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REPORT NO. 3495 (SUMMARY)
PERIOD COVERED: 1 OCTOBER 1966 - 30 NOVEMBER 1967

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT ON WORK SPONSORED BY

THE OFFICE OF NAVAL RESEARCH

CONTRACT Nonr 2655(00)
NR 093-014/9-20-66

JANUARY 1968

COPY NO. [redacted]

CHEMICAL AND BIOLOGICAL PROCESSES
AEROJET-GENERAL CORPORATION
EL MONTE, CALIFORNIA

United States Patent Office Secrecy Order

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January 1968

Report No. 3495
(Summary)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum, V. Grakauskas, H. F. Shuey

Analytical Support: K. Inouye, L. A. Maucieri

A Report On Work Sponsored By
THE OFFICE OF NAVAL RESEARCH

Contract Nonr 2655(00)
NR 093-014/9-20-66

AEROJET-GENERAL CORPORATION
A Subsidiary of The General Tire & Rubber Company

ABSTRACT

(C) During the past year, work was continued on reactions of difluoramine with the objective of synthesizing new types of high-energy NF compounds and obtaining a more thorough understanding of the reactions involved. Work was completed on the synthesis of fluorammonium salts.

Report No. 3495

CONTRACT FULFILLMENT STATEMENT

(U) This summary technical report is submitted in partial fulfillment of the contract and covers the period from 1 October 1966 through 30 November 1967.

AEROJET-GENERAL CORPORATION

W. P. Knight, Manager
Applied Chemistry

R. T. Holzmann, Manager
Chemical and Biological Processes

CONTENTS

I. INTRODUCTION

(U) This report summarizes the research carried out under Contract Nonr 2655(00) during the period 1 October 1966 through 30 November 1967. Experimental details are included only for the work of 1 April 1967 through 30 November 1967, since the work of 1 October 1966 through 31 March 1967 was covered in Report No. 3396 (Semiannual). This work is a direct continuation of the research under Contracts Nonr 2655(00) and N7onr-462 Task Order 1, which has been summarized in Aerojet Reports No. 1163, 1318, 1509, 1685, 1877, 2099, 2381, 2730, 2945, 3132, and 3299.

(C) During the past year, research was continued on reactions of difluoramine with the objective of developing general methods of preparing energetic compounds, and obtaining a more thorough understanding of the reactions involved. A manuscript covering earlier work on reactions of carbonyl compounds with difluoramine is given in Appendix A and will be submitted for journal publication when security clearance is approved. Appendix B describes the work completed on the preparation and characterization of fluorammonium salts.

II. REACTIONS OF DIFLUORAMINE

A. INTRODUCTION

(C) Compounds having geminal bis-difluoramino groups and nitro groups in the same molecule separated by two methylene groups are prepared readily from the corresponding nitroketones. However, no general method is available for the synthesis of higher energy compounds of this type with fewer intervening methylene groups. Another type of difluoramino-nitro that would be of particular interest is the compound with difluoramino and nitro groups on the same carbon atom. In addition to providing an oxygen source for propellant combustion, the nitro groups might alter the sensitivity characteristics of the difluoramino groups.

B. DISCUSSION

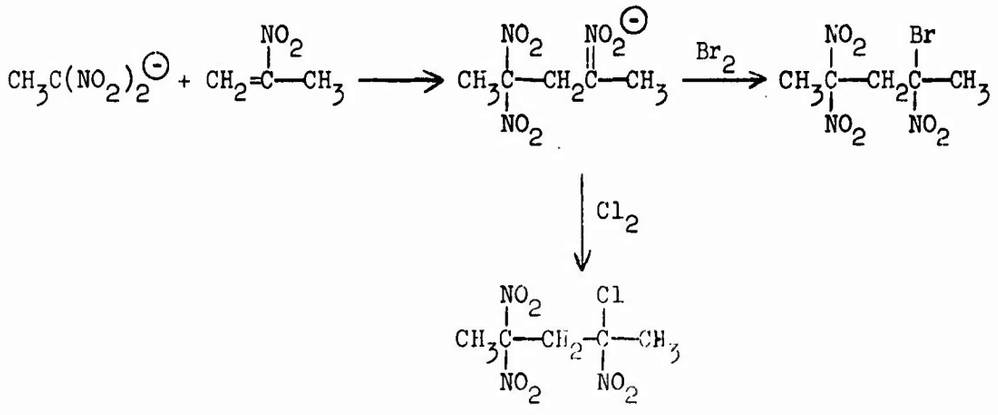
1. Reactions of Halonitroalkanes with Difluoramine

(C) Halogens, nitro groups, and nitroso groups were shown previously to be useful as leaving groups in difluoramine reactions.* For example, 1,1-dichloro-1-nitroalkanes reacted with difluoramine in fuming sulfuric acid to give 1-difluoramino-1,1-dichloroalkanes. The ethane derivative (prepared by adding difluoramine to 1,1-dichloroethylene) was converted in prolonged reactions to 1,1-bis(difluoramino)-1-chloroethane, but higher homologs failed to undergo chlorine replacement. However, the corresponding 1-difluoramino-1,1-dibromoalkanes, prepared from dibromonitroalkanes, readily underwent further reaction to give 1,1-bis(difluoramino)-1-bromoalkanes. Nitroso groups also underwent facile replacement by difluoramine, and 1,1-bis(difluoramino)-1-chloroalkanes were prepared from 1-chloro-1-nitro-1-nitrosoalkanes. Trinitromethyl compounds, gem-dinitro compounds, and halodinitro compounds did not react with difluoramine.

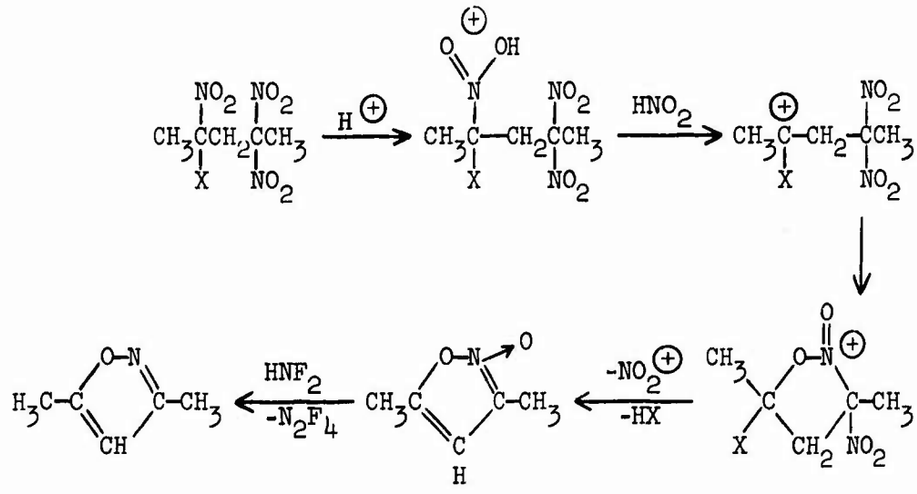
(C) Because of the demonstrated inertness of gem-dinitro compounds to the difluoramine reaction conditions, 2-halo-2,4,4-trinitro compounds were expected to undergo replacement of only the mononitro and halogen. Earlier attempts to isolate 2,2,4-trinitro-4-halohexanes by the halogenation of 2,2,4-trinitrohexane were unsuccessful because the acidities of the hydrogens in the 3 and 4 positions were of comparable magnitude.** This problem was overcome by adding the sodium salt of dinitroethane to 2-nitropropene, and halogenating immediately the resulting nitronate salt without allowing the neutral trinitroalkane to form. In this way both 2-bromo-2,4,4-trinitropentane and 2-chloro-2,4,4-trinitropentane were prepared.

*Aerojet-General Reports: 2730, October 1963; 2945, October 1964; 3132, August 1966 (Confidential).

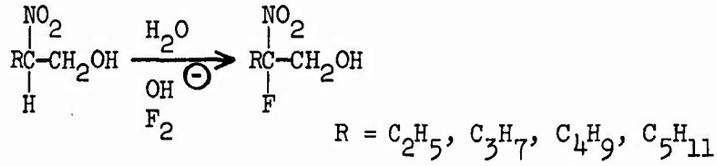
**Aerojet-General Report 3299, October 1966, p. 8 (Confidential).



(C) Both of these compounds reacted with difluoramine in fuming sulfuric acid to give the same products: 2,2,4,4-tetrakis(difluoramino)hexane and 3,5-dimethylisoxazole. Even when reaction conditions were used that resulted in the recovery of some unreacted starting material, no other products were isolated. Since simple gem-dinitro compounds are unreactive under the difluoramine reaction conditions, it appears that the gem-dinitro groups of these halonitro compounds are made reactive by cyclic participation with the initially formed carbonium ion that would result from the removal of the mononitro group. To determine whether 3,5-dimethylisoxazole was an intermediate in the formation of 2,2,4,4-tetrakis(difluoramino)hexane, a sample was treated with difluoramine in fuming sulfuric acid. The tetrakis(difluoramino)pentane was indeed formed. The reaction of the halotrinitro compounds with sulfuric acid did not give the isoxazole, so difluoramine is required for the formation of this intermediate. The isoxazole was apparently formed by the intramolecular interaction of the oxygen of a nitro group with the carbonium ion center resulting from loss of nitrous acid from the protonated mononitro group. Loss of HX and nitronium ion from this intermediate would give the isoxazole-N-oxide, which could be reduced to the isoxazole by difluoramine.

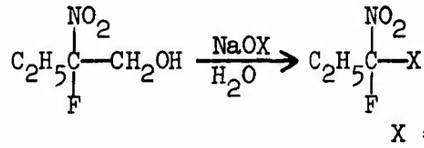


(C) The earlier investigation of nitro and halo leaving groups in the reactions of α-dihalonitro compounds with difluoramine was extended to determine the effect of C-F bonds on these reactions. Simple 1-fluoro-1-nitroalkanes, the desired starting materials for this study, could not be obtained in practical yields by the aqueous fluorination of nitroalkane salts. The corresponding formaldehyde adducts, however, were fluorinated smoothly to give 2-fluoro-2-nitroalcohols in yields of 25 to 50%.



R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}

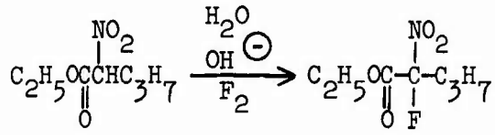
Although attempts to prepare the fluoronitroalkanes by deformylation of the alcohols were unsuccessful, 1-bromo-1-fluoro-1-nitropropane and 1-chloro-1-fluoro-1-nitropropane were prepared by treating the alcohol with sodium hypobromite and sodium hypochlorite, respectively.



X = Cl, Br

The reaction of 1-bromo-1-fluoro-1-nitropropane with difluoramine in fuming sulfuric acid or in fluosulfonic acid gave 1-difluoramino-1-bromo-1-fluoropropane. The infrared spectrum of this product is shown in Figure 1. More severe reaction conditions resulted in degradation rather than higher substitution products.

(C) It was also desired to study the reactions of α-fluoronitro-nitroso compounds with difluoramine. Preliminary attempts to prepare starting materials of this type from the above alcohols were unsuccessful because of difficulty in preparing nitronate anions by deformylation. An alternative approach, based on decarboxylation rather than deformylation, appears more promising. Ethyl 2-fluoro-2-nitropentanoate was prepared as a starting material for this work by the fluorination of the salt of ethyl 2-nitropentanoate.



(C) The possibility of preparing an α-difluoramino nitro compound from an α-iodonitro compound was studied briefly. The syntheses of crude 2-iodo-2-nitropropane and 2-iodo-2-nitrobutane have been reported, but the compounds were too unstable for distillation.* Using the same method, 1-iodo-1-nitrocyclohexane was prepared, which gave analytically pure material by low-temperature crystallization. This compound did not react with liquid difluoramine at its boiling point. In the presence of sulfuric acid, no product extractable from water was formed. This iodo compound was also treated with tetrafluorohydrazine, but no reaction took place at 80°C; at 120°C, the mixture exploded.

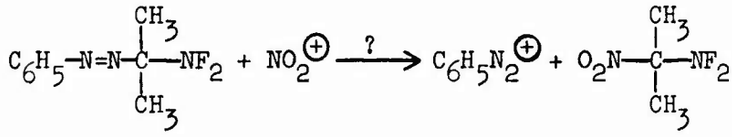
2. Reactions of Azonitro Compounds with Difluoramine

(C) A study was previously conducted** of the reaction of 2-phenylazo-2-nitropropane with difluoramine, with the objective of preparing 2-nitro-2-difluoraminopropane. The only product isolated other than starting material

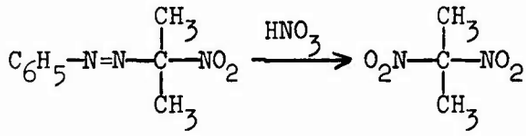
*L. W. Seigle and H. B. Haas, J. Org. Chem., 5, 100 (1940).

**Aerojet-General Report No. 3299, October 1966, p. 10 (Confidential).

was 2-phenylazo-2-difluoraminopropane; the nitro group rather than the phenylazo group was replaced by difluoramine. Work was continued on this reaction, since 2-nitro-2-difluoraminopropane might alternatively be obtained by the nitrolysis of 2-phenylazo-2-difluoraminopropane.

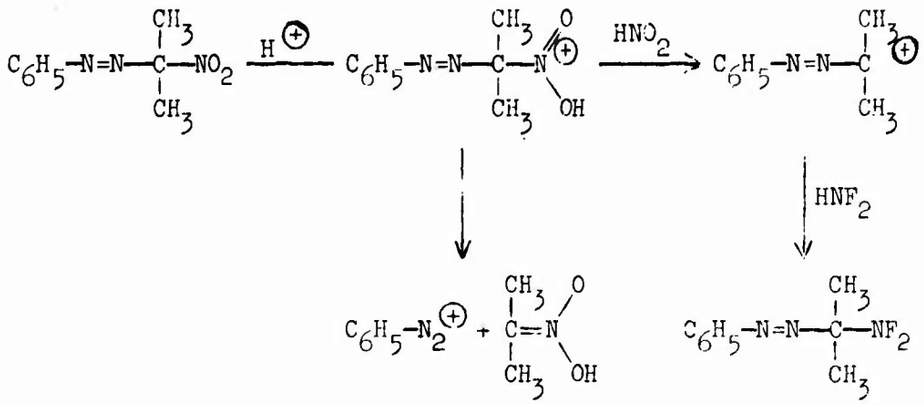


(C) The feasibility of this approach was demonstrated by the nitration of the more readily available starting material, 2-phenylazo-2-nitropropane. No reaction took place between this compound and N_2O_4 in methylene chloride, whereas a mixture of ammonium nitrate and nitric acid gave a complex tarry product. However, anhydrous nitric acid at 0 to 25°C gave a 37% yield of 2,2-dinitropropane:

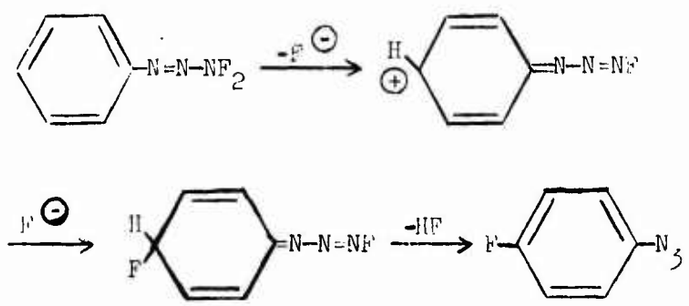


(C) The reaction of 2-phenylazo-2-nitropropane with difluoramine, catalyzed by sulfuric acid, was scaled up and the reaction time was extended in order that sufficient 2-phenylazo-2-difluoraminopropane might be prepared for nitration studies; a 17% yield of analytically pure material was thus isolated (the previously prepared material was somewhat impure). Other products of this reaction were benzene, acetone, acetone oxime, 2,2-bis(difluoramino)propane, phenyl azide, and O-(2-difluoraminopropyl) acetone oxime. The latter compound was identified by elemental analysis, NMR, and infrared spectra.

(C) The observed products appear to arise from the initial protonation of a nitro oxygen of 2-phenylazo-2-nitropropane. The protonated species might then undergo two types of cleavage: loss of nitrous acid to give a secondary carbonium ion, and loss of benzenediazonium ion, leaving aci-2-nitropropane. Alkylation of difluoramine by the secondary carbonium ion would give 2-phenylazo-2-difluoraminopropane:



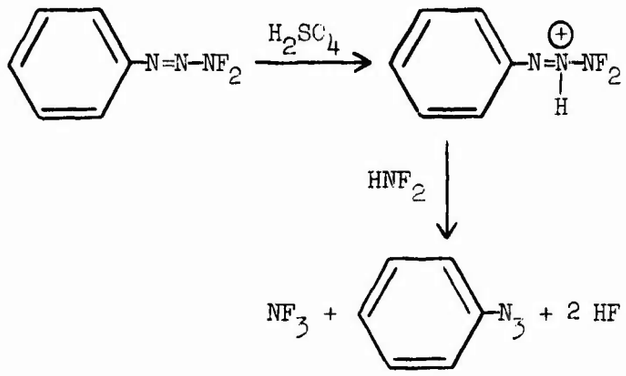
(C) Benzene, o-fluorophenyl azide, and p-fluorophenyl azide have been shown to be products of the reaction of benzenediazonium ion and difluoramine, under mildly basic conditions.* The formation of benzene was rationalized on the basis of reduction of diazonium ion by difluoramine, and the formation of the fluoroazide was ascribed to coupling of the diazonium ion to difluoramine with subsequent rearrangement of the triazene:



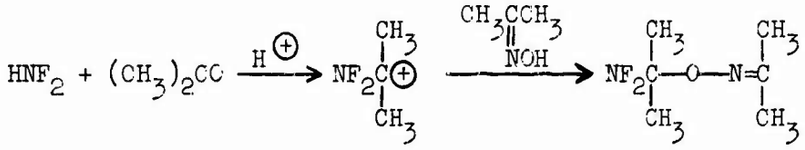
(C) In the present work, in which strongly acidic reaction conditions were used, unsubstituted phenyl azide was formed rather than the fluoro derivatives. This result can be explained on the basis that the initially formed triazene would by protonated by sulfuric acid. Loss of fluoride is then inhibited because it leads to an unstable, doubly-charged cation. Phenyl azide will be formed if fluorine is lost in an electrophylic fluorination reaction (e.g., converting difluoramine, the most abundant substrate available, to trifluoramine).

*Aerojet-General Report No. 0235-01-25/26, September 1966 (Confidential).

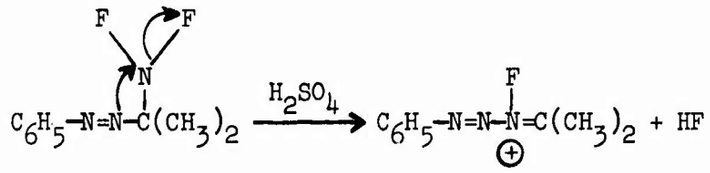
(C) The fact that phenyl azide is formed from benzenediazonium ion and difluoramine in sulfuric acid was confirmed in a control experiment. The addition of benzenediazonium fluoborate to a mixture of concentrated sulfuric acid, and refluxing difluoramine gave phenyl azide and no fluorine-containing derivatives.



(C) The product, acetone, from the reaction of 2-phenylazo-2-nitropropane and difluoramine could be formed by the hydration of the 2-phenylazo-2-propyl cation, or by the Nef reaction of aci-2-nitropropane. The source of the acetone oxime, on the other hand, is less clear. The compound might be formed by the reduction of the aci-2-nitropropane by difluoramine. The C-(2-difluoramino-propyl) acetone oxime could be formed from acetone oxime, difluoramine, and acetone.



(C) To gain additional information about the side reactions, a solution of pure 2-phenylazo-2-difluoraminopropane in sulfuric acid was prepared for NMR studies. The solution was intensely green colored. The F^{19} spectrum consisted of two broadened peaks of about equal intensity at -117.0 and -110.5 ppm from trifluoroacetic acid. The former is at the same position as that of a solution of HF in sulfuric acid. The proton spectrum consisted of a multiplet in the aromatic region at 8.3 to 9.9 δ and 2.2 δ. These spectra suggest that ionization of fluoride from the difluoramino group took place, with migration of the phenylazo group.



This ion might account for the side products in the synthesis of 2-phenylazo-2-difluoraminopropane, since hydrolysis during work-up could give benzenediazonium ion and acetone oxime derivatives.

(C) Attempts were made to nitrate 2-phenylazo-2-difluoraminopropane with 100% nitric acid and with nitronium fluoborate. Degradation of the starting material took place, and 2-difluoramino-2-nitropropane was not isolated.

3. Miscellaneous

(C) The reaction of difluoramine with 2-nitropropene could be expected to result in Michael addition, as was found with other conjugated olefins such as acrylates and vinyl ketones. It was found, however, that no reaction took place between these reagents when no catalyst was used or when the boron trifluoride complex of phosphoric acid was added. The use of concentrated sulfuric acid resulted in the decomposition of the 2-nitropropene. Isopropyl N-fluorocarbamate also failed to add to 2-nitropropene in the presence of pyridine. It appears that the addition is reversible with the equilibrium shifted toward starting materials because of the acidity of the hydrogens adjacent to the nitro group.

(C) Another possible route to α-nitro difluoramino compounds that was investigated briefly is the reaction of α-diazonitro compounds with difluoramine. It was shown previously that the reaction of ethyl diazoacetate with difluoramine in the presence of sulfuric acid gave ethyl difluoraminoacetate.* Ethyl azonitroacetate, contaminated by ethyl nitratoacetate, was prepared by the reaction of nitrogen pentoxide with ethyl diazoacetate.** No reaction took place with difluoramine in the absence of catalysts, and with the addition of sulfuric acid, no fluorine-containing products were found.

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*Aerojet-General Report No. 3299, October 1966, p. 10 (Confidential).

**U. Schollkopf and H. Schafer, Angew. Chem. (Int. ed.) 4, 358 (1965).

$$2\ EtOCOCHN_2 + N_2O_5 \longrightarrow EtOCOC(NC_2)=N_2 + EtOCOCH_2{-}ONO_2 + N_2$$

$$\xrightarrow{HNF_2} \text{no reaction} \xrightarrow[HNF_2]{H_2SO_4} \text{degradation}$$

(C) Some additional work was done on the reaction of pseudo-nitroles with difluoramine. It was shown previously that gem-difluoramines were formed in the presence of fuming sulfuric acid and that fluoroazoxy-nitro compounds were formed in the presence of the boron trifluoride complex of phosphoric acid.* It appeared the nitro-difluoramino compounds should be formed with a catalyst of intermediate activity. Trifluoroacetic acid, concentrated sulfuric acid, and 100% sulfuric acid have now been investigated for the reaction of nitronitrosocyclohexane and difluoramine. With trifluoroacetic acid and with concentrated sulfuric acid, no reaction took place; the nitroso compound was insoluble in the reagent. When 100% sulfuric acid was used as the catalyst and the nitroso compound was dissolved in methylene chloride, a new compound was formed, with an F^{19} NMR signal at -23.4 ϕ. The amount of this material that was formed was not sufficient for complete characterization.

(C) The reaction of ethyl 2-propanenitronate with difluoramine was also attempted. When no catalyst was used, no fluorine-containing product was formed. When concentrated sulfuric acid was used, the product gave very weak F^{19} signals at -28.0 ϕ, -24.4 ϕ, and -19.1 ϕ.

(C) Gem-difluoramines have been shown to hydrolyze reversibly in sulfuric acid to give ketones and difluoramine.** A stronger acid, fluosulfonic acid, was treated with 3,3-bis(difluoramino)pentane, in the hope that a more useful reaction would take place. However, the NMR spectra of the resulting solution showed that 3-pentanone and difluoramine were formed.

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*Aerojet-General Report No. 2945, October 1964, p. 5 (Confidential).

**Aerojet-General Report No. 0235-01-22, May 1965, p. 5 (Confidential).

$$CH_3CH_2\overset{\overset{NF_2}{|}}{\underset{\underset{NF_2}{|}}{C}}CH_2CH_3 \xrightarrow{FSO_3H} CH_3CH_2\overset{\overset{O}{||}}{C}CH_2CH_3 + HNF_2$$

C. EXPERIMENTAL

1. 2-Bromo-2,4,4-trinitropentane (Improved Procedure)

(C) 2-Nitropropene (24.0 g, 0.2 mole) was added with stirring to a solution of 8.8 g (0.22 mole) of sodium hydroxide and 24.0 g (0.20 mole) of 1,1-dinitroethane in 200 ml of water at 5°C. A yellow salt precipitated immediately. To this slurry, 32.0 g (0.2 mole) of bromine was added dropwise over a 25-min period at 0-5°C. The precipitate was filtered and washed with cold water. Recrystallization from 200 ml of ethanol gave 34.3 g of white solid, m.p. 54-55°C. The mother liquor was concentrated to give a second crop, 4.8 g, m.p. 53-54°C (68.1% total yield).

2. Reaction of 2-Bromo-2,4,4-trinitropentane With Difluoramine

(C) A solution of 5.0 g (17.5 mmoles) of 2-bromo-2,4,4-trinitropentane in 10 ml of methylene chloride was added, with stirring, to a mixture of 27 g of refluxing difluoramine in 14 ml of 20-23% fuming sulfuric acid in a glass reactor fitted with glass and Teflon needle valves. The mixture was stirred 19 hours at ambient temperature. The reactor contents were drained onto 250 ml of ice, and the product was extracted with four 25-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate, and distilled through a 25-cm Holzmann column to give 0.69 g of liquid, b.p. 40-58°/13 mm. Analysis by gas chromatography and NMR showed that the sample contained 0.24 g (0.87 mmole, 5.0% yield) of 2,2,4,4-tetrakis(difluoramino)pentane and 0.45 g (4.65 mmole, 26.5% yield) of 3,5-dimethylisoxazole.

3. 2-Chloro-2,4,4-trinitropentane

(C) The suspended salt prepared from 24.0 g (0.20 moles) of 1,1-dinitroethane, 8.8 g (0.22 mole) of sodium hydroxide, and 17.4 g of 2-nitropropene in 200 ml of water at 0-5°C was saturated with chlorine. A green oil separated which was diluted with 80 ml of methylene chloride, washed with three 30 ml portions of sodium bicarbonate solution, and with three 30 ml portions of water. The solution

was dried with sodium sulfate and distilled to yield 27.8 g of pale green oil, b.p. 82°C/0.06 mm. Crystallization and recrystallization from ethanol yielded 5.9 g (0.0244 moles, 12.2% yield) of 2-chloro-2,4,4-trinitropentane, a white solid, m.p. 31-31.5°C.

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

(C) The NMR spectrum of 2-chloro-2,4,4-trinitropentane consisted of an AB quartet at 4.00 δ (CH_2) with J_{AB} = -16.8 cps and inner members separated 6.2 cps, a sharp singlet at 2.22 δ [CH_3-$C(NO_2)_2$-], and a slightly broadened singlet at 2.15 δ (CH_3-C NO_2Cl-).

4. Reaction of 2-Chloro-2,4,4-trinitropentane with Difluoramine

(C) 2-Chloro-2,4,4-trinitropentane (5.0 g, 0.0207 moles) was added with stirring to a mixture of 14 ml of 20-23% fuming sulfuric acid and 27 g of refluxing difluoramine in a glass reactor fitted with glass and Teflon valves. The reactor was sealed and the mixture was stirred at room temperature for 18 hours. The solution became blue during the first hour, and then pale-yellow. The mixture was drained onto 250 ml of ice and the product was extracted with four 30 ml portions of methylene chloride. The combined extracts were dried with sodium sulfate and filtered; the solvent was removed through a 25 cm Holtzmann column. Vacuum distillation gave 0.60 g, b.p. 37-50°C/13 mm, and 0.53 g, b.p. 50-58°C/13 mm.

(C) Analysis of gas chromatography and NMR showed that the first fraction consisted of 0.064 g (0.123 mmole) of 2,2,4,4-tetrakis(difluoramino)pentane and 0.537 g (5.53 mmol) of 3,5-dimethylisoxazole, and that 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 thus were 8% and 34%, respectively. The 2,2,4,4-tetrakis(difluoramino)pentane was identified by comparison with previously reported spectral and chromatographic data,* and the 3,5-dimethylisoxazole by comparison with an authentic sample. The proton NMR spectrum of the former consisted of a broadened signal at 2.93 δ for the methylene and a quintet (J_{HF} = 2.20 cps) at 1.70 δ for the methyl, whereas the fluorine spectrum consisted

*Aerojet-General Report 2730, October 1963 (Confidential).

of a singlet at -29.0 ϕ. The proton spectrum of the latter consisted of a symmetrical broadened band at 5.88 δ for the CH, a broadened singlet at 2.33 δ for $\diagup N{=}\overset{|}{C}\text{-}CH_3$, and a singlet at 2.17 δ for $O\text{-}\overset{\|}{C}\text{-}CH_3$.

5. Reaction of 3,5-Dimethylisoxazole with Difluoramine

(C) 3,5-Dimethylisoxazole (1.0 g, 0.011 mole) was added dropwise over a 1 hour period to a mixture of 4 ml of 20-23% fuming sulfuric acid and 4.5 g of refluxing difluoramine. An upper layer separated during a 2 hour reaction period; it was subsequently taken up in 5 ml of methylene chloride.

(C) The proton NMR spectrum of this solution showed that it contained 2,2,4,4-tetrakis(difluoramino)pentane and 3,5-dimethylisoxazole.

6. 2-Fluoro-2-nitrobutanol

(C) A solution of 230 g (1.93 moles) of 2-nitrobutanol and 85.1 g (2.12 moles) of sodium hydroxide was fluorinated at 5-10°C until fluorine was no longer absorbed (2 liters). The solution was saturated with sodium chloride and was extracted with 2 liters of methylene chloride in five portions. The methylene chloride solution was dried over sodium sulfate and distilled through a 4 in. Vigreaux column to give 110 g of crude 2-fluoro-2-nitrobutanol, b.p. 60°C/0.8 mm and 37 g of 2-nitrobutanol, b.p. 60-73°C/0.8 mm. Redistillation gave 91.3 g (34.5% yield) of 2-fluoro-2-nitrobutanol, b.p. 102-104°C/13 mm. A total of 43.1 g of starting material was recovered.

Anal. Calcd for $C_4H_8NO_3F$: C, 35.04; H, 5.84; N, 10.22

Found: C, 34.90; H, 5.90; N, 10.11

(C) The fluorine NMR spectrum of a CCl_4 solution consisted of a symmetrical complex multiplet centered at 139.8 ϕ. The proton spectrum consisted of a triplet at 1.01 δ (relative area, 139) for the methyl, a multiplet at 2.23 δ (area 95) for the methylene of the ethyl group, a broad singlet at 3.0 δ shifted upfield by dilution (area 45) for the -OH, a singlet at 3.91 δ (area 39) for one of the α-hydrogens, and an AB quartet at 4.18 δ (area 37, J_{HH} = -13.9 cps; J_{HF} = 23.5 cps, inner members separated 7.6 cps) for the other.

(C) The AB pattern for one of the α-hydrogens and the singlet for the other is tentatively explained on the basis of opposite signs of coupling

constants of the two hydrogens to fluorine, with equal magnitudes of the HF and HH coupling constants.

7. 2-Fluoro-2-nitropentanol

(C) A solution of 102 g (0.99 moles) of 1-nitrobutane, 40.0 g (1.0 mole) of sodium hydroxide, and 84 g (1.0 mole) of formalin in 1250 ml of water was fluorinated and worked up as in the above reaction, but using a 25 cm Holzmann column for the distillation, to give 31.0 g (21% yield) of 2-fluoro-2-nitropentanol, b.p. 29-30°/0.025 mm.

Anal. Calcd for $C_5H_{10}NO_3F$: C, 39.74; H, 6.67; N, 9.27

Found: C, 39.71; H, 6.63; N, 9.40

(C) The fluorine NMR spectrum exhibited a profile identical with that of 2-fluoro-2-nitrobutanol, but at 138.1 ϕ. The proton spectrum showed a triplet (J = 7.0 cps) at 1.00 δ for the methyl, a multiplet at 1.5 δ for the adjacent methylene, a multiplet at 2.1 δ for the next methylene, a broad singlet which shifted on dilution at 3.3 δ for the hydroxyl, a singlet at 3.90 δ for one of the carbinol protons, and an AB pattern at 4.19 δ (J_{HH} = -13.8 cps; J_{HF} = 23.6 cps, inner members separated 6.4 cps) for the other.

8. 2-Fluoro-2-nitrohexanol

(C) The fluorination of a solution of 52.0 g (0.445 moles) of 4-nitropentane, 17.8 g (0.445 moles) of sodium hydroxide, and 37.4 g (0.445 moles) of formalin and workup as above gave 21.2 g (28.4% yield) of 2-fluoro-2-nitrohexanol, b.p. 42-43°C/0.025 mm and 14.7 g (0.10 mole) of 2-nitrohexanol, b.p. 74°C/0.05 mm.

Anal. Calcd for $C_6H_{12}NO_3F$: C, 43.63; H, 7.33; N, 8.45

Found: C, 43.67; H, 7.51; N, 8.13

(C) The fluorine NMR spectrum consisted of a multiplet at 138.2 ϕ. The proton spectrum showed a triplet (J = 6.1 cps) at 0.77 δ for the methyl, a multiplet at 1.3 δ for the next two methylene groups, a multiplet at 2.2 δ for the next methylene group, a singlet at 4.27 δ for one carbinol proton, and an AB pattern at 4.59 δ for the other (J_{HH} = -13.6 cps; J_{HF} = 24.4 cps, inner members separated 11.4 cps). Pyridine was the solvent for this spectrum, as satisfactory resolution was not obtained with CCl_4.

9. 2-Fluoro-2-nitroheptanol

(C) The fluorination of a solution of 60 g (0.457 mole) of 1-nitrohexane, 18.3 g (0.457 mole) of sodium hydroxide, and 38.1 g (0.457 mole) of formalin, gave - after three distillations - 20.0 g (24.5% yield) of 2-fluoro-2-nitroheptanol, b.p. 55-57°C/0.025 mm.

Anal. Calcd for $C_7H_{14}NO_3F$: C, 46.90; H, 7.88; N, 7.80

Found: C, 46.76; H, 7.97; N, 7.47

(C) The fluorine NMR spectrum showed a symmetrical multiplet at 137.7 ϕ. The proton spectrum (pyridine solution) showed a triplet (J = 4.9 cps) at 0.82 δ for the methyl, a multiplet centered at 1.2 δ for the next three methylenes, a multiplet at 2.3 δ for the fourth methylene, a singlet at 4.26 δ for one of the carbinol hydrogens, and an AB pattern at 4.58 δ for the other (J_{HH} = -13.6 cps; J_{HF} = 24.8 cps, central members separated 11.2 cps).

10. 1-Bromo-1-fluoro-1-nitropropane

(C) 2-Fluoro-2-nitrobutanol (68.6 g, 0.50 moles) was added dropwise to a freshly prepared solution of 1.25 moles of sodium hypobromite in 1.5 liters of water. A heavy oil separated. After 0.5 hours, the mixture was extracted with three 100 ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled through a 25 cm Holzmann column to give 30.0 g (32% yield) of 1-bromo-1-fluoro-1-nitropropane, b.p. 90°C/47 mm, and 22.4 g (0.185 moles) of 2-fluoro-2-nitrobutanol.

Anal. Calcd for $C_3H_5NO_2BrF$: C, 19.37; H, 2.69; N, 7.53

Found: C, 19.37; H, 2.72; N, 7.63

(C) The proton NMR spectrum consisted of a doublet (J_{HF} = 18 cps) of quartets (J = 7.3 cps) at 2.8 δ and a triplet (J = 7.3 cps) at 1.1 δ. The F^{19} spectrum consisted of a distorted triplet at 85.6 ϕ (J = 18.5 cps).

11. Reaction of 1-Bromo-1-fluoro-1-nitropropane With Difluoramine

(C) 1-Bromo-1-fluoro-1-nitropropane (5.0 g, 0.268 mole) was added with stirring to a mixture of 14 ml of 21-23% fuming sulfuric acid and 27 g of refluxing difluoramine in a glass pressure reactor. The reactor was sealed and the

mixture was stirred at room temperature for 30 min. During this time an intense bromine color appeared. Decane (~40 ml) was added to the mixture and the lower acid layer was drained onto 250 ml of ice. The decane layer was treated with sodium sulfate. Nothing was extractable from the aqueous phase. Distillation of 15 ml of the decane solution at 77°C and 22 mm into a -80°C receiver for 1-1/2 hours yielded 0.7 g of colorless oil, shown to be a mixture of decane and product by infrared and elemental analysis. A pure sample of 1-bromo-1-difluoramino-1-fluoropropane was obtained by gas chromatography (0.117 in. ID by 6 ft column of di-n-butylphthalate on chromosorb-W using a helium flow rate of 30 cu cm/min at 63°C, 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

(C) The proton NMR spectrum consisted of a triplet (J = 7.6 cps) at 1.3 δ for the methyl and an overlapping quartet (J = 7.6 cps) of doublets (J_{HF} = 16.5 cps) at 2.39 δ for the methylene with each element showing an additional 1.5 cps triplet splitting to the NF_2. The fluorine spectrum consisted of a broad symmetrical band at -34.3 ϕ for the NF_2 and a quintet (J_{FF} = 16.5 cps = J_{CH_2F}) at 102.0 ϕ for the CF.

12. Ethyl-2-fluoro-2-nitropentanoate

(C) A solution of 160.0 g (0.913 mole) of ethyl-2-nitropentanoate and 40.0 g (1.0 mole) of sodium hydroxide in 2 liters of water was fluorinated at 0-5°C until 1 mole of fluorine was consumed. The product layer was diluted with methylene chloride, washed with water, and dried with sodium sulfate. Distillation through a 25 cm Holzmann column yielded 96 g (0.5 mole, 50% yield) of ethyl 2-fluoro-2-nitropentanoate (a colorless oil, b.p. 36°C/0.35 mm) and 76 g (0.43 mole) of ethyl 2-nitropentanoate, b.p. 39°C/0.025.

Anal. Calcd for $C_7H_{12}ONF$: C, 43.49; H, 6.26; N, 7.25

Found: C, 43.48; H, 6.03; N, 7.14

(C) The proton NMR spectrum consisted of a quartet (J = 5.4 cps) at 4.3 δ for the ethoxy methylene, a doublet (J_{HF} = 20 cps) of triplets (J = 7 cps) at 2.40 δ for the methylene hydrogens vicinal to F, a triplet at 1.30 δ superimposed

over a multiplet near 1.30 δ, and a distorted triplet (J = 6.4 cps) at 0.98 δ representing the ethoxy CH_3, internal CH_2, and terminal CH_3, respectively. The F^{19} spectrum exhibited a broadened triplet (J_{HF} = 20.8 cps) at 125.2 ppm (C-F).

III. SUMMARY

(C) The reactions of 2-bromo-2,4,4-trinitropentane and 2-chloro-2,4,4-trinitropentane with difluoramine gave 2,2,4,4-tetrakis(difluoramino)pentane, and 3,5-dimethylisoxazole was isolated as an intermediate.

(C) The reaction of 1-bromo-1-fluoro-1-nitropropane with difluoramine gave 1-difluoramino-1-bromo-1-fluoropropane. More severe reaction conditions gave degradation.

(C) The starting materials, 2-fluoro-2-nitroalcohols and ethyl 2-fluoro-1-nitropen noate, were synthesized by the aqueous fluorination of the corresponding nitronate salts.

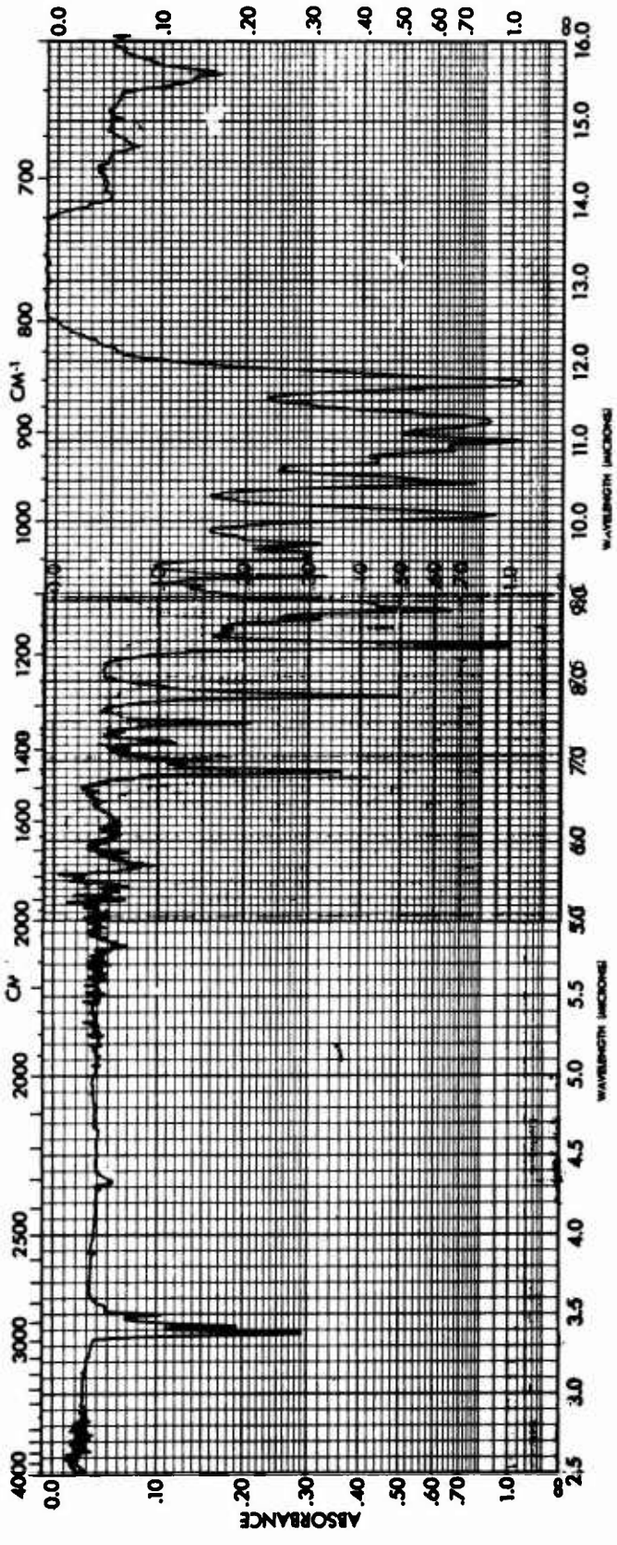
(C) The reaction of 2-phenylazo-2-nitropropane with difluoramine and fuming sulfuric acid gave 2-phenylazo-2-difluoraminopropane, benzene, acetone, 2,2-bis-(difluoramino)propane, and O-(2-difluoraminopropyl)acetone oxime.

(C) The nitration of 2-phenylazo-2-difluoraminopropane has not yielded 2-nitro-2-difluoraminopropane, although 2-phenylazo-2-nitropropane gave 2,2-dinitropropane. No product of interest resulted from the reactions of difluoramine with ethyl nitrodiazoacetate, ethyl 2-butanenitronate, 1-diazo-2-heptanone, 2-nitropropene, diphenyliodium tosylate, and 1-iodo-1-nitrocyclohexane.

(C) The reaction of 3,3-bis(difluoramino)pentane with fluosulfonic acid gave 3-pentanone and difluoramine.

IV. CONCLUSIONS AND RECOMMENDATIONS

(C) The reactions of 2-halo-2,4,4-trinitropentanes and of dimethylisoxazole with difluoramine to give 2,2,4,4-tetrakis(difluoramino)pentane are of general significance. Analogous halonitro compounds and higher homologues of isoxazoles and similar heterocyclics which are known should lead to longer chain compounds with alternating methylene and bis(difluoramino)methylene groups.



Infrared Spectrum of 1-Difluoramino-1-Bromo-1-Fluoropropane (C)

Figure 1

APPENDIX A

REACTIONS OF CARBONYL COMPOUNDS WITH DIFLUORAMINE (C)

Report No. 3495

REACTIONS OF CARBONYL COMPOUNDS WITH DIFLUORAMINE[1] (C)

Kurt Baum

Contribution from Chemical and Biological Processes Division, Aerojet-General Corporation, Azusa, California 91703.

(C) Abstract: Ketones and aldehydes reacted 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 reacted 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-dioxan. Michael addition of difluoramine took place with α,β-unsaturated carbonyl compounds.

(C) 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 difluoramino-carbinols and difluoraminocarbonium ions as intermediates.

(C) 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 (b.p. -23°), although no reaction took place with sulfuric acid of less than 92% concentration. Electron-withdrawing substituents required more

TABLE I (C)

GEM-BIS(DIFLUORAMINO) DERIVATIVES OF KETONES

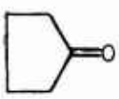
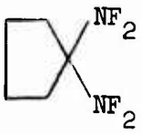
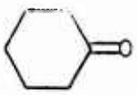
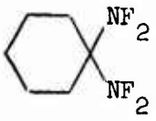
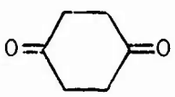
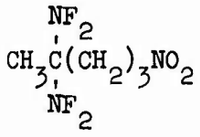
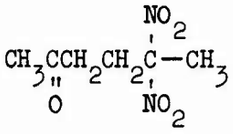
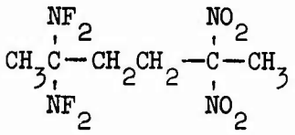
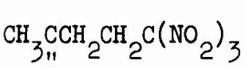
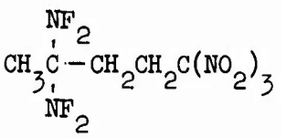
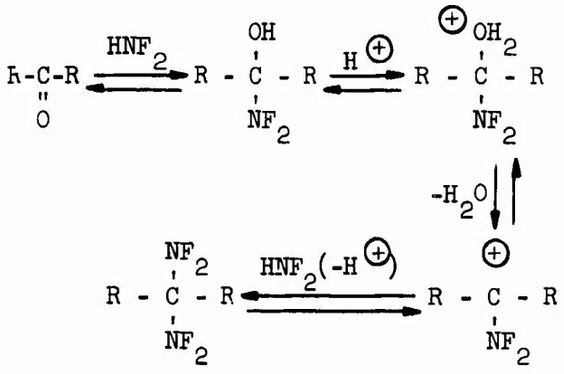
Starting Material	Product	B.P. (or m.p.)
CH_3CCH_3 (O)	$CH_3C(NF_2)_2CH_3$	73°
$C_2H_5CC_2H_5$ (O)	$C_2H_5C(NF_2)_2C_2H_5$	40-41°/30 mm
$CH_3C(CH_2)_5CH_3$ (O)	$CH_3C(NF_2)_2(CH_2)_5CH_3$	38°/0.6 mm
		36°/20 mm
		44°/7 mm
		(103°)
$ClCH_2CCH_3$ (O)	$ClCH_2C(NF_2)_2CH_3$	41°/60 mm
$CH_3C(CH_2)_3CO_2C_2H_5$ (O)	$CH_3C(NF_2)_2(CH_2)_3CO_2C_2H_5$	93°/2 mm

TABLE I (cont.) (C)

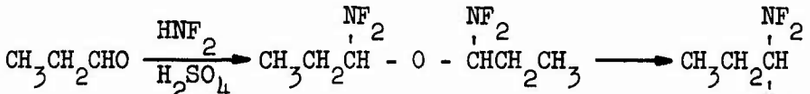
Starting Material	Product	B.P. (or m.p.)
		65°/0.25 mm
		(47°)
		(42°)

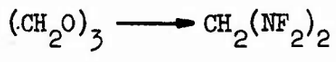
forcing conditions, such as a more acidic medium (oleum) or a higher reaction temperature (attained by using a closed reactor). The sequence leading to bis(difluoramino)alkanes was shown to be reversible; 2-octanone was recovered when 2,2-bis(difluoramino)octane was shaken with sulfuric acid for 1 hour 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:



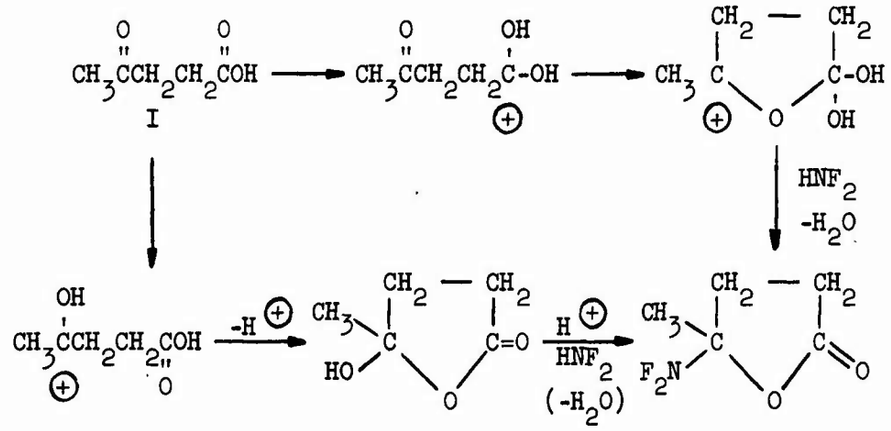
In general, a high concentration of difluoramine, a solvent with a strong affinity for water, and a low solubility for the product are favorable factors. The importance of reaction conditions in the case of 5,5,5-trinitro-2-pentanone is illustrative. No reaction took place with refluxing difluoramine and concentrated sulfuric acid in 4 hours. Using 100% sulfuric acid, 4 ml/mmole ketone, and an eightfold excess of difluoramine at room temperature gave a 53% conversion in 40 hours, and starting material was recovered. Using 20% fuming sulfuric acid, only 0.7 ml/mmole ketone, and a threefold excess of difluoramine at its reflux temperature gave a 99.5% yield in only 2 hours.

(C) 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)butane, and α,α'-bis(difluoramino)propyl ether was isolated as an intermediate. Trioxane similarly was converted to 1,1-bis(difluoramino)-methane, a highly explosive gas.

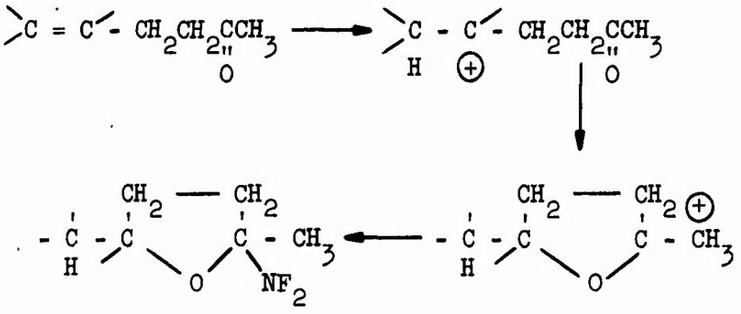




(C) Carbonyl compounds with carbonium ion precursors in suitable positions gave difluoramino-substituted lactones, tetrahydrofurans, and dioxanes. The reactions listed in Table II were carried out in the presence of refluxing difluoramine, using concentrated sulfuric acid as the solvent. These reactions 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 would be formed by the protonation of either the carboxyl or keto carbonyl groups.



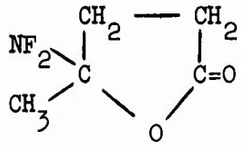
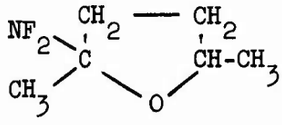
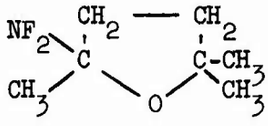
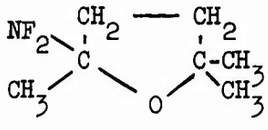
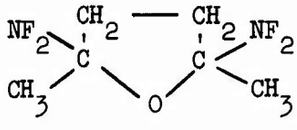
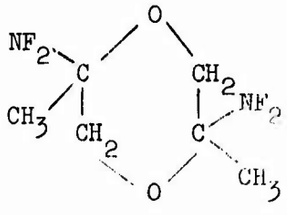
For the olefinic starting materials in Table II, the observed products can arise only by protonation of the olefinic bonds; initial attack on the carbonyls would give carbocyclic products.



(C) 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.[4] Tetrahydrofuran derivatives were formed by the acid catalyzed ring closure of both 4-hydroxyolefins, and 5-hydroxyolefins.[5] Also, γ-hydroxyaldehydes[6] have been

TABLE II (C)

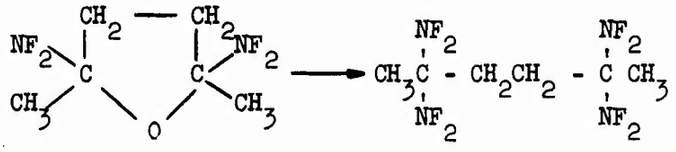
CYCLIZATION REACTIONS

Starting Material	Product	B.P. (or m.p.)
$CH_3CCH_2CH_2COOH$ (O)		55-56°/0.5 mm
$CH_3CCH_2CH_2CH=CH_2$ (O)		34°/8 mm
$CH_3CCH_2CH_2C(CH_3)(NO_2)-CH_3$ (O)		50-51°/19 mm
$CH_3CCH_2CH_2C(CH_3)=CH_2$ (O)		50-51°/19 mm
$CH_3CCH_2CH_2CCH_3$ (O, O)		35°/2.7 mm
CH_3CCH_2OH (O)		(70°)

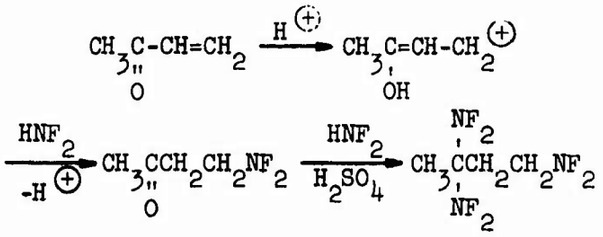
report to give 2-alkoxytetrahydrofurans on reaction with alcohols. The reaction of acetol with alcohols gave 2,5-dialkoxy-2,5-dimethyl-1,4-dioxans.[7]

(C) 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 S_Ni mechanism involving an O-acyl intermediate.[8] The direct nucleophilic displacement of nitro groups by anions has also been reported.[9]

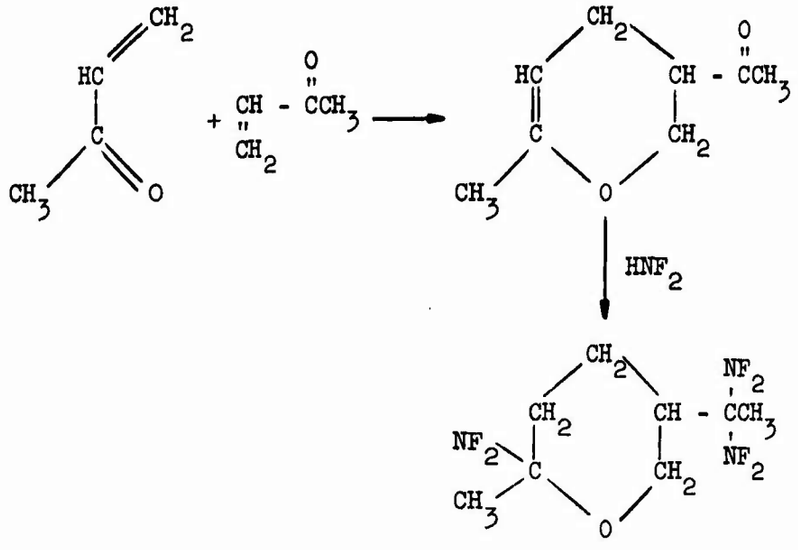
(C) In a prolonged reaction of acetonylacetone with difluoramine in fuming sulfuric acid at room temperature, ring-opening of the initially formed tetrahydrofuran derivative took place, and 2,2,5,5-tetrakis(difluoramino)hexane was prepared. In this experiment, some acetonylacetone was recovered, although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



(C) 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.[10]



A high-boiling by-product of this reaction was identified as 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran, which could be formed by dimerization of methyl vinyl ketone and reactions of the double bond and carbonyl with difluoramine.



Other examples of the Michael reaction 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.

(C) Since simple primary, secondary, and tertiary alkyldifluoramines rearrange rapidly in sulfuric acid to give fluorimmonium ions,[11,3] 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[12] of gem-bis(difluoramino)-alkanes would likewise give a lower electron density on the adjacent carbon than for the simple derivatives.

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

Experimental Section

(C) 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.

(C) 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 1-1/4-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 vent 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.

(C) A simpler reactor using similar valves has been reported previously.[13]

(C) Extensive attempts were not made to optimize yields in the following preparations.

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

(C) 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.

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

(C) The proton nmr spectrum consisted of a quintet at 1.52 δ, J = 2 cps. The fluorine spectrum showed a broadened singlet at -27.9 ϕ.

(C) 3,3-Bis(difluoramino)pentane. 3-Pentanone (1.0 g, 0.0116 moles) was added dropwise with stirring to 4.5 g of difluoramine and 15 ml of concentrated sulfuric acid. After 3.5 hours, 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 moles, 49.5% yield) of 3,3-bis(difluoramino)pentane, b.p. 54°/52 mm.

(C) 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.

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

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

(C) 2,2-Bis(difluoramino)octane. 2-Octanone (30.0 g, 0.234 moles) 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 hour. The reactor was closed and kept at ambient temperature for 3.5 hours. 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, b.p. 38°/0.6 mm.

(C) 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.

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

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

(C) 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.

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

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

(C) 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.

(C) The proton nmr spectrum consisted of multiplets and 2.06 δ and 1.72 δ with area ratio 2:3. The fluorine spectrum contained a single broadened signal at -22.79 ϕ.

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

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

(C) 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.

(C) The proton nmr spectrum showed a broadened singlet at 2.41 δ, and the fluorine spectrum showed a broadened singlet at -25.22 ϕ.

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

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

(C) 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.

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

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

(C) Ethyl 5,5-Bis(difluoramino)hexanoate. Ethyl 5-ketohexanoate (9.3 g, 0.059 moles) was added slowly to 50 ml of 20% fuming sulfuric acid and 27 g of difluoramine in a pressure reactor. After a 20-hour reaction period, excess difluoramine was vented and the reaction mixture was added to 1 liter 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, b.p. 90-93°/1.9-2 mm (mixture analyzed by capillary gc).

(C) 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.

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

(C) 2,2-Bis(difluoramino)-5-nitropentane. 5-Nitro-2-pentanone[14] (5.0 g, 0.038 moles) was added dropwise, with stirring to 27 g of difluoramine and 17 ml of 20% fuming sulfuric acid. After 2.5 hours, 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, b.p. 65°/0.25 mm.

(C) Anal. Calcd for $C_6H_9N_3F_4O_2$: 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.

(C) Infrared bands in the NF region were 10.02 μ(s), 10.23 μ(s), 11.05 μ(s), and 11.58 μ(s). The proton nmr spectrum consisted of a quintet at 1.63 δ (J = 2 cps) for the methyl, an irregular triplet at 4.37 δ for the methylene adjacent to the nitro, and a complex multiplet with maximum intensity at 131 cps (60 mc) for the other methylenes. The fluorine spectrum consisted of a slightly broadened signal at -26.94 ϕ.

(C) 2,2-Bis(difluoramino)-5,5-dinitrohexane. To a solution of 1.90 g (0.010 moles) of 5,5-dinitro-2-hexanone[15] 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 hours, 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), m.p. 47°. An analytical sample (same mp) was obtained by subliming the material at 100°/0.1 mm.

(C) 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.

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

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

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

(C) 2,2-Bis(difluoramino-5,5,5-trinitropentane. 5,5,5-Trinitro-2-pentanone[16] (15.0 g, 0.068 moles) 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 hours and 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, m.p. 42°.

(C) 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; H, 22.60; F, 24.8.

(C) Infrared bands (all m) in the NF region were 10.0 μ, 10.21 μ, 10.64 μ, 10.85 μ, 11.08 μ, 11.38 μ, 11.70 μ, and 11.99 μ. The proton nmr spectrum (CCl_4 solution) consisted of a quintet (J = 2 cps) at 1.71 δ for the methyl and signals at 3.16 δ and 2.54 δ 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.

(C) 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.

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

(C) 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.

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

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

(C) 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 (b.p. 25°/17 mm) was isolated.

(C) 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.

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

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

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

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

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

(C) 2-Difluoramino-2,5-dimethyltetrahydrofuran. 5-Hexene-2-one (2.45 g, 0.025 moles) 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 hours, unreacted difluoramine was removed, and the sulfuric acid solution was drained onto 150 ml of crushed ice. The product was extracted with 4 - 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, b.p. 34°/8 mm.

(C) 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.

(C) The compound had infrared peaks at 3.45 μ(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 (w).

(C) The proton nmr spectrum displayed a sextet (J = 6 cps) at 4.31 δ 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 δ) representing methyls adjacent to the NF_2 groups, and two almost superimposed doublets (J = 6 cps) at 1.25 δ for methyls on methine carbons. The fluorine nmr spectrum consisted of an AB quartet centered at -23.66 ϕ (with the central members separated by 228 cps and J_{FF} = 574 cps) and a singlet at -24.09 ϕ. The data indicate a mixture of cis and trans isomers. The F^{19} AB quartet would result from asymetry of the center at which the NF_2 is attached[17] in one isomer; the singlet would indicate accidental equivalence of the fluorines in the other isomer.

(C) 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 moles) of 5-methyl-5-nitro-2-hexanone[14] 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 hours. Unreacted difluoramine was removed, and the solution was added to 200 ml of crushed ice. The product was extracted with 4 - 50 ml portions of methylene chloride. The methylene chloride solution was dried and

distilled to give 3.3 g of colorless liquid, b.p. 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).

(C) 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.

(C) The infrared spectrum was as follows: 3.35 μ(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), 13.0 (w).

(C) The proton nmr spectrum (carbon tetrachloride solution) consisted of singlets at 1.24 and 1.33 δ and a triplet (J = 2.5 cps) at 1.45 δ. The fluorine spectrum consisted of an AB quartet centered at 23.6 ϕ, J_{FF} = 498 cps. The separation of the central peaks was 187 cps.

(C) B. From Methallylacetone. Methallylacetone (1.43 g, 0.0125 moles) 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 3 - 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, b.p. 50°/20 mm identical with that above.

(C) 4-Difluoramino-4-methylbutyrolactone. Levulinic acid (1.45 g, 0.0125 moles) 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 hours, 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, b.p. 55 to 56°/0.5 mm.

(C) 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.

(C) The infrared spectrum showed bands at 3.30-3.40 μ(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 (w).

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

(C) 2,5-Bis(difluoramino)-2,5-dimethyl-1,4-dioxan. Concentrated sulfuric acid (15 ml) was added dropwise with stirring to a solution of 1.85 g (0.025 moles) 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 hours 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-dioxan, a white solid, m.p. 62-64°. This solid was sublimed at room temperature at 0.3 mm onto a -80° coldfinger to give 1.15 g (42% yield), m.p. 70°.

(C) 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.

(C) The infrared spectrum consisted of peaks at 3.40 μ(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).

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

(C) 2,5-Bis(difluoramino)-2,5-dimethyltetrahydrofuran. Acetonylacetone (1.0 g, 0.0088 moles) 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, b.p. 43°/4 mm.

(C) 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.

(C) The infrared spectrum consisted of the following peaks: 3.30 μ(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 (w).

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

(C) 2,2,5,5-Tetrakis(difluoramino)hexane. Acetonylacetone (2.32 g, 0.020 moles) 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-hour 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 5 - 50 ml portions of methylene chloride and the solution was dried over sodium sulfate and distilled to give 2.03 g of liquid, b.p. 70°/4 mm.

(C) Gas chromatography (2.5 m column of 5% diethyleneglycol succinate on Fluoropak 80, 85°, 60 ml He/min) showed four components with the following retention times and relative areas: 7 min, 13%; 11 min, 13.1%; 21 min, 59.9%; and 39 min, 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.

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

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

(C) 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.

(C) The N-F portion of the ir spectrum showed bands at 10.0 μ(s), 10.25 μ(s), 10.5 μ(sh), 11.05 μ(s), 11.35 μ(s), and 11.77 μ(sh). The proton nmr spectrum (CCl_4 solution) consisted of a quintet at 1.63 δ (J = 2 cps) for the methyls and a poorly resolved quintet at 2.28 δ for the methylenes. The fluorine spectrum consisted of a single peak at 246 ϕ.

(C) The last gc component was identified as acetonylacetone by comparing its retention time and ir spectrum with an authentic sample.

(C) Methyl β-(difluoramino)propionate. Methyl acrylate (2.92 g, 0.034 moles) was added to 9 g of difluoramine and 17 ml of concentrated sulfuric acid. After 3.5 hours, the mixture was added to 150 ml of ice and the product was extracted with 4 - 50 ml portions of methylene chloride and dried over sodium sulfate. Distillation gave 3.50 g (74% yield) of methyl β-difluoraminopropionate, b.p. 47°/20 mm.

(C) 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.

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

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

(C) β-(Difluoramino)propionic Acid. Acrylic acid (4.0 g, 0.055 moles) was added dropwise to 9 g of difluoramine and 15 ml of concentrated sulfuric acid. After 2 hours, 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, b.p. 60°/1 mm.

(C) 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.

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

(C) The proton nmr spectrum showed a singlet at 11.6 δ for the OH, a triplet of triplets (J_{HF} = 29 cps, J_{HH} = 8 cps) at 3.70 δ for the β-methylene, and a triplet (J = 8 cps) at 2.80 δ for the α-methylene. The fluorine spectrum exhibited a triplet at -53.15 ϕ, J = 28.4 cps.

(C) 1,3,3-Tris(difluoramino)butane. Freshly distilled methyl vinyl ketone (5.0 g, 0.084 moles) was added slowly to 75 ml of 100% sulfuric acid and 27 g of difluoramine. After 3 hours, 75 ml of pentane was added and difluoramine was

removed. Distillation of the pentane solution through a 25-cm Holzmann column gave 10.65 g (60% yield) of 1,3,3-tris(difluoramino)butane, b.p. 50°/30 mm.

(C) 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.

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

(C) 2-Methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran. Methyl vinyl ketone (3.0 g, 0.043 moles) was added dropwise to 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. After 3 hours, 50 ml of pentane was added and difluoramine was removed. The lower layer was drained onto 50 g of ice, and extracted with 3 - 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.

(C) 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.

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

(C) The proton nmr spectrum showed a triplet (J = 2 cps) at 1.44 δ assigned to the $>C(NF_2)\underline{CH_3}$, a quintet (J = 2 cps) for the other methyl, a broadened doublet at 4.61 δ for $>CH\text{-}\underline{CH_2}O$-, and a complex multiplet (maximum intensity at 108 cps) for the remaining ring protons. The fluorine spectrum showed an AB quartet (-11.35 ϕ and -17.39 ϕ, J = 593 cps) for the single difluoramino group and a singlet at -27.80 ϕ for $>C(NF_2)_2$.

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

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APPENDIX B

THE SYNTHESIS OF FLUORAMMONIUM SALTS

Report No. 3495

THE SYNTHESIS OF FLUORAMMONIUM SALTS[1]

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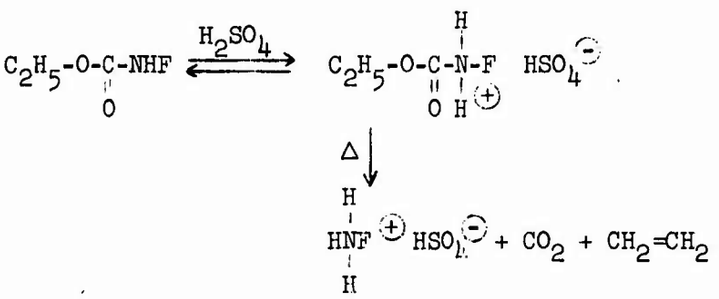
(U) Abstract: The reaction of alkyl N-fluorocarbamates with sulfuric acid gave fluorammonium bisulfate, which was identified by nmr spectra and by reactions with cyclohexanone and n-butyraldehyde to give ε-caprolactam and n-butyronitrile, respectively. Fluorammonium perchlorate and fluorammonium methanesulfonate were isolated as salts from reactions of N-fluorocarbamates with perchloric acid and methanesulfonic acid, respectively. Ethyl N-fluoro-N-methylcarbamate and sulfuric acid gave methylfluorammonium bisulfate, which reacted with cyclohexanone to give N-methylcaprolactam. Nmr spectra of fluorammonium perchlorate indicated rapid hydrogen exchange in acetonitrile and ethyl acetate, but not in sulfuric acid.

(U) Of the four possible fluorine-substituted ammonium ions, only the tetrafluoro derivative has been reported as a stable salt.[2,3] Difluoramine and trifluoramine have been reported to form reversible complexes with Lewis acids at low temperatures. Fluoramine was claimed to be a by-product of the electrolysis of ammonium bifluoride[5,6] but the results have been shown to be in error.[7] Dimethylfluoramine was synthesized by the fluorination of unsymmetrical dimethylsulfamide and the compound was sufficiently basic to form a stable hydrochloride.[8] Fluorimonium salts prepared by the rearrangement of alkyldifluoramines[9] can also be considered as alkylidene derivatives of substituted fluoramines.

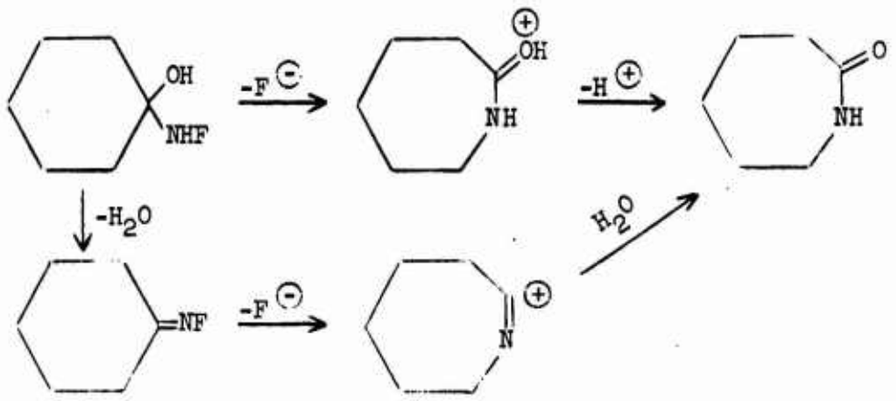
(U) Simple salts of fluoramine have now been prepared by the reaction of alkyl N-fluorocarbamates with strong acids. The starting materials are synthesized readily by the fluorination of alkyl carbamates.[10]

(U) Fluorammonium Bisulfate. Fluorimonium salts have been prepared and characterized in sulfuric acid. Under these conditions, the hydrolysis of N-fluorocarbamates in sulfuric acid would be expected to give the fluorammonium ion, which also should be stable.

(U) When a solution of ethyl N-fluorocarbamate in concentrated sulfuric acid was heated at 85 to 90°, carbon dioxide and ethylene were evolved. The F^{19} nmr spectrum of the sulfuric acid solution consisted of a quartet at 36.8 ppm relative to external trifluoroacetic acid, with a coupling constant of 38 cps. Thus, the fluorine was coupled to three equivalent hydrogens, and it is noteworthy that the hydrogens did not exchange rapidly with the solvent. By contrast, the F^{19} spectrum of an unheated solution of ethyl N-fluorocarbamate in sulfuric acid consisted of a single broadened signal at 27.5 ppm; the NH protons of the starting material thus exchanged with the solvent rapidly by the nmr time scale.



(U) Additional evidence for the fluorammonium ion structure was obtained from reactions with carbonyl compounds. The reaction of cyclohexanone with a sulfuric acid solution of fluorammonium bisulfate gave ε-caprolactam, isolated by quenching the mixture with ice. A probable intermediate was α-fluoraminocyclohexanol, which could lose a fluoride ion and undergo nucleophic ring expansion. Alternatively, the dehydration of this alcohol could give fluoriminocyclohexane, which, in turn, would undergo a similar ring expansion. The Beckmann fragmentation of fluorimines has been reported recently.[11]



(U) When n-butyraldehyde was treated similarly with the fluorammonium bisulfate solution, n-butyronitrile was formed. A related reaction, carried out in the presence of base instead of acid is the synthesis of nitriles from aromatic aldehydes and chloramine.[12]

$$CH_3CH_2CH_2CHO \xrightarrow[H_2O]{NH_3F^{\oplus}} CH_3CH_2CH_2C{\equiv}N$$

(U) Attempts to isolate pure fluorammonium bisulfate, by diluting the sulfuric acid solution with organic solvents, were unsuccessful.

(U) Fluorammonium Perchlorate. Perchloric acid, which is more volatile than sulfuric acid, appeared to offer better possibilities for the isolation of a pure fluorammonium salt. Accordingly, a solution of ethyl N-fluorocarbamate in 70% perchloric acid was heated until gas was evolved (68°), and the excess perchloric acid was then removed under vacuum. However, the product was contaminated by organic material of low volatility. Isopropyl N-fluorocarbamate reacted with 70% perchloric acid at a lower temperature than the ethyl ester (35 to 40°), and gave a less contaminated, but still unsatisfactory product. Unexpectedly, fluorammonium perchlorate was found to have appreciable vapor pressure, subliming slowly at 46°/.02 mm; the sublimed salt was analytically pure.

(U) It is well-recognized that the maximum acid strength of a solution is limited by the acidity of the conjugate acid of the solvent. For this reason, perchloric acid is a stronger acid in acetic acid than in aqueous solution.[13] Perchloric acid is soluble in chloroform[14]; therefore, this solvent, which has very low basicity, should enhance the acidity. Indeed, isopropyl N-fluorocarbamate reacted more

rapidly with a 10% solution of anhydrous perchloric acid in chloroform, than with the 70% commercial reagent. An additional advantage was that fluorammonium perchlorate was insoluble in chloroform. Analytically pure product was isolated directly in quantitative yield. The fate of the isopropyl group was not determined, but inasmuch as carbon dioxide free of propylene was liberated, it appears likely that isopropyl perchlorate was formed; if it was formed, it would remain in solution.[15]

$$(CH_3)_2CHOCNHF + 2\ HClO_4 \xrightarrow[42\text{-}43^{\circ}]{CHCl_3} (CH_3)_2CHOClO_3 + CO_2 \uparrow + \underline{NH_3FClO_4}$$

(U) Fluorammonium perchlorate was a white solid which melted with decomposition at 104 to 105°. Differential thermal analysis showed a sharp exotherm at this temperature. The impact sensitivity was the same as that of RDX. The salt was hygroscopic and decomposed rapidly in the presence of atmospheric moisture. Although the synthesis and isolation was carried out in glass equipment under an atmosphere of dry nitrogen, some etching of the glass was visible after several hours of contact with the salt. However, samples have been stored at room temperature for several months, without decomposition, in fluorocarbon or passivated-nickel containers.

(U) Fluoroammonium perchlorate was insoluble in hydrocarbons and halocarbons; it was soluble in simple esters, nitriles, nitroalkanes, and in such ethers as monoglyme and tetrahydrofuran. It formed a 1:1 complex with dioxane. Concentrated solutions (e.g., 30 to 50%) in any solvents were unstable, and in several instances, fumed off shortly after they were prepared. Addition of chloroform to the ethyl acetate solution precipitated unchanged fluorammonium perchlorate.

(U) The fluorine nmr spectrum of fluorammonium perchlorate in sulfuric acid consisted of a quartet (J = 44.1 cps) at 34.3 ppm from trifluoracetic acid (ϕ = 110.8), while the proton spectrum showed a doublet (J = 44 cps) at 10.28 δ.[16] However, when acetonitrile was used as the nmr solvent, the proton spectrum gave a broadened singlet at 10.7 δ, while the fluorine spectrum gave a slightly unsymmetrical singlet at 122.4 ϕ. In ethyl acetate, the proton signal was a sharp singlet at

11.5 δ, and the fluorine signal was a sharp singlet at 122.8 ϕ. Thus, rapid hydrogen exchange took place in the organic solvents but not in sulfuric acid. If the mechanism of exchange were direct displacement of protons, a higher rate could be expected in sulfuric acid than in the organic solvents. The more basic solvents apparently allow dissociation of fluorammonium perchlorate, to a small extent, to fluoramine and perchloric acid. The high volatility of fluorammonium perchlorate, compared to that of ammonium perchlorate might also be the result of dissociation.

$$H_3\overset{\oplus}{N}F\ ClO_4^{\ominus} \rightleftharpoons H_2NF + HClO_4$$

(U) Fluorammonium Methanesulfonate - Fluorammonium methanesulfonate was synthesized by heating ethyl N-fluorocarbamate and methanesulfonic acid at 90°. The salt was precipitated by the addition of ether. The melting point and dta exotherm were essentially the same as those of the perchlorate, and of the perchlorate-dioxane complex; this temperature range appears to be the stability limit of the fluorammonium ion.

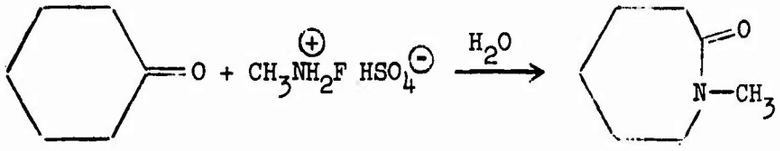
$$(CH_3)_2CHOCNHF + CH_3SO_3H \longrightarrow H_3NF^{\oplus}\ CH_3SO_3^{\ominus}$$

(U) The infrared spectrum is described in the Experimental Section.

(U) Methylfluorammonium Bisulfate - To determine whether substituted fluorammonium salts could be prepared by these methods, the reaction of ethyl N-fluoro-N-methylcarbamate with sulfuric acid was studied. Gas was evolved at 85 to 95°. The F^{19} nmr spectrum of the sulfuric acid solution consisted of an incompletely resolved triplet of quartets at -29.5 ppm (external trifluoroacetic acid reference), with coupling constants of 42 cps to the NH_2 and 28 cps to the methyl.

$$FN(CH_3)CO_2C_2H_5 \xrightarrow[\Delta]{H_2SO_4} F\text{-}\overset{\oplus}{N}H_2CH_3\ HSO_3^{\ominus}$$

A sulfuric acid solution prepared in this manner reacted with cyclohexanone and water to give N-methylcaprolactam.



(U) These reactions are analogous to those of the unsubstituted fluorocarbamates and indicate broad applicability of the synthesis methods.

Experimental Section

(U) Fluorammonium Bisulfate Solution. Ethyl N-fluorocarbamate (6.42 g, 0.060 moles) was added dropwise to 20 ml of concentrated sulfuric acid at room temperature, and the solution was heated at 85 to 90° until gas evolution ceased (20 min). A sample of the evolved gas was collected in an infrared cell and was shown by its spectrum to consist of carbon dioxide and ethylene. The 56.4 mc F^{19} nmr spectrum of the sulfuric acid solution consisted of a quartet at +36.8 ppm, referred to external trifluoroacetic acid, with J_{HF} = 38 cps. No ethyl N-fluorocarbamate remained. The F^{19} spectrum of a 10% solution of ethyl N-fluorocarbamate in sulfuric acid, freshly prepared at room temperature, consisted of a single broadened signal at +27.5 ppm.

(U) ε-Caprolactam. A fluorammonium bisulfate solution was prepared from 6.42 g (0.060 mole) of ethyl N-fluorocarbamate and 30 ml of concentrated sulfuric acid as above. To this solution at 0 to 2°, 4.9 g (0.050 moles) of cyclohexanone was added dropwise with stirring over a 25-min period. The resulting mixture was stirred at 5 to 10° for 30 min and was then poured onto 70 g of crushed ice. The mixture was neutralized with sodium hydroxide and extracted with five 50-ml portions of ether. The ether solution was dried over sodium sulfate and the solvent was distilled off. The residue was recrystallized from pentane to give 3.5 g (50% yield) of ε-caprolactam, mp 68° (not depressed in mixed mp with an authentic sample).

(U) n-Butyronitrile. A solution of fluorammonium bisulfate prepared from 4.3 g (0.04 moles) of ethyl N-fluorocarbamate and 25 ml of concentrated sulfuric acid was added to a mixture of 80 g of crushed ice and 1.44 g (0.020 moles) of n-butyraldehyde. The mixture was allowed to stand for 18 hr at room temperature, and was then extracted with four 30-ml portions of methylene chloride. The combined methylene chloride solutions were dried and distilled to give 1.1 g (76%

yield) of n-butyronitrile, bp 118°. Its infrared spectrum was identical with that of an authentic sample.

(U) Fluorammonium Perchlorate from Anhydrous Perchloric Acid. To a solution of 94 g (0.95 mole) of anhydrous perchloric acid[17] in 900 ml of chloroform (Baker's reagent grade, containing 0.6% methanol) was added dropwise, at 24° to 28° a solution of 56.6 g (0.468 moles) of isopropyl N-fluorocarbamate in 40 ml of chloroform. The addition was conducted behind a safety barricade. The liberation of carbon dioxide (identified by ir) began immediately. The reaction mixture was heated at 42° to 43° until the gas evolution ceased (15 to 20 min) and was then cooled to 25°. The product was filtered under nitrogen, washed with five 100-ml portions of chloroform, and dried at 0.2 mm Hg to give 63 g (0.465 moles, 99.5% yield) of fluorammonium perchlorate, mp 104 to 105° (dec).

(U) Anal. Calcd for NH_3ClFO_4: C, 0.0; H, 2.2; N, 10.4; F, 14.1. Found: C, 0.1; H, 2.3; N, 10.3; F, 14.0.

(U) Fluorammonium Perchlorate from 70% Perchloric Acid. Isopropyl N-fluorocarbamate (2 g) was added dropwise, with stirring at 25 to 30° to 2.8 g of 70% perchloric acid and the solution was heated for 1 hr at 35 to 40°. The solution was concentrated to half of its original volume at 40 to 43°/0.05 mm and cooled to 20°. The product which precipitated was filtered under nitrogen and dried under vacuum to give 0.5 g of impure fluorammonium perchlorate.

(U) Anal. Found: C, 0.7; H, 2.6; F, 13.1.

A less pure product was obtained when the original reaction mixture was stripped to dryness.

(U) When ethyl N-fluorocarbamate rather than the isopropyl derivative was used as the starting material, a reaction temperature of 68° was required, and product purity was affected adversely. Small samples of analytically pure fluorammonium perchlorate were isolated by subliming the crude material at 46°/0.02 mm. The addition of dioxane to a tetrahydrofuran solution of the crude product resulted in the precipitation of a 1:1 complex, mp 100 to 103° (dec.)

(U) Anal. Calcd for $C_4H_{11}NClFO_6$: C, 21.5; H, 4.90; N, 6.6; F, 8.55. Found: C, 21.5; H, 5.06; N, 6.2; F, 8.2.

(U) Fluorammonium Methanesulfonate. A solution of 1.5 g (0.014 moles) of ethyl N-fluorocarbamate in 6.2 ml of methanesulfonic acid was heated under nitrogen for

5 hr at 90 to 94°. The solution was cooled to room temperature and ether was added until the mixture became cloudy. After 1 hr, the crystalline product was filtered under nitrogen, washed with ether and dried under vacuum to give 1.05 g (57% yield) of white platelets, m.p. 103 to 105° (dec.).

(U) Anal. Calcd for CH_6NSO_3F: C, 9.16; H, 4.57; N, 10.7; F, 14.5. Found: C, 9.33; H, 4.77; N, 10.8; F, 14.6.

(U) The infrared spectrum of fluorammonium methanesulfonate, obtained using Fluorolube (2 to 7.5μ) and Nujol (7.5 to 16μ) mulls consisted of peaks at 3.0μ (sh), 3.20 (m), 3.30 (m), 3.58μ (w), 6.2 to 6.6μ (w), 7.15μ (m), 7.50μ (w), 8.05μ (sh), 8.2 to 8.6μ (s), 9.44μ (s), 9.69μ (s), 12.4μ (sh), 12.67μ (m), 12.90μ (w), 13.9μ (w), and 14.7μ (w).

(U) The F^{19} nmr spectrum in sulfuric acid was identical with that of the bisulfate solution.

(U) Methylfluorammonium Bisulfate Solution. A solution of 6.0 g (0.050 moles) of ethyl N-fluoro-N-methylcarbamate in 20 ml of concentrated sulfuric acid was heated at 85 to 95° until gas evolution ceased (20 min). The F^{19} nmr spectrum of this solution consisted of an incompletely resolved triplet of quartets at -29.5 ppm (external trifluoroacetic acid reference), $J_{NH_2\text{-}F}$ = 42 cps and $J_{CH_3\text{-}F}$ = 28 cps.

(U) N-Methylcaprolactam. A methylfluorammonium bisulfate solution prepared from 6.1 g (0.05 moles) of ethyl N-fluoro-N-methylcarbamate and 30 ml of sulfuric acid was cooled to 0° and added to a mixture of 150 g of crushed ice and 4.4 g (0.045 moles) of cyclohexanone. The resulting solution was allowed to stand at room temperature for 4 hr, and then was extracted with four 25 ml portions of methylene chloride. The combined methylene chloride solutions were dried with Drierite and distilled to give 2.5 g (44% yield) of N-methylcaprolactam, b.p. 50°/0.3 mm, N_D^{25} 1.4814 (literature values[18], bp 20°/19 mm, N_D^{25} 1.4818).

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The reactions of 2-bromo-2,4,4-trinitropentane and 2-chloro-2,4,4-trinitropentane with difluoramine gave 2,2,4,4-tetrakis(difluoramino)pentane, and 3,5-dimethylisoxazole was isolated as an intermediate. The reaction of 1-bromo-1-fluoro-1-nitropropane with difluoramine gave 1-difluoramino-1-bromo-1-fluoropropane. More severe reaction conditions gave degradation. The starting materials, 2-fluoro-2-nitroalcohols and ethyl 2-fluoro-1-nitropentanoate, were synthesized by the aqueous fluorination of the corresponding nitronate salts. The reaction of 2-phenylazo-2-nitropropane with difluoramine and fuming sulfuric acid gave 2-phenylazo-2-difluoraminopropane, benzene, acetone, 2,2-bis(difluoramino)propane, and O-(2-difluoraminopropyl)acetone oxime. The nitration of 2-phenylazo-2-difluoraminopropane has not yielded 2-nitro-2-difluoraminopropane, although 2-phenylazo-2-nitropropane gave 2,2-dinitropropane. No product of interest resulted from the reactions of difluoramine with ethyl nitrodiazoacetate, ethyl 2-butylnitronate, 1-diazo-2-heptanone, 2-nitropropene, diphenyliodium tosylate, and 1-iodo-1-nitrocyclohexane. The reaction of 3,3-bis(difluoramino)pentane with fluosulfonic acid gave 3-pentanone and difluoramine.

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