AD NUMBER
AD337753
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AUTHORITY
30 Jun 1975, Group 4, 30 Jun 1975; ONR ltr dtd 16 Feb 1979

AD 337 753

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CAMERON STATION, ALEXANDRIA, VIRGINIA

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(1) Grade

AZUSA PLANT

CHEMICAL PRODUCTS DIVISION

RESEARCH IN FLUORO-NITRO COMPOUNDS(U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

CONTRACT Nonr-2655(00)
ARPA ORDER NO. 170-61
PROJECT CODE 9100

REPORT NO. 0235-01-17 / JUNE 1963 / COPY NO. AF-11

AEROJET GENERAL TIRE GENERAL

AEROJET-GENERAL CORPORATION

AZUSA, CALIFORNIA

[redacted]

United States Patent Office Secrecy Order

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(4) NA

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AEROJET GENERAL TIRE GENERAL

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(9) Quarterly rept. no. 17, 1 MAR-31 MAY 63.

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

(7) NA
(8) U
(12) IV
(13) NA

(10) by K. Baum,
F. Gerhart,
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A. Remanick and
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(15) Contract Nonr 2655(00)
(16) ARPA ORDER 170-61
(17-19) NA
(20) C
(21) NA

a report to

U.S. NAVY
OFFICE OF NAVAL RESEARCH
WASHINGTON, D.C.

(14) Report No. 0235-01-17

(11) June 1963

AEROJET-GENERAL CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

CONFIDENTIAL

Report No. 0235-01-17

This is the seventeenth quarterly report prepared under Contract Nonr-2655(00). The ARPA Order No. is 170-61; the Project Code is 9100. It covers the period 1 March through 31 May 1963.

AEROJET-GENERAL CORPORATION

J R Fischer
for
L. R. Rapp, Manager
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ABSTRACT

5,5-Dinitro-2,2-bis(difluoramino)pentane was prepared by the reaction of 5,5,5-trinitro-2,2-bis(difluoramino)pentane with alkaline hydrogen peroxide. The reaction of this product with refluxing hydrochloric acid gave 4,4-bis(difluoramino)pentanoic acid.

The reduction of 1-methyl-1-(difluoramino)cyclohexane with lithium aluminum hydride gave N-methylcyclohexylamine and partially identified amines which appear to be 2-methylhexamethylenimine and 1-methylcyclohexylamine. The reduction of difluoraminocyclohexane gave hexamethylenimine and cyclohexylamine.

Attempts to convert ethyl 2,2-bis(difluoramino)propionate to a hydrazide by reaction with methanolic hydrazine, and to an alcohol by lithium borohydride reduction, were unsuccessful.

N,N-Difluorourea was obtained in the aqueous fluorination of formamide, methylisourea, and aminoiminomethanesulfinic acid.

Methyl N-fluorocarbamate was prepared by the fluorination of methyl carbamate. Its reaction with P_2O_5 gave methyl N,N'-difluoroallophanate.

The previously prepared N-fluoroammonium salt from ethyl N-fluorocarbamate and sulfuric acid was found to contain carbonaceous material. A virtually carbon-free salt was prepared from sulfuric acid and excess methyl N-fluorocarbamate.

Azine fluoride was treated with alkali fluorides. No evidence for an adduct was found.

CONTENTS

I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military applications.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum, F. J. Gerhart)

1. Discussion

An investigation of the synthetic usefulness of 5,5,5-trinitro-2,2-bis(difluoramino)pentane was begun in the previous report period.* The trinitromethyl group could not be hydrolyzed to a carboxyl group with refluxing hydrochloric acid. Preliminary evidence indicated, however, that one nitro group could be removed by the action of alkaline peroxide. Since terminal dinitro compounds are hydrolyzed more easily than are unactivated trinitromethyl compounds,** this route was followed in an attempt to prepare a γ-bis(difluoramino) carboxylic acid.

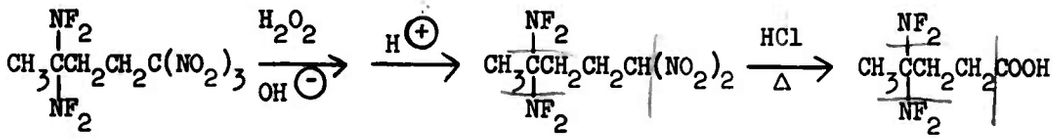
The reaction of 5,5,5-trinitro-2,2-bis(difluoramino)pentane with alkaline hydrogen peroxide was carried out in methanol in the temperature range 0 to 10°C. The product, isolated in 71.5% crude yield, was a high-boiling liquid which could not be fractionally distilled. The elemental analysis of a sample purified only by molecular distillation was in moderately good agreement with the theoretical values for 5,5-dinitro-2,2-bis(difluoramino)pentane. The infrared spectrum (Figure 1) obtained conforms to that for such a structure, with some hydroxyl- and carbonyl-containing impurities.

*Aerojet-General Report 0235-01-16, March 1963, p. 7 (Confidential).

**M. J. Kamlet, L. A. Kaplan and J. C. Dacons, J. Org. Chem., 26, 4371 (1961).

II Technical Discussion, A (cont.)

This material was heated with constant boiling hydrochloric acid for 4 hours to form 4,4-bis(difluoramino)pentanoic acid. This product was a high-boiling liquid which was difficult to purify. Elemental analysis, infrared (Figure 2), proton (Figure 3) and fluorine (Figure 4) NMR spectra all confirmed the structural assignment, but indicated that some impurities were present.



The preparation of the starting material, 5,5,5-trinitro-2,2-bis(difluoramino)pentane, was found to be very sensitive to experimental conditions. The use of a large excess of 100% sulfuric acid as the solvent for the reaction of difluoramine with 5,5,5-trinitro-2-pentanone required a pressure reactor and a 40-hour reaction period.* Even then a considerable amount of starting material was recovered. When a relatively small amount of 20% fuming sulfuric acid was used as the solvent, the reaction was complete after 2 hours at the reflux temperature of difluoramine, and a quantitative yield was obtained.

The study of the effect of reducing agents on NF compounds was also continued. The lithium aluminum hydride reduction product of 1-methyl-1-(difluoramino)cyclohexane was previously found to be a mixture of two amines with the empirical formula $C_7H_{15}N$.** The Hinsberg test of this mixture gave no acid-soluble or base-soluble products, indicating a mixture of secondary amines. The NMR spectrum of the mixture of benzenesulfonamides contained signals identical to those of an authentic sample of the benzenesulfonamide of N-methylcyclohexylamine. In addition, there were signals assignable to the derivative

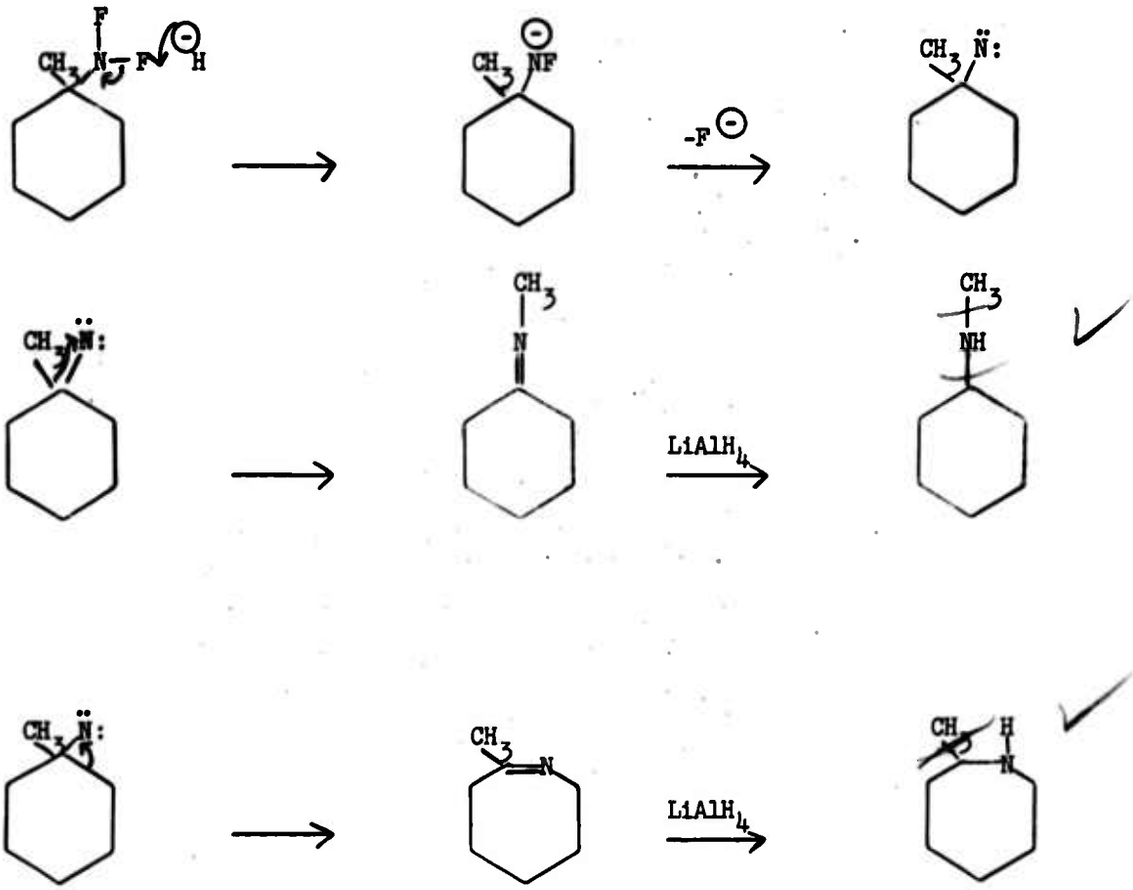
*Aerojet-General Report 0235-01-13, March 1962, p. 9 (Confidential).

**Aerojet-General Report 0235-01-16, March 1963, p. 5 (Confidential).

II Technical Discussion, A (cont.)

of 2-methylhexamethyleneimine. There was also a second methyl peak, possibly due to the benzenesulfonamide of 1-methyl-1-cyclohexylamine (this hindered sulfonamide might have unusual solubility properties). Attempts will be made to resolve the mixture of amines by gas chromatography.

The rearranged amines might be formed from the nitrene resulting from hydride attack on fluorine followed by loss of fluoride.



II Technical Discussion, A (cont.)

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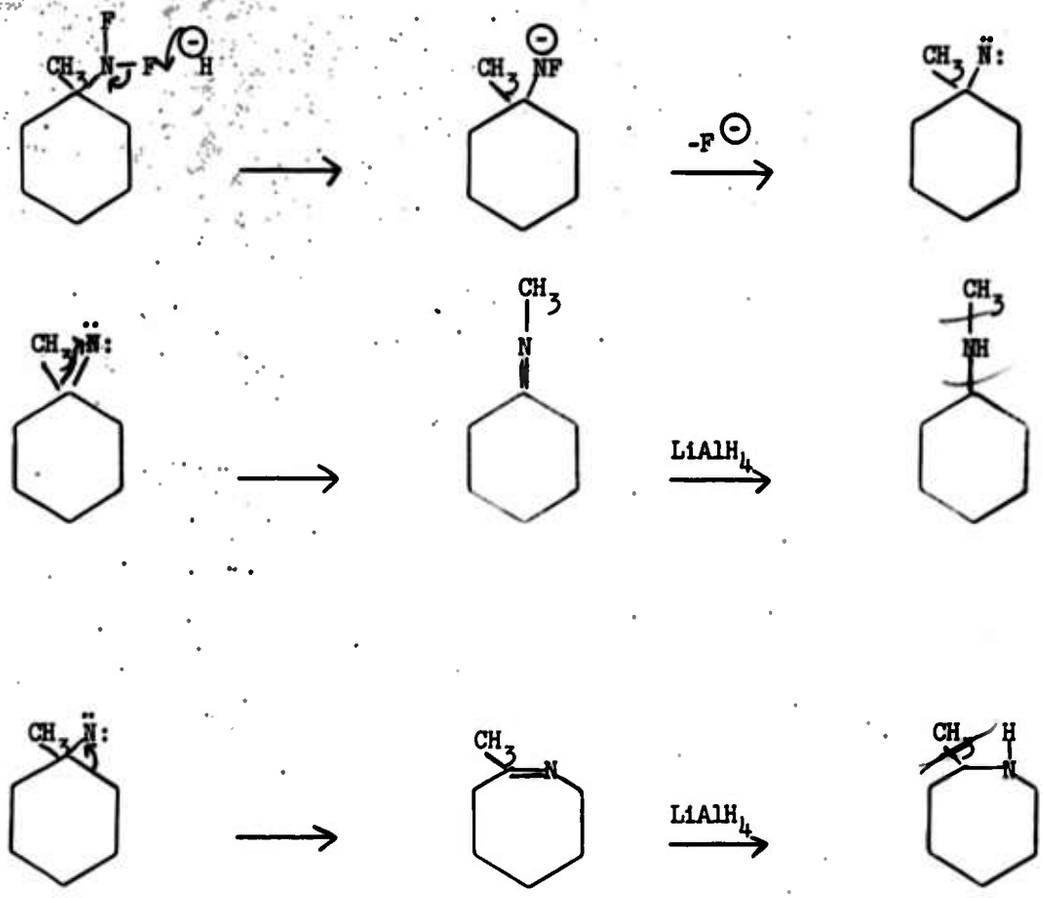
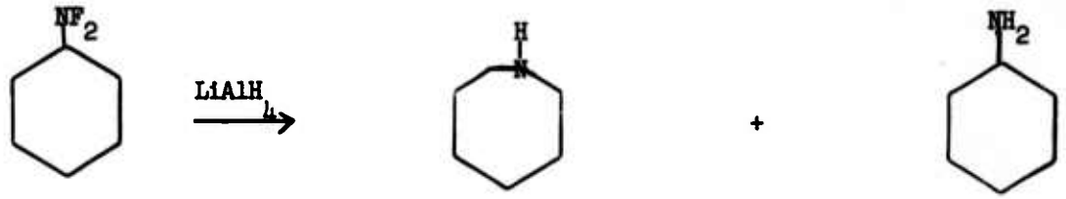
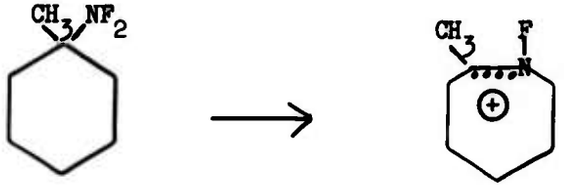


II Technical Discussion, A (cont.)

The reduction of difluoraminocyclohexane with lithium aluminum hydride followed a similar course. The product was a 70:30 mixture of hexamethylenimine and cyclohexylamine. It was identified by comparing the NMR spectra and gas chromatograph retention times with those of authentic samples.



The reaction of 1-methyl-1-difluoraminocyclohexane with acids results in fluoride loss and ring expansion to give a stable cation.*



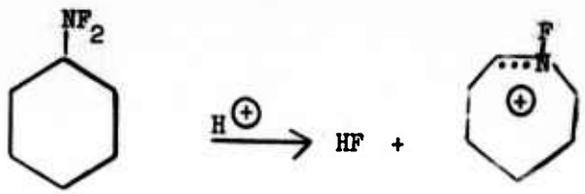
Since secondary alkyl difluoramines are also known to be unstable to strong acids,** it was of interest to examine the structure of the decomposition products.

When a sample of difluoraminocyclohexane was shaken with sulfuric acid, it reacted exothermically to give a clear solution. The F^{19} NMR spectrum of this sulfuric acid solution (Figure 5a) contained an HF peak at -6758 cps (relative to trifluoroacetic acid) and a multiplet at -9804 cps, which at lower sweep (Figure 5b) was found to consist of five components. If these are regarded as overlapping triplets, they are consistent with the ring-expanded cation (coupling constants of 12 and 24 cps to $-CH_2-$ and $-\overset{\oplus}{C}H-$).

*Aerojet-General Report 0235-01-16, March 1963, p. 5 (Confidential).

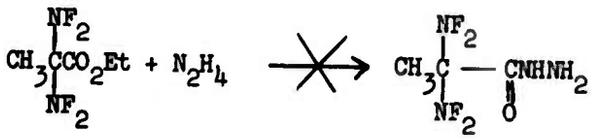
**Aerojet-General Report 2381, October 1962, p. 11 (Confidential).

II Technical Discussion, A (cont.)



The proton NMR spectrum (Figure 6) contains a pair of triplets at 2.52 ppm (relative to H_2SO_4) assigned to $-NF-\overset{\oplus}{C}H-CH_2-$, a broad poorly resolved doublet at 6.83 ppm assigned to $-CH_2-CH_2-NF-$, a broad signal at 8.46 ppm assigned to $-CH_2-CH_2\overset{\oplus}{C}H-$, and a large peak at 9.56 ppm assigned to the remaining six protons.

The feasibility of converting a gem-difluoramino ester into an isocyanate by the hydrazide route has been demonstrated, using ethyl 5,5-bis(difluoramino)hexanoate.* The extension of this reaction series to ethyl 2,2-bis(difluoramino)propionate, which has recently been prepared,** was attempted since the product would be a valuable intermediate. However, several attempts to prepare the hydrazide were unsuccessful, and inorganic fluorides were formed. The results are similar to those reported by Rohm & Haas** for the reaction of ammonia with ethyl 2,2-bis(difluoramino)propionate.



The reaction of this ester with lithium borohydride was also attempted, under the conditions that were used to reduce ethyl 5,5-bis(difluoramino) hexanoate to the corresponding alcohol.***

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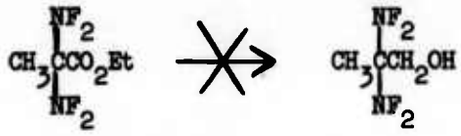
* Aerojet-General Report 0235-01-16, March 1963, p. 6 (Confidential).

** Rohm & Haas, Quarterly Progress Report on ARPA Projects, No. P-62-26, p. 5 (Confidential).

*** Aerojet-General Report 0235-01-15, January 1963, p. 9 (Confidential).

II Technical Discussion, A (cont.)

Although an exothermic reaction occurred, no ether-soluble compound other than starting material was formed.



2. Experimental

a. 5,5,5-Trinitro-2,2-bis(difluoramino)pentane

A solution of 15 g (0.068 moles) of 5,5,5-trinitro-2-pentanone in 50 ml of 20% fuming sulfuric acid was prepared by partially freezing the acid with dry ice and adding the ketone with stirring. The mixture was then frozen and connected to a difluoramine generator. Difluoramine (approximately 27 g) was allowed to reflux over the mixture for 2 hours. A white precipitate began to form as soon as the acid was melted. The excess difluoramine was removed after 50 ml of methylene chloride was added and the lower (sulfuric acid) layer was discarded. The methylene chloride layer was dried over sodium sulfate and diluted to 100 ml. Stripping an aliquot of solvent showed that the solution contained 20.9 g (0.0676 moles, 99.5% yield) of 5,5,5-trinitro-2,2-bis(difluoramino)pentane, mp 42°C.*

b. 5,5-Dinitro-2,2-bis(difluoramino)pentane

A solution of 3 g (0.0097 moles) of 5,5,5-trinitro-2,2-bis(difluoramino)pentane in 12 ml of methanol was prepared in a 100-ml three-necked flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel. The flask was cooled with an ice-salt bath, and a 1.7 ml portion of 30% aqueous hydrogen peroxide (0.0146 moles) was added rapidly. A solution of 1.88 g (0.0285 moles) of 85% potassium hydroxide in 15 ml of methanol was added slowly during a 30-min time span while the temperature of the reaction

*Aerojet-General Report 0235-01-13, March 1962, p. 9 (Confidential).

II Technical Discussion, A (cont.)

mixture was kept under 10°C. The solution was stirred at 0°C for 15 min, then diluted with 15 ml of water and acidified with 25% sulfuric acid. The solution was extracted with three 25-ml portions of methylene chloride which were combined and dried over sodium sulfate. The solvent was removed, leaving 1.83 g (0.00693 moles, 7?.5% yield) of crude 5,5-dinitro-2,2-bis(difluoramino) pentane. An analytical sample was prepared by molecular distillation.

Anal. Calc'd for $C_5H_8N_4F_4O_4$: C, 22.7; H, 3.03; N, 21.2; F, 22.8.

Found: C, 23.2; H, 3.37; N, 18.0; F, 26.7.

The infrared spectrum of the analytical sample (Figure 1) was virtually identical with that of the undistilled material.

c. 4,4-Bis(difluoramino)pentanoic Acid

Crude 5,5-dinitro-2,2-bis(difluoramino)pentane, (1.5 g, 0.0057 moles) was refluxed with 40 ml of constant boiling hydrochloric acid for 4 hours. The resulting solution was cooled to room temperature and extracted with three 30-ml portions of methylene chloride. The extracts were combined and dried over sodium sulfate. The solvent was distilled off through a 25-cm platinum spiral column. The residue was then vacuum-distilled to give 0.25 g (0.00126 moles, 22.1% yield) of 4,4-bis(difluoramino)pentanoic acid, bp 90°C/ 0.05 mm.

Anal. Calc'd for $C_5H_8N_2F_4O_2$: C, 29.4; H, 3.92; N, 13.7; F, 37.2.

Found: C, 27.4; H, 3.61; N, 13.0; F, 34.9.

The 60-mc proton NMR spectrum (Figure 2) was obtained using a CCl_4 solution with TMS added as an internal reference. The quintet at 1.68 ppm is assigned to the terminal methyl group $\underline{CH_3}C(NF_2)_2$- and the multiplet (or pair of overlapping multiplets) with peaks at 152 and 157 cps are tentatively assigned to the methylene groups. The broadened signal at 11.83 ppm is assigned to the carboxylic acid proton. No assignments are

II Technical Discussion, A (cont.)

obvious for the weak multiplets indicated by question marks and presumably they are due to impurities. The 56.4 mc F^{19} spectrum was obtained using the same sample with $CFCl_3$ added as an internal reference. The spectrum consists of an intense signal at -26.86 ppm accompanied by relatively weak signals at -27.15 ppm (an unresolved shoulder) and -28.24 ppm. The intense signal may be assigned to the difluoramino groups in the desired product. The shoulder at -27.15 ppm indicates the presence of a few percent of starting material. The -28.24 ppm signal presumably results from an impurity.

d. Reduction of Difluoraminocyclohexane

Difluoraminocyclohexane (2.40 g, 0.0179 moles) was added dropwise to a solution of 2.85 g (0.0716 moles) of 95% lithium aluminum hydride in 75 ml of diethyl ether. The solution was stirred for 20 hours at ambient temperature. Water was then added carefully to the reaction mixture to decompose the unreacted lithium hydride. The product was extracted with three 30-ml portions of ether which were combined and dried over sodium sulfate. The solvent was distilled off through a 25 cm platinum spiral column. Vacuum distillation of the residue gave 1.30 g of colorless liquid, bp 37°C/7 mm. Proton NMR spectra and gas chromatograms corresponded to a 70:30 mixture of hexamethylenimine and cyclohexylamine.

e. Reaction of Hydrazine with Ethyl 2,2-Bis(difluoramino) propionate

To 1.8 g (0.0088 moles) of ethyl 2,2-bis(difluoramino)propionate dissolved in 6 ml of methanol was added 0.58 g (0.0176 moles) of 97% hydrazine while the reaction vessel was cooled to 0°C. The solution turned yellow with the formation of a white precipitate which was filtered off. The solid was non-oxidizing and contained no carbon. The methanol solution was dried over sodium sulfate and the solvent was distilled off through a 25-cm platinum spiral column. The residue was flash-distilled at 1 mm to give 0.42 g (23.4% recovery) of ethyl 2,2-bis(difluoramino)propionate as indicated by its infrared spectrum.

II Technical Discussion, A (cont.)

f. Reaction of Lithium Borohydride with Ethyl 2,2-Bis(difluoramino)propionate

Ethyl 2,2-bis(difluoramino)propionate (1.1 g, 0.0054 moles) dissolved in 5 ml of pentane was added dropwise over a 15 min period to 0.47 g (0.022 moles) of lithium borohydride in 15 ml of tetrahydrofuran. The temperature rose to 55°C during the addition. The solution was cooled to room temperature and 20 ml of water was added. The layers were separated and the water mixture was extracted three times with 20 ml portions of ether. The extracts were combined, dried over sodium sulfate, and distilled to give 0.47 g of starting material (42.7% recovery), bp 43°C/5 mm.

B. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

It has been shown that the fluorination of aqueous primary amides results in the formation of the corresponding amines by the Hofmann rearrangement of the N-fluoroamide intermediates.* Since the Hofmann rearrangement of N-haloformamides has not been reported in the literature, it was of interest to examine the aqueous fluorination of formamide. The fluorination product in this case was identified as N,N-difluorourea. Formamide apparently underwent fluorination to give the monofluoro derivative. The elimination of hydrogen fluoride and hydrogen migration in the resulting nitrene would give cyanic acid, which would form urea. The fluorination of the latter then accounts for the product.

$$HCONH_2 + F_2 \xrightarrow{(H_2O)} [HCONHF] \xrightarrow{-HF} [HCO\ddot{N}:] \longrightarrow HNCO$$

$$HNCO \xrightarrow{(H_2O)} NH_2CONH_2 \xrightarrow{F_2} NF_2CONH_2$$

Some attempts were made to synthesize perfluoroamidine derivatives by the fluorination of amidines:

$$NH_2C(=NH)X + F_2 \xrightarrow{(H_2O)} NF_2C(=NF)X$$

*Aerojet-General Report No. 0235-01-16, March 1963, p. 14, (Confidential).

II Technical Discussion, B (cont.)

The fluorination of methylisourea sulfate ($X=OCH_3$) and aminoiminomethanesulfinic acid ($X=SO_2H$), however, yielded N,N-difluorourea, apparently as a result of the hydrolysis of partially fluorinated intermediates.

Some side reactions that have been observed in reactions of ethyl N-fluorocarbamate might be avoided by the use of methyl N-fluorocarbamate. The latter was, therefore, synthesized by the fluorination of aqueous methyl carbamate; its infrared, its proton and its fluorine NMR spectra are shown in Figure 7, 8, and 9, respectively.

The reaction of ethyl N-fluorocarbamate with phosphorous pentachloride was attempted previously with the objective of preparing FNCO. The product, however, was a complex mixture which was not identified*. Recently, the reaction between methyl N-fluorocarbamate and phosphorus pentoxide was investigated. After a mixture of these reagents was heated at 65 to 75°C for 48 hours, approximately 70% of the N-fluorocarbamate was recovered. The reaction product, a white solid, was tentatively identified as methyl N,N'-difluoroallophanate on the basis of its elemental analysis and infrared spectrum (Figure 10). Since NMR spectra of the material have not yet been obtained, the positions of fluorines in the molecule remain to be confirmed. Fluorine isocyanate was not detected in this reaction. The allophanate might be formed by the <u>in situ</u> reaction of FNCO with N-fluorocarbamate, or by a simple condensation:

$$NHFCOOCH_3 \xrightarrow[\Delta]{P_2O_5} NHFCONFCOOCH_3$$

Methyl N,N'-difluoroallophanate is the first known urea derivative fluorinated on both nitrogens. Since this compound is of interest for fluorination studies, attempts were made to improve the yield of the material. But when a mixture of methyl N-fluorocarbamate and phosphorus pentoxide was heated to 100°C, the mixture fumed off. When gaseous carbamate was passed through hot phosphorus pentoxide, no reaction occurred, even at 170°C.

*Aerojet-General Report No. 2099 (Annual Summary), November 1961, p. 31 (Confidential).

II Technical Discussion, B (cont.)

The reaction between thionyl chloride and N-fluorocarbamate appeared to offer an alternative route to N,N'-difluoroallophanates via either fluorine isocyanate or N-fluorocarbamyl chloride:

$$NHFCOOR + SOCl_2 \xrightarrow{?} FNCO \text{ or } NFCOCl \longrightarrow NHFCONFCOOR$$

R = CH3 R = CH3

No reaction took place when a mixture of thionyl chloride and methyl N-fluorocarbamate was refluxed for several hours. When a trace of pyridine was added, a reaction occurred at 70 to 75°C, liberating sulfur dioxide but no FNCO. The pot residue, a viscous nondistillable liquid, did not contain methyl N,N'-difluoroallophanate. The structure of this material is under investigation.

In another experiment, methyl N-fluorocarbamate was found to react readily with hydrogen chloride at ambient temperature with the formation of ammonium fluoride. The generation of hydrogen chloride in the thionyl chloride-N-fluorocarbamate reaction obviously adds to the complexity of side reactions.

2. Experimental

a. Methyl N-Fluorocarbamate

A solution of 75 g (1.0 mole) of methyl carbamate in 500 ml water was fluorinated at 0 to 5°C with fluorine diluted with nitrogen (1:3) until 22.5 liters of fluorine was consumed. The reaction mixture was extracted with ten 50-ml portions of diethyl ether. The combined ethereal extracts were dried, filtered, and concentrated; the residual pale-yellow liquid fractionated to give 22 g of a colorless liquid, bp 62-4°C/26 mm, n_D^{25} 1.3895.

Anal. Calc'd for $C_2H_4FNO_2$: C, 25.81; H, 4.33; N, 15.05; F, 20.42.

Found: C, 25.4; H, 4.4; N, 15.0; F, 20.4.

The infrared spectrum of methyl N-fluorocarbamate is shown in Figure 7.

II Technical Discussion, B (cont.)

Since the material is only slightly soluble in carbon tetrachloride, the NMR spectra were obtained in chloroform. The 60 mc proton NMR spectrum (Figure 8) was obtained using TMS as an internal reference. The spectrum consists of signals at 4.02 ppm (sharp singlet assigned to CH_3O_2CNHF) and a doublet at 10.10 ppm (splitting 58 cps, assigned to $NHFCO_2CH_3$) whose components are very broad and weak. This portion of the spectrum was repeated at higher RF level and recorder gain to obtain the shift and the splitting.

The 56.4 mc F^{19} NMR spectrum (Figure 9) was obtained using the same sample with Freon-11 added as an internal reference. The spectrum consists of a single signal, a doublet (splitting 56 cps) at +6920 cps (+119.1 ppm) from Freon-11. The doublet is assigned to $NHFCO_2CH_3$. The proton and F^{19} NMR spectra are consistent with each other and with the structure.

b. Fluorination of Formamide

A solution of 22.5 g (0.5 mole) of formamide in 350 ml water was fluorinated at 0 to 5°C until 12 liters of fluorine gas was consumed. The reaction mixture was extracted with six 50-ml portions of diethyl ether. The etheral solution was worked up to give 2.5 g of a white solid (sublimed), mp 42-3°C. The material was identified as N,N-difluorourea by its infrared spectrum.

c. Fluorination of Methylisourea Sulfate

A solution of 28 g of methylisourea sulfate in 350 ml water was fluorinated at 0 to 5°C until 12 liters of fluorine gas was consumed. The reaction mixture was extracted with five 50-ml portions of diethyl ether, and the combined ethereal extracts was dried, filtered, and concentrated. The residual yellow solid was recrystallized from carbon tetrachloride to give 4.5 g of a white solid, mp 42°C, identified (infrared spectrum) as N,N-difluorourea.

d. Fluorination of Aminoiminomethanesulfinic Acid

A solution of 54 g (0.5 mole) of aminoiminomethanesulfinic acid in 600 ml water was fluorinated at 0 to 5°C until 28 liters of fluorine

II Technical Discussion, B (cont.)

gas was consumed. The reaction mixture was extracted with diethyl ether and the ethereal solution worked up to give 5.0 g of a white solid, mp 41°C, identified (infrared spectrum) as N,N-difluorourea.

e. Methyl N,N'-Difluoroallophanate

A mixture of 8.0 g of phosphorus pentoxide and 8.0 g methyl N-fluorocarbamate was heated at 65 to 75°C for 48 hours. Only little gassing occurred during the heating period and no products accumulated in a -80°C trap connected in series with the reaction flask. The mixture was then distilled at reduced pressure to yield 6.5 g of methyl N-fluorocarbamate. A viscous liquid (1.0 g) distilled at 0.1 mm at a pot temperature of 75 to 95°C and solidified at room temperature. The material was purified by crystallization from carbon tetrachloride to give a white solid with a mp of 64°C. Its infrared spectrum (Figure 10) is in agreement with the proposed allophanate structure.

Anal. Calc'd for $C_3H_4N_2F_2O_3$: C, 23.38; H, 2.62, N, 18.18; F, 24.7.

Found: C, 23.3; H, 3.2; N, 17.8; F, 23.8.

f. Reaction of Methyl N-Fluorocarbamate with Hydrogen Chloride

Dry hydrogen chloride was passed at 3 to 5 bubbles a second into 3 g of methyl N-fluorocarbamate at 30 to 35°C for 20 min. The reaction mixture gradually turned turbid and a white solid precipitated. The solid was removed by filtration and was recrystallized from water-ethanol. The non-oxidizing solid did not melt at 300°C and contained 55% fluorine (calculated for NH_4F, 51.4%). Its infrared spectrum (in KBr) was identical with that of ammonium fluoride.

C. FLUORAMMONIUM SALTS (A. H. Remanick and V. Grakauskas)

1. Discussion

Previous work has shown that the reaction of ethyl N-fluorocarbamate with concentrated sulfuric acid gave a white solid, tentatively

II Technical Discussion, C (cont.)

identified as fluorammonium bisulfate*. It was found that modification of the experimental conditions previously described improved product yield. Thus, reaction of ethyl N-fluorocarbamate with excess 100% sulfuric acid followed by careful addition of diethyl ether gave a white solid which was essentially identical with that obtained in the earlier work.

Further characterization of this material confirmed the presence of the fluorammonium cation, but a mixture of cations apparently was present.

Elemental analysis revealed a 1 to 1 ratio of N and F. In addition, reaction of the solid with aqueous potassium iodide gave an oxidation equivalent which was 90% of theoretical based on the reaction:

$$H_3NF^{\oplus} + 2I^{\ominus} \longrightarrow NH_3 + I_2 + F^{\ominus}$$

Previously, the F^{19} NMR spectrum of the solid in concentrated sulfuric acid had shown a symmetrical quartet (j=45 cps) as expected for the fluorammonium cation. The H^1 NMR spectrum in concentrated sulfuric acid (Figure 11) showed a doublet centered at +0.25 ppm, relative to H_2SO_4 (j=45 cps), a pair of weak irregular triplets at +6.09 ppm and +7.05 ppm, and a weaker quartet and triplet at +6.36 and +9.42 ppm, respectively. The presence of a doublet, having the same "j" value as that for the quartet in the F^{19} NMR spectrum confirmed the structure of the fluorammonium cation.

The other signals which were present in the H^1 NMR spectrum suggested the presence of XCH_2CH_2Y and CH_3CH_2Z structures. Elemental analysis revealed that carbon and nitrogen were present in equimolar quantities. The amount of sulfate precipitated by Ba^{++} was only about half of that indicated by combustion sulfur analysis, suggesting the presence of carbon-sulfur compounds. The H^1 NMR spectrum of sodium isethionate ($NaSO_3CH_2CH_2OH$) in concentrated sulfuric acid showed a pair of irregular triplets of the same form

*Aerojet-General Report No. 0235-01-16, March 1963, p. 22 (Confidential).

II Technical Discussion, C (cont.)

shown by the fluorammonium salt, but with slightly displaced shifts (i.e., +6.26 ppm and +7.22 ppm, relative to H_2SO_4). The difference in the chemical shifts may be due to a concentration effect. Since isethionate and ethylsulfate are isomeric, elemental analysis could only give the total amount of these materials. It was estimated, by NMR, and they were present in the ratio of 9 to 1.

Attempted purification of the salt by recrystallization was prevented by its instability in hydroxylic solvents and insolubility in other common organic solvents. Reprecipitation from concentrated sulfuric acid did not improve the purity of the solid.

The solid was stable at room temperature for several days under anhydrous conditions although it decomposed rapidly at 90°C. The material was relatively inert to impact, friction, and static charge.

For the purpose of eliminating some of the side reactions which occurred in the solvolysis of ethyl N-fluorocarbamate, the reaction of methyl N-fluorocarbamate with concentrated sulfuric acid was investigated. The use of excess sulfuric acid gave a solid of lower F to N ratio than in the case of the ethyl derivative. However, preliminary results indicated the use of excess methyl N-fluorocarbamate afforded a product, substantially free of carbon, corresponding to $H_2NF^{\oplus}HSO_4^{\ominus}$ by elemental analysis (calculated for $FNH_3^{\oplus}HSO_4^{\ominus}$; H,3.0; N,10.5; F,14.31. Found: C,0.2; H,4.4; N,11.6; F,14.6. There was insufficient material for sulfate analysis. The solid appeared to be somewhat soluble in the carbamate, suggesting the use of the latter as a solvent for recrystallization and metathetical reactions. The details of this reaction are being examined more closely.

The possibility of liberating fluoramine by the reaction of the salt from ethyl N-fluorocarbamate with a weak base was examined. Since it was expected, by analogy with chloramine, that fluoramine would be an unstable gas, the gaseous products were passed directly into a sulfuric acid trap. The

II Technical Discussion, C (cont.)

bases employed in the reactions were s-collidine and dibutyl carbitol. In neither case did the F^{19} NMR spectrum of the sulfuric acid from the trap indicate the presence of the fluorammonium cation.

2. Experimental

a. Reaction of Ethyl N-Fluorocarbamate with Sulfuric Acid

To 7.35 g (0.075 mole) of 100% sulfuric acid was added, with stirring, 1.5 g (0.014 mole) of ethyl N-fluorocarbamate. The reaction mixture was protected from the atmosphere by a sulfuric acid bubbler and heated to 90°C over a 15 min period. After gas evolution had ceased (about 10 min), the mixture was allowed to cool to room temperature. Diethyl ether (ca. 15 ml) was added until the mixture became cloudy. During the ether addition, the temperature of the solution rose to 45°C. After about 30 min, the oil which had initially formed solidified. The suspension was centrifuged and the resulting solid was washed twice with diethyl ether. Possible traces of ether were removed under vacuum, leaving 0.8 g of solid. Found: C, 7.82; H, 3.08; N, 9.7; F, 13.4; $SO_4^=$ (precipitated by Ba^{++}), 32.1; combustion sulfur (as $SO_4^=$) 75.1; F (by KI) = 12.3.

b. Reaction of Methyl N-Fluorocarbamate with Sulfuric Acid

A mixture of 3.0 g of methyl N-fluorocarbamate and 0.25 g of 100% sulfuric acid was heated at 95 to 98°C for 30 min. The originally clear solution became turbid after 15 min and a white solid was gradually deposited. The reaction mixture was cooled to room temperature and the solid was filtered off, washed with methyl N-fluorocarbamate followed by diethyl ether and was then vacuum dried. The material melted at 132 to 134°C with slow decomposition.

Anal. Calc'd for $NH_3F^{\oplus}HSO_4^{\ominus}$: C, 0.0; H, 3.0; N, 10.5; F, 14.3

Found: C, 0.2; H, 4.4; N, 11.6; F, 14.6

II Technical Discussion, C (cont.)

c. Attempted Preparation of Fluoramine

In a 5-ml flask containing a magnetic stirrer and syringe inlet and protected from the atmosphere by a sulfuric acid trap (which contained 1.2 ml of 100% sulfuric acid) was placed 0.61 g of the solid mentioned in paragraph II,C,2,a and 5.0 ml of diethyl ether. The system was flushed with nitrogen and 0.75 g of s-collidine (sufficient to liberate 85% of the fluoramine in the mixed salt) in 2.0 ml of ether was slowly added. After gas evolution ceased, the sulfuric acid was examined by NMR. No F^{19} signal was present.

In a similar manner, s-collidine in decalin was reacted with a suspension of the mixed salt in decalin. In this experiment, the pressure in the system was maintained at 33 mm and the gaseous products were passed through a -20°C trap before entering the sulfuric acid trap. No F^{19} signals were present in the NMR spectrum of the sulfuric acid solution.

In a 25 ml flask equipped with a magnetic stirrer and connected through a 0°trap to another trap containing 1.2 ml of 100% sulfuric acid, was placed 0.5 g of the mixed fluorammonium salt and 15 ml of dry dibutyl carbitol. The system was evacuated to 0.1 mm through the sulfuric acid trap and maintained at this pressure for 3 hours. The system was then opened to the atmosphere and the contents of the sulfuric acid trap submitted for NMR analysis. No F^{19} signals were present. The 0° trap was then replaced by a reflux condenser containing ice and connected to a trap containing 1.2 ml of 100% sulfuric acid. The system was evacuated to 0.1 mm and the dibutyl carbitol suspension slowly heated to 85°C and maintained at this temperature for 1.5 hours. NMR analysis of the contents of the sulfuric acid trap revealed no F^{19} signal.

D. REACTION OF AZINE FLUORIDE WITH ALKALI FLUORIDES (R. K. Robeson)

1. Discussion

Haller found that azine fluoride was adsorbed by KF at room temperature and that the resulting material exploded when it was heated to 80°C*.

*J. F. Haller, Doctoral Thesis, Cornell University, 1942.

II Technical Discussion, D (cont.)

The possibility that the complex contained the $F_2N_3^{\ominus}$ ion led us to attempt to determine the structure of the material.

Attempts to form this complex have been unsuccessful to date. The method employed involved the reaction of hydrazoic acid, prepared from sodium azide and stearic acid, with helium-diluted fluorine in a flow system to produce FN_3. When the latter was purified by distillation from cold Freon-11 and passed over KF, no adsorption (evidenced by weight gain) took place.

Similar experiments involving RbF and CsF also indicated that no FN_3-alkali fluoride complex had formed under the conditions employed. In one experiment, FN_3 was not dissolved in Freon-11, but was passed directly over KF. Although an explosion of the HN_3 generator occurred before the experiment was completed, a small gain in weight of the KF tube was observed. This experiment will be repeated.

2. Experimental

The alkali-metal fluorides were prepared for use by washing the commercially available anhydrous materials with spectro-grade CCl_4 in a dry box, filtering the solutions, and subsequently drying the solids at 125°C overnight.

In a typical experiment, HN_3 was generated over a 45 min period from a mixture of 98.5 g (0.347 moles) of stearic acid and 15.5 g (0.249 moles) of NaN_3 at 125°C. The HN_3 stream (diluted with He) was subsequently mixed with excess F_2 (also diluted with He) in a stainless steel reaction coil maintained at about 25°C, and the reaction products were passed through traps maintained at 0° (to remove unreacted HN_3), and at -80°C (containing 300 ml of Freon-11). The FN_3 collected in the latter trap to give a pale green solution containing little or no elemental fluorine. On warming, the FN_3 volatilized and was passed through tared tubes containing a large excess of alkali metal fluorides. Infrared spectra of the gas stream entering and leaving the tubes

II Technical Discussion, D (cont.)

confirmed the presence of FN_3. No gain in weight of the tubes was observed, and no iodine was formed when the contents of the tubes were emptied into acidified KI solution.

III. PERSONNEL

The experimental synthesis work was performed by F. J. Gerhart, M. Mascari, A. H. Remanick, E. D. Gilley, R. K. Robeson, V. Grakauskas and K. Baum. Analytical support was provided by H. Nelson (NMR), K. Inouye (Microanalysis), D. I. Matson (IR) and H. W. Pust (Gas Chromatography).

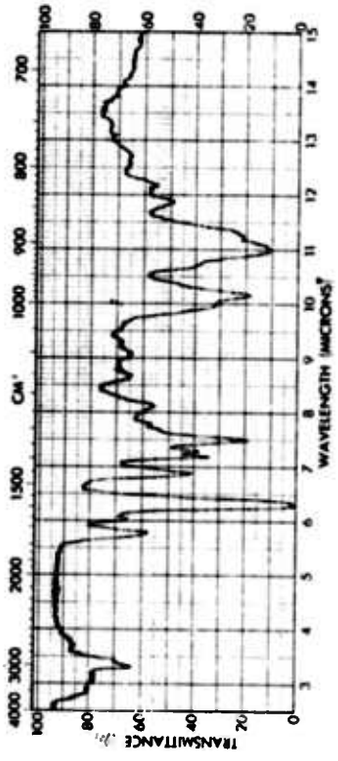


Figure 1. Infrared Spectrum of 5,5-Dinitro-2,2-Bis(difluoramino)pentane

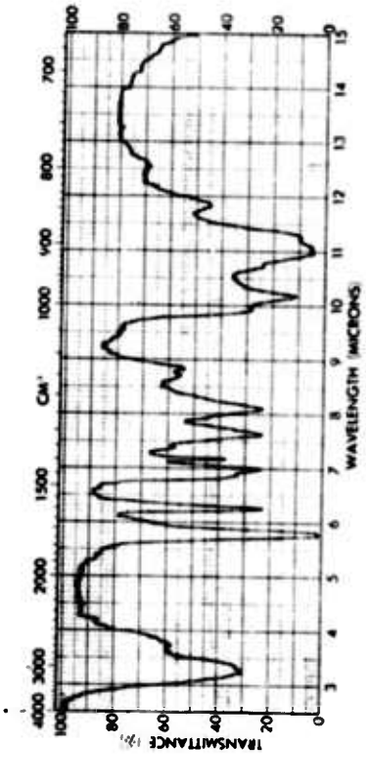


Figure 2. Infrared Spectrum of 5,5-Bis(difluoramino)pentanoic Acid

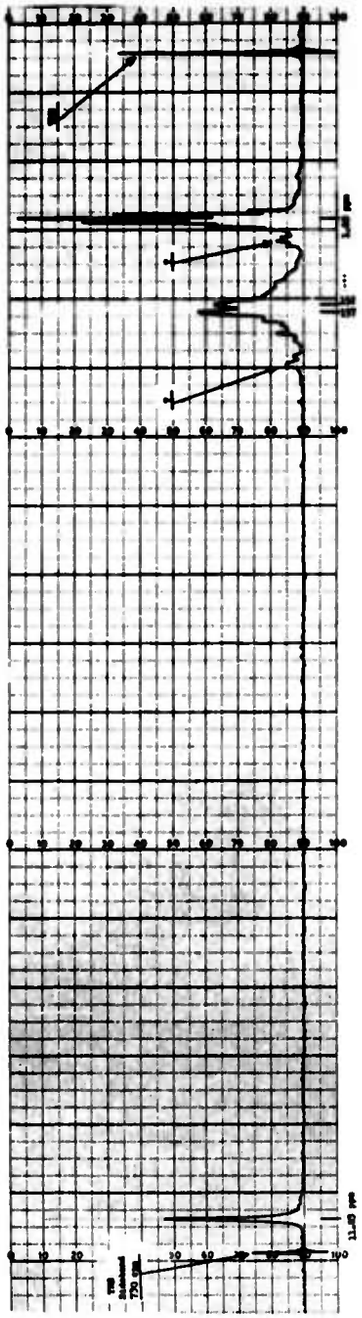


Figure 3. Proton NMR Spectrum of 5,5-Bis(difluoramino)pentanoic Acid

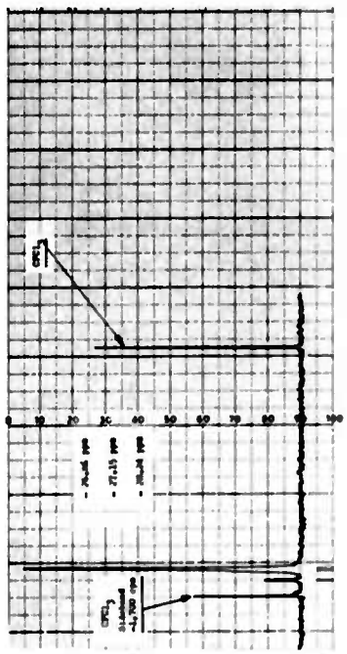


Figure 4. Fluorine NMR Spectrum of 5,5-Bis(difluoramino)pentanoic Acid

Figures 3 and 4

Figure 5a. Fluorine NMR Spectrum of Difluoraminocyclohexane-Sulfuric Acid Reactions Product

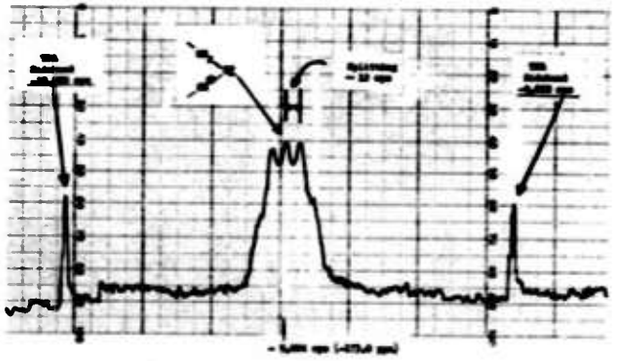


Figure 5b. Fluorine NMR Spectrum of Difluoraminocyclohexane-Sulfuric Acid Reaction Product

Figures 5a and 5b

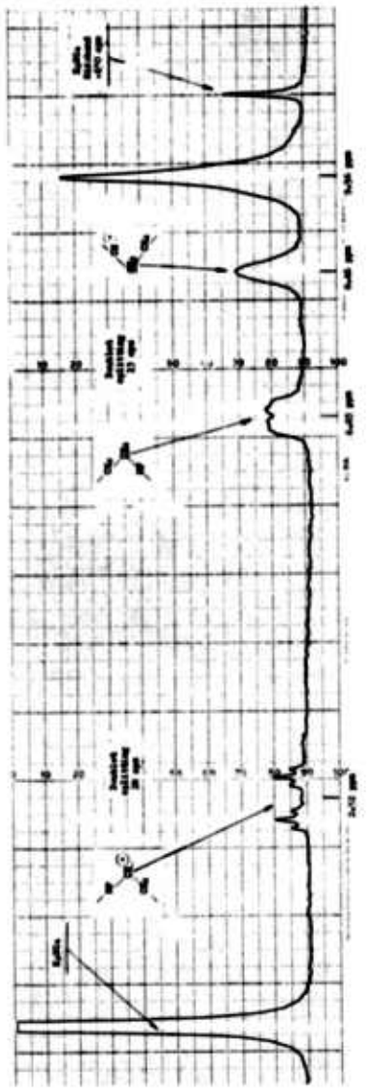


Figure 6. Proton NMR Spectrum of Difluoraminocyclohexane-Sulfuric Acid Product

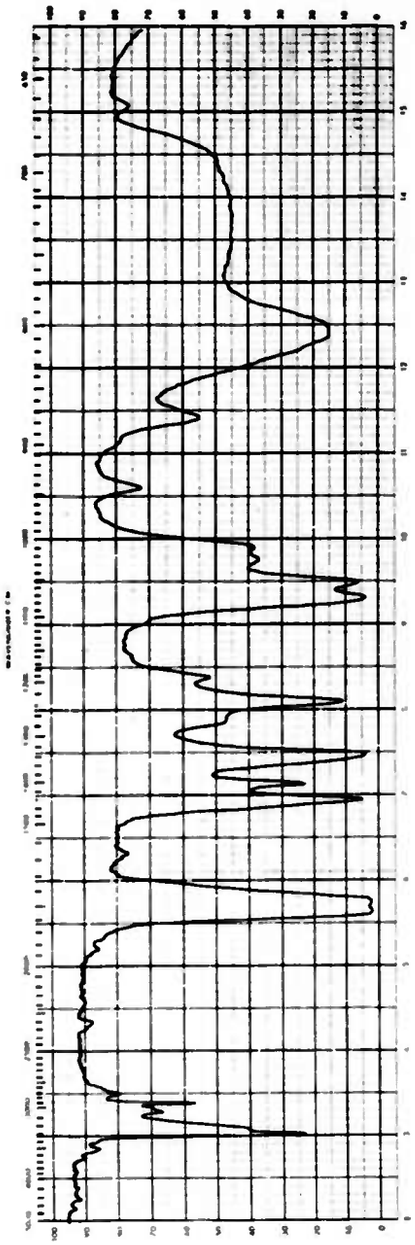


Figure 7. Infrared Spectrum of Methyl N-Fluorocarbamate

Figures 6 and 7

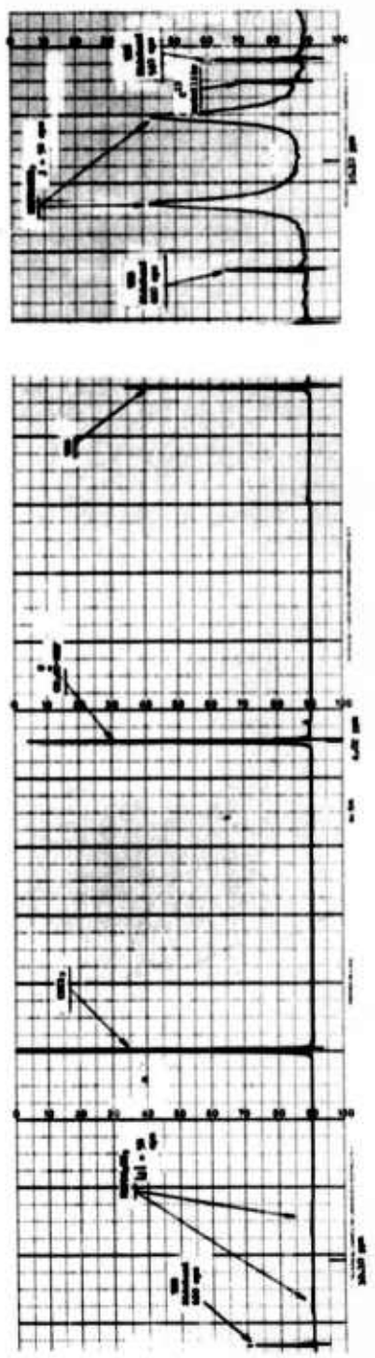


Figure 8. Proton NMR Spectrum of Methyl N-Fluorocarbamate

Figure 8

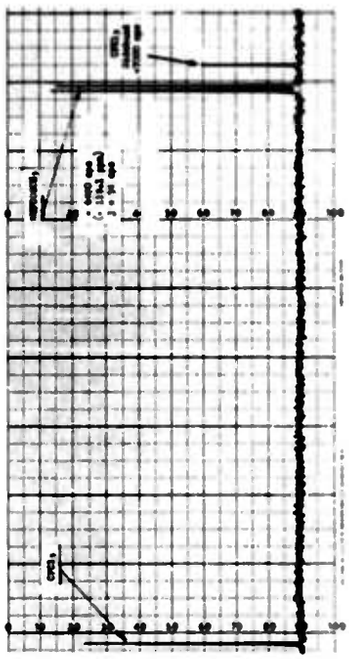


Figure 9. F^{19} NMR Spectrum of Methyl N-Fluorocarbamate

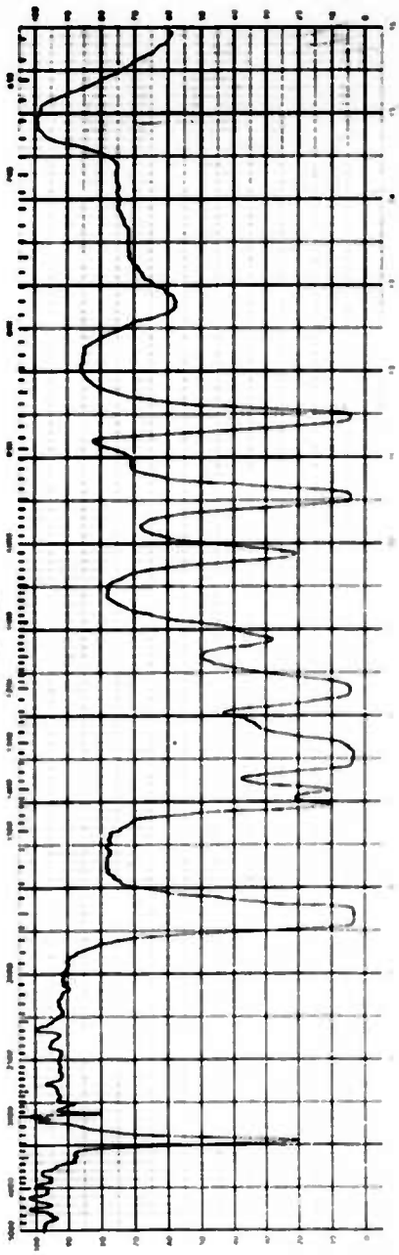


Figure 10. Infrared Spectrum of Methyl N,N'-Difluoroallophanate

Figures 9 and 10

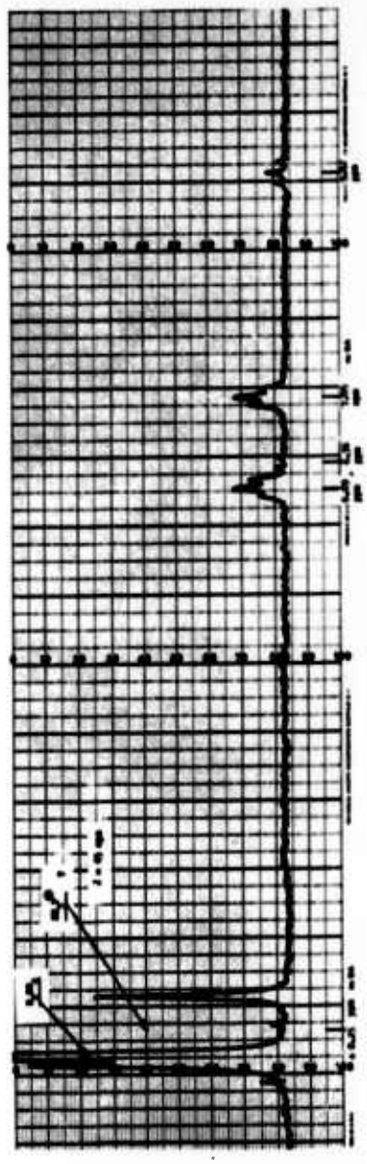


Figure 11. Proton NMR Spectrum of the Reaction Product of Ethyl N-Fluorocarbamate and Sulfuric Acid

Figure 11

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