g, 0.028 mol) was added dropwise with stirring to 27 g of refluxing difluoramine and 10 ml of 20% fuming sulfuric acid. After 3 hr, 50 ml of pentane was added and the unreacted difluoramine was removed. The pentane layer was separated, dried over sodium sulfate, and distilled through a 25-cm Holzmann column to give 3.64 g (57% yield) of 1,1-dichloro-3,3-bis(difluoramino)-1-butene, bp 51° (18 mm).

Anal. Calcd for $C_4H_4N_2F_4Cl_2$: C, 21.14; H, 1.76; N, 12.3; F, 33.5. Found: C, 20.91; H, 2.04; N, 12.2; F, 34.1.

The proton nmr spectrum consisted of a quintet (J = 2.5 cps) at δ 1.97 for the methyl and a broadened singlet at 6.31 for the olefinic hydrogen. The fluorine spectrum consisted of a singlet at ϕ^* −30.02. The infrared spectrum showed an olefin band at (μ) 6.15 and NF bands at 9.92, 10.15, 10.40, 10.70, 11.02, 11.3, and 11.7.

N-[2,2-Dichloro-1,2-bis(difluoramino)ethyl]acetamide.—1,1-Dichloro-1-buten-3-one (20 g, 0.144 mol) was added dropwise with stirring to 27 g of difluoramine and 65 ml of 20% fuming sulfuric acid. After 3 hr, 60 ml of pentane was added and the excess difluoramine was removed. The acid layer was drained onto 200 ml of ice and the mixture was extracted with three 30-ml

(12) I. M. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1430 (1949).

(13) P. Straus, L. Kollek, and W. Heyn, *Ber.*, **63**, 1877 (1930).

(14) R. Ettinger, *J. Phys. Chem.*, **67**, 1558 (1963).

(15) M. Julia, *Ann. Chim.* (Paris), [12] **5**, 595 (1950).

portions of methylene chloride. Distillation of the pentane layer gave no products. The methylene chloride solution was dried over sodium sulfate and the solvent was removed. An undistillable oil (14.6 g) remained. Crystallization and recrystallization from cyclohexane gave 8.8 g (24% yield) of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide, mp 92–93°.

Anal. Calcd for $C_4H_5N_3F_4OCl_2$: C, 18.60; H, 1.94; N, 16.3; F, 29.4. Found: C, 19.04; H, 2.04; N, 16.2; F, 28.4.

The proton spectrum showed a singlet at δ 2.19 for the methyl, a broad doublet (J = 9 cps) at 6.86 for the NH, and a five-line pattern centered at 6.19 for $NHCH(NF_2)$. The latter signal is interpreted as double doublet splitting (J = 22.3, 11.3 cps) by the nonequivalent NF_2 fluorines and doublet splitting by the NH. Near equality of coupling to the NH and one of the fluorines results in overlapping to give five evenly spaced lines. When D_2O was added to remove the amide hydrogen, the δ 6.86 doublet disappeared and the 6.19 signal reverted to a doublet of doublets (J = 11.8, 23.4 cps). The fluorine nmr spectrum in $DCCl_3$ showed a "doublet" (J = 23 cps) at ϕ^* −42.66 for NF_2CCl_2 which is interpreted in terms of the rotational nonequivalence of the two fluorines, with the outer members of the resulting AB quartet invisible over the background. The other difluoramino group, attached to an asymmetric center, gave an AB quartet, with each member split by the adjacent hydrogen [ϕ^*_A −27.37, ϕ^*_B −45.34 (J_{AB} = 614 cps, J_{AH} = 22.3 cps, J_{BH} = 11.4 cps)]. The infrared spectrum showed the expected amide bands, and bands in the NF region at (μ) 9.73 (s), 10.13 (m), 10.56 (m), 11.18 (s), 11.42 (s), 11.80 (s), and 12.0 (s).

1,1-Dichloro-1-(difluoramino)ethane and 1-Chloro-1,1-bis(difluoramino)ethane.—1,1-Dichloroethylene (3.0 g, 0.031 mol) was added to 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid in a 500-ml glass reactor fitted with needle valves[2] and the mixture was allowed to stand at ambient temperature for 18 hr. Difluoramine was removed and the product was extracted with 50 ml of pentane. Distillation through a 25-cm Holzmann column gave 0.51 g of colorless liquid, bp 30° (160 mm). Gas chromatography (10 ft × 1/4 in. column, 10% dioctyl phthalate on Fluoropak 80, 60 ml/min He, 25°) showed that the distillate consisted of 66% 1,1-dichloro-1-(difluoramino)ethane (7.2% yield), retention time 27 min, and 33% 1-chloro-1,1-bis(difluoramino)ethane (3.3% yield), retention time 18 min.

Anal. Calcd for $C_2H_3Cl_2NF_2$: C, 16.00; H, 2.00; N, 9.34; F, 25.3. Found: C, 15.80; H, 2.26; N, 8.91; F, 25.3.

The proton nmr spectrum of 1,1-dichloro-1-(difluoramino)-ethane in CCl_4 consisted of a triplet (J = 2.2 cps) at δ 2.31, and the fluorine spectrum consisted of a broadened singlet at ϕ^* −43.4. Infrared bands in the NF region were at (μ) 9.90 (s), 10.35 (w), 11.0 (s), and 11.8 (m).

Anal. Calcd for $C_2H_3N_2F_4Cl$: N, 16.8. Found: N, 17.3.

The proton nmr spectrum of 1-chloro-1,1-bis(difluoramino)-ethane in CCl_4 consisted of a quintet (J = 2.3 cps) at δ 1.61 and the fluorine spectrum consisted of a broadened singlet at ϕ^* −27.7. Infrared bands in the NF region were at (μ) 9.9 (m), 10.25 (s), 11.0–11.4 (vs).

In another experiment 3.0 g (0.031 mol) of 1,1-dichloroethylene was added to 6 g of refluxing difluoramine and 4 ml of 20% fuming sulfuric acid. After 1 hr, 15 ml of *n*-decane was added and the acid layer was quenched with ice. Distillation of the *n*-decane solution gave 0.35 g (8% yield) of 1,1-dichloro-1-(difluoramino)-ethane, bp 35° (250 mm), identical with the above product.

Registry No.—Difluoramine, 10405-27-3; 2,2,4,4-tetrakis(difluoramino)pentane, 19955-08-9; 2-chloro-2,4,4-tris(difluoramino)pentane, 19955-09-0; 2-chloro-3,4,4-tris(difluoramino)pentane, 19955-10-3; 3-chloro-3-(difluoramino)butyric acid, 19955-11-4; 1,1-dichloro-3,3-bis(difluoramino)-1-butene, 19955-12-5; N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide, 19955-13-6; 1,1-dichloro-1-(difluoramino)ethane, 19955-14-7; 1-chloro-1,1-bis(difluoramino)ethane, 19955-15-8.

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Reactions of Nitro and Nitroso Compounds with Difluoramine[1]

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Nitro and nitroso compounds were used as alkylating agents for difluoramine in the presence of strong acid. 1,1-Dibromo-1-nitrobutane, 1,1-dichloro-1-nitrobutane, 1-bromo-1-fluoro-1-nitropropane, and α,α-dibromo-α-nitrotoluene gave 1,1-dibromo-1-(difluoramino)butane, 1,1-dichloro-1-(difluoramino)butane, 1-bromo-1-difluoramino-1-fluoropropane, and α,α-dibromo-α-(difluoramino)toluene, respectively. Prolonged reactions converted the dibromo derivatives into 1-bromo-1,1-bis(difluoramino) compounds. 2-Halo-2,4,4-trinitropentane gave 3,5-dimethylisoxazole and 2,2,4,4-tetrakis(difluoramino)pentane, rationalized by a mechanism involving intramolecular nitro O alkylation. 1-Chloro-1-nitrosocyclohexane and 1-nitro-1-nitrosocyclohexane gave 1,1-bis(difluoramino)cyclohexane with fuming sulfuric acid but, with $BF_3 \cdot H_3PO_4$ as catalyst, 1-nitro-1-nitrosocyclohexane gave nitrocyclohexane and 1-nitrocyclohexyl-N′-fluorodiimide N-oxide. The latter was shown not to be an intermediate in the sulfuric acid catalyzed reaction. Unstable nitroso derivatives were prepared from 1-chloro-1-nitroalkanes, which reacted with difluoramine and fuming sulfuric acid to give 1-chloro-1,1-bis(difluoramino)alkanes. Alkyl nitrites acted as nitrosation agents toward difluoramine.

In a study of reactions of carbonyl compounds with difluoramine in sulfuric acid, several nitro ketones were examined.[2] Although 5-nitro-2-pentanone, 5,5-dinitro-2-hexanone, and 5,5,5-trinitro-2-pentanone gave the corresponding *gem*-bis(difluoramino)alkanes with nitro groups intact, 5-methyl-5-nitro-2-hexanone gave 2-difluoramino-2,5,5-trimethyltetrahydrofuran, rationalized on the basis of a carbonium-ion intermediate resulting from the protonation of the nitro group and loss of nitrous acid. Nitroso compounds are known to react with difluoramine in the presence of pyridine to give N′-fluorodiimide N-oxides,[3] but acid-catalyzed reactions have not been reported previously. In the present study, the scope of utility of nitro and nitroso compounds as alkylating agents for difluoramine was explored.

α,α-Dihalonitro Compounds.—1,1-Dihalo-1-nitroalkanes were found to react readily with difluoramine and fuming sulfuric acid to give 1,1-dihalo-1-(difluoramino)alkanes (Scheme I). Thus, 1,1-dichloro-1-(difluoramino)butane, 1,1-dibromo-1-(difluoramino)butane, 1-bromo-1-difluoramino-1-fluoropropane, and α,α-dibromo-α-(difluoramino)toluene were prepared

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