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.

Acknowledgment.—The author is grateful to Dr. H. M. Nelson for nmr analyses, Mr. K. Inouye for elemental analyses, and Mr. F. J. Gerhart for assistance in the synthesis work.

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.

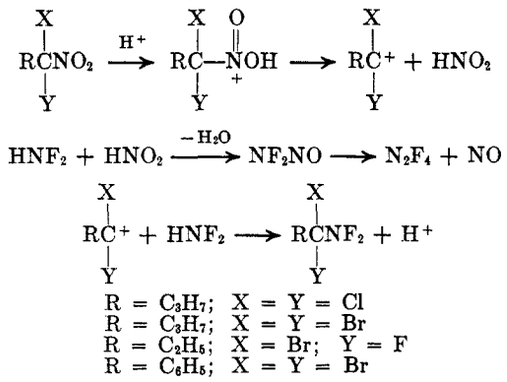
α,α-Dihalonitro Compounds.—1,1-Dihalo-1-nitroalkanes were found to react readily with difluoramine and fuming sulfuric acid to give 1,1-dihalo-1-(difluoramino)alkanes (Scheme I). Thus, 1,1-dichloro-1-(difluoramino)butane, 1,1-dibromo-1-(difluoramino)butane, 1-bromo-1-difluoramino-1-fluoropropane, and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

(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) T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

SCHEME I



from 1,1-dichloro-1-nitrobutane, 1,1-dibromo-1-nitrobutane, 1-bromo-1-fluoro-1-nitropropane, and α,α-dibromo-α-nitrotoluene, respectively, in yields of 33–61%.

Transient blue-purple colorations in the solutions were indicative of nitrosyl difluoramine, formed by the nitrosation of difluoramine. Nitrosyl difluoramine has been prepared reversibly from NO and N_2F_4 at low temperatures.[4]

1,1,1-Bromodinitroalkanes and chlorodinitroalkanes did not react with difluoramine in fuming sulfuric acid. 1-Iodo-1-nitrocyclohexane[5] was degraded under these conditions, but did not react with neat difluoramine.

The reaction of vinylidene chloride with difluoramine and fuming sulfuric acid gave 1,1-dichloro-1-(difluoramino)ethane and 1-chloro-1,1-bis(difluoramino)ethane.[6] The reaction of dihalonitroalkanes with difluoramine thus provided a convenient source of starting material to determine the scope of reactivity of halogens in α,α-dihalodifluoramines toward substitution. Only the dibromo derivatives were found to undergo halogen substitution. In fact, to obtain a sample of 1,1-dibromo-1-(difluoramino)butane free of the bis(difluoramino) derivative, it was necessary to quench the reaction (conducted at -10 to $-20°$) within 10 min. On the other hand, the corresponding dichloro derivative gave no chlorine substitution product after 4 days in a sealed reactor at ambient temperature. α,α-Dichloro-α-(difluoramino)toluene was previously prepared from benzotrichloride and difluoramine in trifluoroacetic acid.[7] In the present work the same product was obtained using fuming sulfuric acid and no chlorine substitution took place under forcing conditions. Likewise, no further substitution products could be obtained from 1-bromo-1-difluoramino-1-fluoropropane. The greater reactivity of 1,1-dichloro-1-(difluoramino)ethane compared with the butane and toluene analogs must be attributed to steric factors.

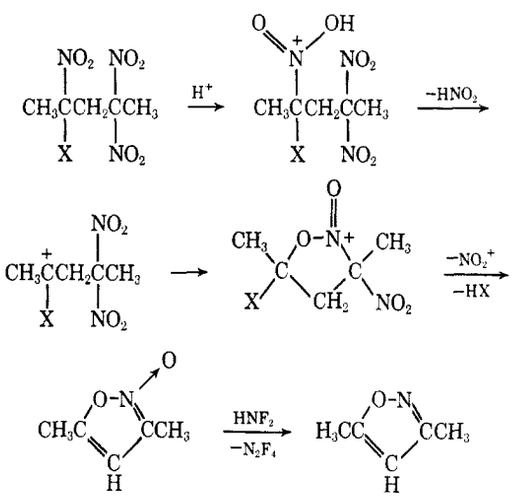
$$RCBr_2NF_2 \xrightarrow[H_2SO_4,\ SO_3]{HNF_2} RCBr(NF_2)_2$$

R = C_3H_7 (13% yield)
R = C_6H_5 (72% yield)

2-Halo-2,4,4-trinitropentanes.—Because of the demonstrated inertness of *gem*-dinitro compounds, 2-halo-2,4,4-trinitropentanes were expected to undergo replacement only of the 2-nitro and possibly the halogen. The starting materials were prepared by adding bromine and chlorine *in situ* to the adduct of the sodium salt of 1,1-dinitroethane and 2-nitropropene.[8] The chloro and bromo compounds both reacted with difluoramine in fuming sulfuric acid to give the same products, 2,2,4,4-tetrakis(difluoramino)pentane[6] (5–8% yield) and 3,5-dimethylisoxazole (26–34% yield). Even when reaction conditions were used that resulted in the recovery of some unreacted starting materials, no other products were isolated. The isoxazole also gave 2,2,4,4-tetrakis(difluoramino)pentane, but it is not known whether the reaction proceeded entirely through this intermediate.

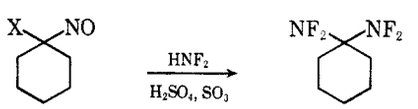
A possible path for the formation of 3,5-dimethylisoxazole is given in Scheme II. Protonation of the

SCHEME II



most basic nitro group and loss of nitrous acid would give a halocarbonium ion. Intramolecular alkylation of the oxygen of a nitro group, followed by loss of nitronium ion and HX would give 3,5-dimethylisoxazole N-oxide, which could be reduced to the isoxazole by difluoramine. Amine oxides are deoxygenated by a variety of reagents,[9] and, since isoxazoles are resistant to oxidation,[10] the deoxygenation of this oxide should be particularly facile. Difluoramine has been shown to act as a reducing agent toward reagents such as ferric ion[11] and diazonium salts.[12]

Nitroso Compounds.—The only product isolated from the reactions of 1-chloro-1-nitrosocyclohexane or 1-nitro-1-nitrosocyclohexane with difluoramine and fuming sulfuric acid was 1,1-bis(difluoramino)cyclo-



X = Cl or NO_2

(4) C. B. Colburn and F. A. Johnson, *Inorg. Chem.*, **1**, 715 (1962).

(5) An undistillable oil prepared according to L. W. Seigle and H. B. Haas, *J. Org. Chem.*, **5**, 100 (1940). Analytically pure material was obtained by low temperature crystallization.

(6) K. Baum, *ibid.*, **34**, 2046 (1969).

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

(8) S. S. Novikov, *et al.* [*Dokl. Akad. Nauk SSSR*, **125**, 560 (1959)] reported a similar synthesis of 2-bromo-2,4,4,4-tetranitrobutane by adding nitroform to 2-nitropropene and brominating the resulting acidic *aci*-nitro compound.

(9) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 27.

(10) K. K. Kochetkov and S. D. Sokolov, *Advan. Heterocycl. Chem.*, 418 (1963).

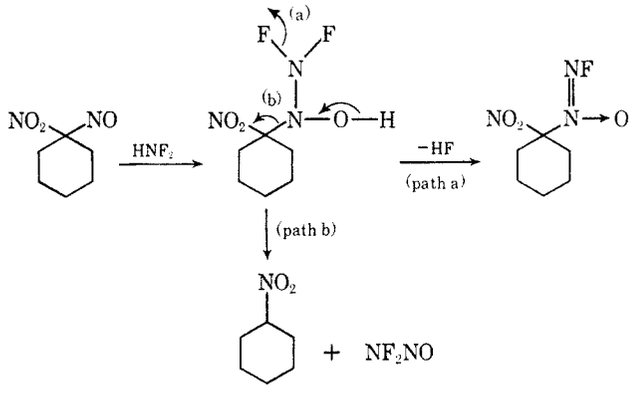
(11) K. J. Martin, *J. Amer. Chem. Soc.*, **87**, 394 (1965).

(12) K. Baum, *J. Org. Chem.*, **33**, 4333 (1968).

hexane, even when the reaction, in the latter case, was quenched within 5 min.

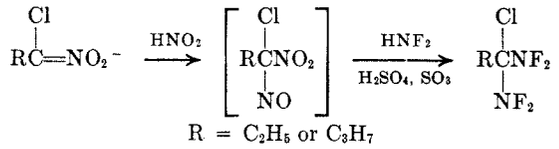
With the objective of isolating possible intermediates, the reaction of 1-nitro-1-nitrosocyclohexane with difluoramine was repeated using a more selective catalyst, the boron trifluoride complex of phosphoric acid.[7,12] Under these conditions,[13] 1,1-bis(difluoramino)cyclohexane was not formed, but nitrocyclohexane and 1-nitrocyclohexyl-N′-fluorodiimide N-oxide were isolated. These products could be formed from a common intermediate, the adduct of difluoramine to the N=O bond, by cleavage of either the N–F or the C–N bond (Scheme III).

SCHEME III



A sample of 1-nitrocyclohexyl-N′-fluorodiimide N-oxide was treated with difluoramine in fuming sulfuric acid to determine if this compound could be an intermediate in the formation of 1,1-bis(difluoramino)cyclohexane. The unchanged starting material was recovered. The reaction thus appears to involve initial solvolysis of a protonated nitro or nitroso group, or of the hydroxylamine function postulated above. When one group is replaced, the remaining one becomes sufficiently reactive that intermediates are not isolated.

This reaction was used to prepare 1-chloro-1,1-bis(difluoramino)alkanes not obtainable from the dichloronitroalkanes. The 1-chloro-1-nitro-1-nitrosoalkanes have not been reported previously. Nitrosation of aqueous solutions of the sodium salts of 1-chloro-1-nitropropane and 1-chloro-1-nitrobutane at 0° gave dark blue oils which were too unstable for the isolation of analytical samples. Reactions of the crude oils with difluoramine in fuming sulfuric acid gave 1-chloro-1,1-bis(difluoramino)propane and 1-chloro-1,1-bis(difluoramino)butane, respectively.



R = C_2H_5 or C_3H_7

Alkyl Nitrites.—Octyl nitrite reacted with liquid difluoramine to give a blue-purple solution indicative of nitrosyldifluoramine. Removal of the difluoramine left *n*-octanol. No catalyst was necessary for this reaction. The nitrite thus acted as a nitrosation agent rather than an alkylating agent toward difluoramine.

(13) Methylene chloride was used as a solvent for the 1-nitro-1-nitrosocyclohexane; thus the catalyst was present as a separate phase. The diimide N-oxide was obtained in one uncatalyzed reaction, but this result was not repeatable.

Experimental Section

Difluoramine.—The previously described[2,14] apparatus for the difluoramine reaction was used. *Adequate explosion shielding is essential* for the difluoramine reactions and for isolation of the products.

1,1-Dichloro-1-(difluoramino)butane.—1,1-Dichloro-1-nitrobutane (4.0 g, 0.0232 mol) was added with stirring to 27 g of difluoramine and 11 ml of 20% fuming sulfuric acid in a 500-ml reactor fitted with glass and Teflon needle valves.[2] The reaction was allowed to proceed for 1 hr at the reflux temperature of difluoramine; a purple color developed during this period. The valves were closed and the reaction was continued at room temperature for 2 hr. The mixture was drained onto 100 ml of ice and extracted with three 30-ml portions of methylene chloride. The solution was dried over sodium sulfate and distilled through a 25-cm Holzmann column to give 2.80 g (61% yield) of 1,1-dichloro-1-(difluoramino)butane, bp 45° (40 mm).

Anal. Calcd for $C_4H_7NF_2Cl_2$: C, 26.97; H, 3.96; H, 7.86; F, 21.4. Found: C, 27.10; H, 4.03; N, 7.65; F, 20.7.

The proton nmr spectrum showed an irregular triplet (J = 6 cps) at δ 1.03 for the methyl and complex multiplets at 1.82 and 2.21 for the methylenes. The fluorine spectrum consisted of a broadened singlet at ϕ^* −41.92. Infrared bands in the NF region were (μ) 9.90 (m), 10.98 (m), 11.30 (s), and 11.69 (m).

1,1-Dibromo-1-(difluoramino)butane.—To 6 g of refluxing difluoramine and 5 ml of 20% fuming sulfuric acid, 1.0 g (0.00384 mol) of 1,1-dibromo-1-nitrobutane was added dropwise with stirring. After 10 min, the mixture was drained onto 100 ml of ice. The product was extracted with two 20-ml portions of methylene chloride, dried over sodium sulfate, and distilled through a 25-cm Holzmann column to give 0.48 g (47% yield) of 1,1-dibromo-1-(difluoramino)butane, bp 24° (1 mm).

Anal. Calcd for $C_4H_7NF_2Br_2$: C, 17.98; H, 2.62; N, 5.24. Found: C, 18.21; H, 2.60; N, 5.26.

The proton nmr spectrum consisted of a triplet (J = 7 cps) for the methyl at δ 1.05, a distorted triplet at 2.52 for $CH_2CBr_2NF_2$, and a multiplet centered at 1.84 for the other methylene. The fluorine spectrum consisted of a broadened singlet at ϕ^* −56.0. Infrared bands in the NF region were (μ) 10.0 (s), 10.80 (w), 10.93 (m), 11.09 (m), 11.40 (s), and 11.78 (m).

1-Bromo-1-difluoramino-1-fluoropropane.—A mixture of 5.0 g (0.268 mol) of 1-bromo-1-fluoro-1-nitropropane,[15] 14 ml of 20% fuming sulfuric acid, and 27 g of difluoramine was stirred at ambient temperature and autogenous pressure for 30 min. Decane (40 ml) was added and difluoramine was removed. The decane solution was heated at 77° for 1.5 hr at 22-mm pressure and the product, 1.95 g of colorless liquid, was collected in a −80° trap. Elemental analysis and gas chromatography showed that the product consisted of 98% 1-bromo-1-difluoramino-1-fluoropropane (37% yield) and 2% *n*-decane. Distillation of the mixture at 50° (209 mm) did not change its composition. An analytical sample was obtained by gas chromatography ($^3/_{16}$ in. × 6 ft column, 10% dibutyl phthalate on Chromosorb W, 30 ml/min helium, 63°, retention time 118 sec).

Anal. Calcd for $C_3H_5NBrF_3$: C, 18.77; H, 2.62; N, 7.30. Found: C, 19.07; H, 2.19; N, 7.72.

The proton nmr spectrum consisted of a triplet (J_{HH} = 7.6 cps) at δ 1.3 for the methyl and an overlapping quartet (J_{HH} = 7.6 cps) of doublets (J_{HF} = 16.5 cps) of triplets (J_{HNF_2} = 1.5 cps) at 2.39 for the methylene. The fluorine spectrum consisted of a broad symmetrical band at ϕ^* −34.3 for the NF_2 and a quintet (J_{FF} = 16.5 cps = J_{CH_2F}) at 102.0 for CF. Infrared bands in the NF region were (μ) 10.10 (s), 10.49 (s), 10.75 (m), 10.80 (m), 11.00 (s), 11.25 (s), and 11.73 (s).

1-Bromo-1,1-bis(difluoramino)butane.—1,1-Dibromo-1-nitrobutane (4.0 g, 0.0153 mol) was added to 27 g of difluoramine and 11 ml of 20% fuming sulfuric acid in a glass pressure reactor. The mixture was stirred at atmospheric pressure for 2 hr and then at autogenous pressure at ambient temperature for 2 hr. Bromine color in this solution became pronounced. Pentane (100 ml) was added and difluoramine was removed. Distillation of the pentane solution gave 0.47 g (13% yield) of 1-bromo-1,1-bis(difluoramino)butane, bp 36° (15 mm).

Anal. Calcd for $C_4H_7N_2F_4Br$: C, 20.08; H, 2.93; N, 11.70. Found: C, 20.52; H, 3.15; N, 11.40.

The proton nmr spectrum consisted of an irregular triplet at δ 0.99 for the methyl and multiplets at 2.3 and 1.8 for the methy-

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

(15) K. Baum, paper in preparation.

lenes. The fluorine spectrum consisted of an AB quartet, ϕ^*_A −35.11, ϕ^*_B −46.27 (J_{AB} = 604 cps). Infrared bands in the NF region were (μ) 9.80 (m), 9.93 (m), 10.62 (s), 10.80 (sh), 11.38 (s), 11.5 (sh), 12.2 (m), and 12.3 (m).

α-Bromo-α,α-bis(difluoramino)toluene.—α,α-Dibromo-α-nitrotoluene (5.0 g, 0.0170 mol) was added dropwise with stirring to 27 g of refluxing difluoramine and 12 ml of 20% fuming sulfuric acid. After 4 hr, 50 ml of methylene chloride was added and difluoramine was removed. The methylene chloride solution was dried over sodium sulfate and distilled to give 3.35 g (72% yield) of α-bromo-α,α-bis(difluoramino)toluene, bp 32° (0.4 mm).

Anal. Calcd for $C_7H_5N_2F_4Br$: C, 30.77; H, 1.83; N, 10.25; F, 27.8. Found: C, 30.90; H, 1.84; N, 10.40; F, 28.3.

The fluorine nmr spectrum consisted of an AB quartet, ϕ^*_A −42.17, ϕ^*_B −45.04 (J_{FF} = 601 cps). Infrared bands in the NF region were (μ) 9.95 (m), 10.19 (m), 10.28 (m), 10.50 (m), 10.70 (m), 11.05 (s), 11.25 (s), and 11.50 (vs).

α,α-Dibromo-α-(difluoramino)toluene and α-Bromo-α,α-bis(difluoramino)toluene.—α,α-Dibromo-α-nitrotoluene (15 g, 0.051 mol) was added dropwise with stirring to 58 g of refluxing difluoramine and 36 ml of 20% fuming sulfuric acid. After 4 hr, 100 ml of pentane was added and difluoramine was removed. The pentane solution was dried over sodium sulfate and distilled to give 5.52 g (40% yield) of α-bromo-α,α-bis(difluoramino)toluene and 4.98 g (32.5% yield) of α,α-dibromo-α-(difluoramino)toluene, bp 53° (0.25 mm).

Anal. Calcd for $C_7H_5Br_2NF_2$: C, 27.91; H, 1.66; N, 4.65; F, 12.62. Found: C, 28.02; H, 1.63; N, 4.70; F, 12.80.

The fluorine nmr spectrum consisted of a singlet at ϕ^* −57.5. Infrared bands in the NF region were (μ) 10.0 (m), 10.73 (w), 10.96 (m), 11.52 (s), and 12.34 (s).

α,α-Dichloro-α-(difluoramino)toluene.—Benzotrichloride (15.0 g, 0.078 mol) was treated with 40 g of refluxing difluoramine and 36 ml of 20% fuming sulfuric acid for 4 hr. Pentane (100 ml) was added and difluoramine was removed. Distillation of the pentane solution gave 10.55 g (64% yield) of α,α-dichloro-α-(difluoramino)toluene, bp 38° (0.4 mm).

Anal. Calcd for $C_7H_5NF_2Cl_2$: C, 39.63; H, 2.36; N, 6.60; F, 17.9. Found: C, 39.60; H, 2.02; N, 6.64; F, 17.8.

The fluorine nmr spectrum consisted of a singlet at ϕ^* −44.88. The infrared spectrum showed NF bands at (μ) 9.98 (m), 10.65 (w), 10.83 (m), 11.14 (s), 11.40 (vs), and 11.80 (s).

1-Iodo-1-nitrocyclohexane.[5]—Nitrocyclohexane (3.87 g, 0.030 mol) was dissolved in 6.6 ml of 5 *N* sodium hydroxide at 50°. The solution was cooled to room temperature and was added dropwise to a solution of 7.62 g (0.030 mol) of iodine and 4.98 g (0.030 mol) of potassium iodide in 30 ml of water. After 10 min, the dark oil which separated was crystallized from pentane at −80° and recrystallized twice. The residual solvent was removed at 20 mm. The product, 1-iodo-1-nitrocyclohexane (5.4 g, 64% yield), was an amber oil at room temperature.

Anal. Calcd for $C_6H_{10}NO_2I$: C, 28.25; H, 3.93; N, 5.50. Found: C, 28.19; H, 3.82; N, 5.32.

This compound did not react with difluoramine in the absence of catalysts, and, in the presence of sulfuric acid, no products extractable from water were formed.

2-Bromo-2,4,4-trinitropentane.—2-Nitropropene (17.4 g, 0.2 mol) was added with stirring to a solution of 8.8 g (0.22 mol) of sodium hydroxide and 24.0 g (0.20 mol) of 1,1-dinitroethane in 200 ml of water at 5°. A yellow salt precipitated. Bromine (32.0 g, 0.20 mol) was added dropwise over a 25-min period at 0–5°. The solid product was filtered, washed with water, and recrystallized from 200 ml of ethanol to give 34.3 g of white solid, mp 54–55°. Concentration of the ethanol gave an additional 4.8 g, mp 53–54° (68% total yield).

Anal. Calcd for $C_5H_8N_3O_6Br$: C, 20.99; H, 2.80; N, 14.69. Found: C, 20.67; H, 2.67; N, 14.36.

The nmr spectrum consisted of singlets at δ 4.06, 2.29, and 2.12, assigned to the CH_2, $CH_3C(NO_2)_2$, and CH_3CNO_2Br, respectively.

2-Chloro-2,4,4-trinitropentane.—The slurry prepared from dinitroethane, sodium hydroxide, and 2-nitropropene, as above, was saturated with chlorine. A green oil which separated was diluted with 80 ml of methylene chloride and washed with sodium bicarbonate solution and with water. Distillation gave 28 g of green oil, bp 82° (0.06 mm). Crystallization and recrystallization from ethanol gave 5.9 g (12.2% yield) of 2-chloro-2,4,4-trinitropentane, a white solid, mp 31–31.5°.

Anal. Calcd for $C_5H_8N_3O_6Cl$: C, 24.85; H, 3.31; N, 17.39. Found: C, 24.59; H, 3.32; N, 16.99.

The nmr spectrum showed an AB quartet centered at δ 4.00 (J_{AB} = 16.8 cps, inner member separation (6.2 cps) for the methylene, a sharp singlet at 2.22 for $CH_3C(NO_2)_2$, and a slightly broadened singlet at 2.15 for CH_3CNO_2Cl.

Reactions of 2-Chloro-2,4,4-trinitropentane and 2-Bromo-2,4,4-trinitropentane with Difluoramine.—2-Chloro-2,4,4-trinitropentane (5.0 g. 0.0207 mol) in 10 ml of methylene chloride was stirred at ambient temperature, under autogenous pressure, with 14 ml of 20% fuming sulfuric acid and 27 g of difluoramine for 18 hr. The mixture was drained onto 250 ml of ice and extracted with four 30-ml portions of methylene chloride. The methylene chloride solution was dried and distilled through a 25-cm Holzmann column to give 0.60 g of colorless liquid, bp 37–50° (13 mm), and 0.53 g, bp 50–58° (13 mm). Gas chromatography (10% six-ring polyphenyl ether on Chromosorb W, 110°) and nmr analysis showed that the first fraction consisted of 0.064 g (0.123 mmol) of 2,2,4,4-tetrakis(difluoramino)pentane[6] and 0.537 g (5.53 mmol) of 3,5-dimethylisoxazole while the second fraction consisted of 0.39 g (1.41 mmol) of 2,2,4,4-tetrakis(difluoramino)pentane and 0.14 g (1.45 mmol) of 3,5-dimethylisoxazole (total yields, 8 and 34%, respectively). Infrared spectra were identical with those of authentic samples.

The reaction of 2-bromo-2,4,4-trinitropentane (5.0 g, 0.0175 mol) with difluoramine as above gave a 5% yield of 2,2,4,4-tetrakis(difluoramino)pentane and a 26.5% yield of 3,5-dimethylisoxazole.

Reaction of 1-Chloro-1-nitrosocyclohexane with Difluoramine.—1-Chloro-1-nitrosocyclohexane (5.0 g, 0.040 mol) was added dropwise to 27 g of refluxing difluoramine and 10 ml of 20% fuming sulfuric acid. The blue color of the nitroso compound disappeared instantaneously. After 2 hr, the reaction was quenched with 100 ml of ice and the product was extracted with three 30-ml portions of methylene chloride and dried over sodium sulfate. Distillation through a 25-cm Holzmann column gave 2.06 g (31% yield) of 1,1-bis(difluoramino)cyclohexane, identical with an authentic sample.[2]

Reaction of 1-Nitro-1-nitrosocyclohexane with Difluoramine and Fuming Sulfuric Acid.—A solution of 5.0 g (0.0316 mol) of 1-nitro-1-nitrosocyclohexane in 15 ml of methylene chloride was added with stirring to 27 g of refluxing difluoramine and 11 ml of 20% fuming sulfuric acid. The nitroso color disappeared instantaneously. Five minutes after the addition was completed, the mixture was worked up as above to give 1.92 g (31% yield) of 1,1-bis(difluoramino)cyclohexane.[2]

Reaction of 1-Nitro-1-nitrosocyclohexane with Difluoramine and Boron Trifluoride–Phosphoric Acid Complex.—Boron trifluoride complex of phosphoric acid (2 ml) was added dropwise to a solution of 5.0 g (0.0316 mol) of 1-nitro-1-nitrosocyclohexane in 27 g of refluxing difluoramine. After 45 min, 80 ml of methylene chloride was added and difluoramine was removed. The methylene chloride solution was dried over sodium sulfate and distilled to give 1.50 g (39.4% yield) of nitrocyclohexane, bp 30° (3 mm), and 3.22 g (53.4% yield) of 1-nitrocyclohexyl-N′-fluorodiimide N-oxide, bp 69° (3 mm).

Anal. Calcd for $C_6H_{10}N_3O_3F$: C, 37.70; H, 5.23; N, 22.0; F, 9.95. Found: C, 38.09; H, 5.57; N, 21.7; F, 10.0.

The infrared spectrum showed a nitro band at 6.4 (μ), an azoxy band at 6.68, and bands in the NF region at 9.70 (m), 9.90 (s), 10.46 (m), 10.98 (m), and 11.40 (s).

1-Chloro-1,1-bis(difluoramino)propane.—1-Chloro-1-nitropropane (10.0 g, 0.081 mol) was dissolved in a solution of 5.0 g (0.125 mol) of sodium hydroxide in 40 ml of water at 0–5° with vigorous stirring (1.5 hr). This solution was added dropwise to a partially frozen nitrous acid solution prepared by slowly adding 8.6 g. (0.122 mol) of sodium nitrite to a solution of 15 g of concentrated sulfuric acid in 100 ml of water with intermittent cooling in a −80° bath. A dark blue oil (7.6 g) separated; it was extracted with 25 g of pentane and stored overnight at −80°.

The pentane solution was added dropwise to 27 g of refluxing difluoramine and 13 ml of 20% fuming sulfuric acid. After 4 hr, the mixture was drained onto 200 ml of ice. The pentane layer was separated and the aqueous layer was extracted with 25 ml of pentane. The pentane solution was dried and distilled to give 0.2 g of colorless liquid, bp 31° (60 mm). Gas chromatography (10 ft × 1/4-in. column, 10% Ucon 50HB100 on Fluoropak 80, 70°) was used to isolate the major component (60% of the sample).

Anal. Calcd for $C_3H_5N_2F_4Cl$: C, 20.3; H, 2.82; N, 15.8. Found: C, 20.4; H, 3.33; N, 16.1.

The proton nmr spectrum consisted of a triplet (J = 7.0 cps) at δ 1.26 for the methyl and a quartet (J = 7.0 cps) at 2.45, with additional coupling detectable to the fluorines. The fluorine spectrum consisted of an AB quartet with ϕ^*_A −29.91, ϕ^*_B −36.91 (J_{AB} = 611 cps).

1-Chloro-1,1-bis(difluoramino)butane.—1-Chloro-1-nitrobutane (5.0 g, 0.0364 mol) was dissolved in a solution of 1.64 g (0.041 mol) of sodium hydroxide in 50 ml of water at 0–5° (2 hr) and 3.79 g (0.055 mol) of sodium nitrite was added. A 25% sulfuric acid solution (20 ml) was added slowly at 0–5°. A dark blue oil (6.2 g) separated and was stored overnight at −80° in 25 g of pentane.

The pentane solution was added to 10 ml of 20% fuming sulfuric acid and 27 g of refluxing difluoramine. After 4 hr the mixture was drained onto 100 ml of ice and pentane layer was separated. The aqueous layer was extracted with two 50-ml portions of methylene chloride. The combined organic solution was distilled to give 0.82 g of colorless liquid, bp 33–34° (35 mm). Gas chromatography (10 ft × 1/4 in. column of 10% Ucon 50-HB100 on Fluoropak 80, 70°) was used to trap the major component (90% of the sample, 10% yield), identified as 1-chloro-1,1-bis(difluoramino)butane.

Anal. Calcd for $C_4H_7N_2F_4Cl$: C, 24.7; H, 3.60; N, 14.4. Found: C, 24.9; H, 3.89; N, 14.0.

The proton nmr spectrum consisted of an irregular triplet at δ 1.01 for the methyl, a multiplet at 1.78 (approximately a septet) for CH_3CH_2, and a multiplet at 2.24 for the other methylene. The fluorine spectrum consisted of an AB quartet, ϕ^*_A −30.42, ϕ^*_B −37.35 (J_{AB} = 609 cps). The infrared spectrum showed peaks in the NF region at (μ) 9.80 (m), 10.60 (s), 11.2–11.4 (s), 12.03 (m), and 12.30 (m).

Reaction of *n*-Octyl Nitrite with Difluoramine.—*n*-Octyl nitrite (5.0 g, 0.0314 mol) was added dropwise to 27 g of refluxing difluoramine. A purple solution was formed, which became colorless after 30 min. After 4 hr, difluoramine was removed and the residue was distilled to give 3.14 g (77% yield) of *n*-octanol, bp 54° (1 mm), infrared spectrum identical with that of an authentic sample.

Registry No.—Difluoramine, 10405-27-3; 1,1-dichloro-1-(difluoramino)butane, 19955-19-2; 1,1-dibromo-1-(difluoramino)butane, 19955-20-5; 1-bromo-1-difluoramino-1-fluoropropane, 19955-21-6; 1-bromo-1,1-bis(difluoramino)butane, 19955-22-7; α-bromo-α,α-bis(difluoramino)toluene, 19955-23-8; α,α-dibromo-α-(difluoramino)toluene, 19955-24-9; 1-chloro-1,1-bis-(difluoramino)butane, 19955-25-0; α,α-dichloro-α-(difluoramino)toluene, 14092-53-6; 2-bromo-2,4,4-trinitropentane, 19955-54-5; 2-chloro-2,4,4-trinitropentane, 19955-55-6; 1-nitrocyclohexyl-N′-fluorodiimide N-oxide, 19955-56-7; 1-chloro-1,1-bis(difluoramino)-propane, 19955-57-8.

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Heterocyclic Ring-Closure Reactions. II.[1] Reactions of α-Mercapto Acids with Cyanogen[2a]

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The reaction of α-mercapto acids with cyanogen has been studied and shown to give 2-[(S-carboxyalkyl)-thioimidyl]-Δ^2-thiazolin-4-one in good yields. The reaction product undergoes unusual N-methylation in addition to esterification when treated with diazomethane and could be cyclized to afford bicyclic symmetrical 4,4′-diketo-Δ^2-bithiazolinyl, which could be converted into its dienol diacetate. Proof of structure has been obtained by X-ray crystallography and supporting evidence obtained from uv, ir, nmr, and pK_a determinations and dipole moment measurements.

Cyanogen reacts with mercaptans in the presence of catalytic amounts of *n*-butylamine at low temperature to yield S,S′-disubstituted dithiooxaldiimidates.[1,3] This is a general reaction for the preparation of dithiooxaldiimidic esters.

Primary aliphatic amines react with cyanogen to yield symmetrically disubstituted oxamidines,[4] whereas secondary amines normally give only cyanoformamidines and under vigorous conditions oxamidine derivatives.[5] But when ethylenediamine and its C-alkyl derivatives are allowed to react with cyanogen the product obtained was characterized as bis(Δ^2-2-imidazolinyl).[6]

In the light of these results it was interesting to investigate the behavior of α-mercapto acids (**1**) with cyanogen, since the geminal mercapto and carboxylic acid groups could react separately or in conjunction. When 2 mol of mercaptoacetic acid (**1a**) were treated with 1 mol of cyanogen, a white crystalline product, henceforth referred to as the monocyclic product, was obtained. This substance analyzed for condensation of these three molecules accompanied by loss of 1 mol of water ($C_6H_6N_2S_2O_3$). This indicated that the expected diaddition product (**2a**) was formed but reacted further to afford a monocyclic product. Cyclization of **2a** can result in formation of **3a** having a five-membered ring or **4a** having a six-membered ring. When it is dissolved in water and treated with 5% aqueous sodium bicarbonate, carbon dioxide is liberated, indicating the presence of a strongly acidic function. It has a neutralization equivalent of 109 when titrated with sodium hydroxide (potentiometric titration) and has two acidic functions of apparent pK_a = 4.1 and 6.7 (50% acetone in water). It gives a red color when treated with a solution of ferric chloride, which indicates that the compound may be phenolic although there are other possibilities for complex formation with the various functional groups in either of the two structures. The

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