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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. 0235-01-16 / MARCH 1963 / COPY NO. AF-12-9

AEROJET GENERAL TIRE GENERAL

AEROJET-GENERAL CORPORATION

AZUSA, CALIFORNIA

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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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a report to

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

Report No. 0235-01-16 March 1963

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

Report No. 0235-01-16

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AEROJET-GENERAL CORPORATION

for L. R. Fischer
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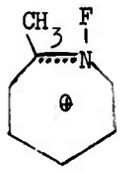
Report No. 0235-01-16

ABSTRACT

3-Fluoro-3-(difluoramino)hexane and 2-fluoro-2-(difluoramino)hexane were identified as products of the reactions of 3-hexyne and 1-hexyne, respectively, with difluoramine in the presence of $BF_3 \cdot H_3PO_4$. The former product was also prepared by the reaction of 3-hexyne with difluoramine and hydrogen fluoride.

1-Methyl-1-(difluoramino)cyclohexane was prepared from 1-methyl-1-cyclohexene and difluoramine. It reacted with sulfuric acid and boron trifluoride to give the bisulfate and fluoborate, respectively, of the stable cation,



The reduction of 1,3,3-bis(difluoramino)butane with lithium borohydride gave an almost quantitative yield of 1-amino-3,3-bis(difluoramino)butane.

Ethyl 5,5-bis(difluoramino)hexanoate was converted to the hydrazide, which gave the corresponding isocyanate by nitrosation followed by the Curtius rearrangement. Addition of ammonia to the isocyanate gave 4,4-bis(difluoramino)-pentyl urea.

The aqueous fluorination of acetamide in the presence of cyclohexanone gave methylamine and ϵ-caprolactone. The latter was formed by the fluorination of cyclohexanone. The fluorination of cyclohexanecarboxylic acid amide gave cyclohexylamine and some cyclohexyl isocyanate, indicating a Hofmann rearrangement under acidic conditions.

The fluorination of cyclohexylurea gave cyclohexyl isocyanate, difluoraminocyclohexane and N,N-difluorocyclohexylurea. No NF compound was isolated from the fluorination of thiourea. The fluorination of diethyl tetramethylenedicarbamate gave 1,4-bis(difluoramino)butane.

A solid, apparently impure N-fluoroammonium bisulfate, was isolated by treating the reaction product of ethyl N-fluorocarbamate and sulfuric acid with diglyme.

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I. INTRODUCTION

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

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

a. Addition of Difluoramine to Acetylenes

The reaction of 3-hexyne with difluoramine - catalyzed by the boron trifluoride complex of phosphoric acid - has been reported to give a mixture of products including 3,3-bis(difluoramino)hexane and 3-hexanone*. Another component of this mixture, which could not be separated completely from 3-hexanone by gas chromatography using a silicone column, was resolved with a dioctyl phthalate column. It was identified as 3-fluoro-3-(difluoramino)hexane by elemental analysis, by its infrared (Figure 1), proton (Figure 2), and fluorine (Figure 3) NMR spectra, and by its mass spectral cracking pattern (Table 1). The NMR and mass spectra are discussed in the experimental section.

The most likely mechanism for the formation of 3-fluoro-3-(difluoramino)hexane is the addition of hydrogen fluoride to 3-hexyne to form 3-fluoro-3-hexene followed by the addition of difluoramine. This course was confirmed in a separate experiment by bubbling anhydrous hydrogen fluoride into a refluxing mixture of 3-hexyne and difluoramine to give the same compound.

The source of the 3,3-bis(difluoramino)hexane in this reaction does not appear to be the reaction of the ketone with difluoramine, since one experiment using 3-pentanone in the presence of $BF_3 \cdot H_3PO_4$ failed to give the

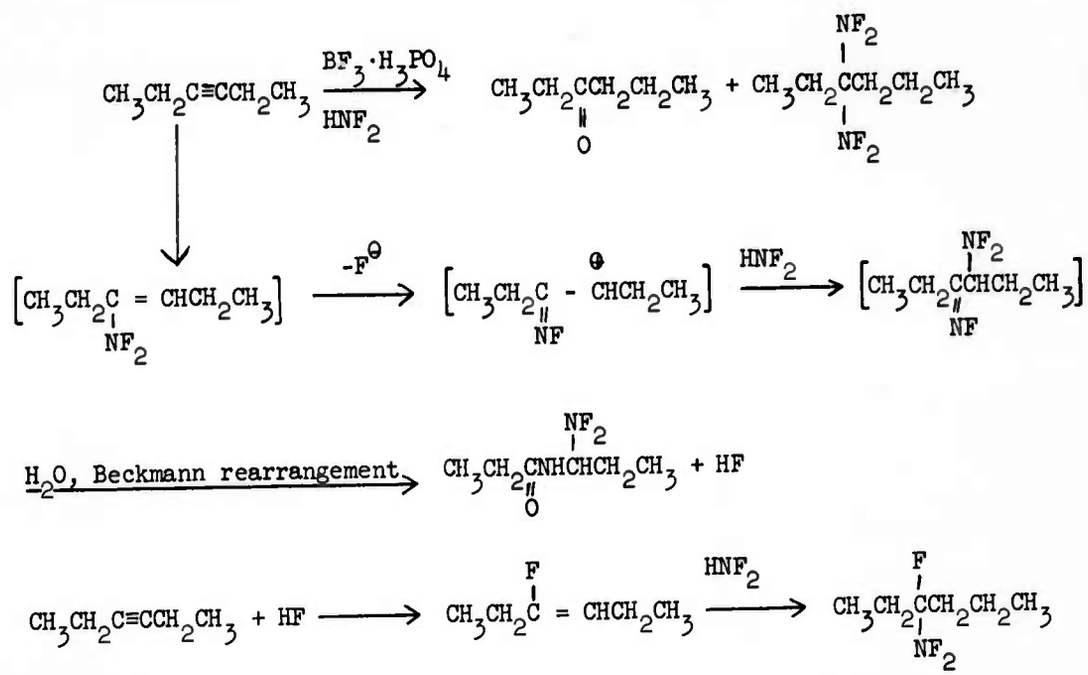
*Aerojet-General Report No. 0235-01-15, January 1963, p. 4 (Confidential).

II Technical Discussion, A (cont.)

gem-difluoramine. Rohm & Haas has also reported an unsuccessful attempt to convert a ketone to a gem-difluoramine with this catalyst*. The possibility that the gem-difluoramine might be formed from 3-fluoro-3-(difluoramino)hexane will be investigated.

A previously isolated product of the reaction of 3-hexyne with difluoramine in the presence of $BF_3 \cdot H_3PO_4$ was tentatively assigned the structure N-(1-difluoraminopropyl) propionamide on the basis of its infrared and NMR spectra, although its elemental analysis was in only fair agreement with the theoretical values*.

This oil has recently been crystallized from ether-pentane to yield a solid, mp 50 to 51.5°C, which gave the correct analytical data for this structure.



*Rohm & Haas Co., Report No. P-62-12, July 15, 1962, p. 10 (Confidential).

II Technical Discussion, A (cont.)

The analogous products from the reaction of 1-hexyne with difluoramine were also isolated and identified. The two volatile, previously unresolved components were separated with a dioctyl phthalate column. The first of these was identified by elemental analysis and by its infrared (Figure 4), proton (Figure 5), and fluorine (Figure 6) NMR spectra as 2-fluoro-2-(difluoramino)hexane. The second product was identified by its infrared spectrum as 2-hexanone.

The high-boiling product which was tentatively identified as N-(difluoraminomethyl)valeramide on the basis of its infrared and NMR spectra could not be purified further by low-temperature recrystallization. The elemental analysis of the previously obtained sample was in fair agreement with this structure.

b. Reactions of Alkyl Difluoramines

In previous reports*, the stability of the gem-difluoramino function toward some commonly used synthetic reagents was studied, using 2,2-bis(difluoramino)octane and ethyl 5,5-bis(difluoramino)hexanoate as model compounds. This study has been continued and has also been extended to isolated difluoramino groups.

1-Methyl-1-(difluoramino)cyclohexane was prepared as a model t-alkyl difluoramine. It was synthesized in 83% yield by the reaction of 1-methyl-1-cyclohexene with difluoramine in the presence of $BF_3 \cdot H_3PO_4$, and was characterized by elemental analysis and its infrared (Figure 7), proton (Figure 8), and fluorine (Figure 9) NMR spectra.

This compound was desired mainly to show how t-alkyl difluoramines are degraded by sulfuric acid. It was previously found that

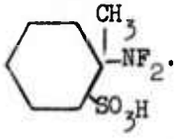
*Aerojet-General Report 2381, October 1962 (Confidential);
Aerojet-General Report 0235-01-15, January 1963 (Confidential).

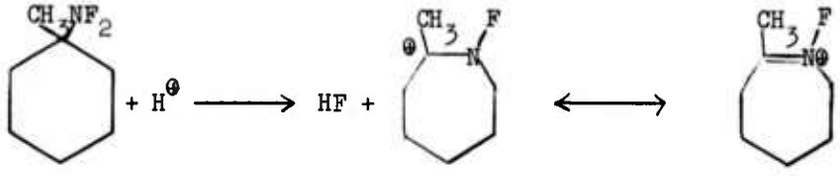
II Technical Discussion, A (cont.)

t-butyl difluoramine reacted with sulfuric acid to form a soluble intermediate which gave acetone on dilution with water.*

It was postulated that the intermediate was the sulfonation product, which might be hydrolyzed to methanesulfonic acid and acetone. Since methanesulfonic acid cannot be separated easily from sulfuric acid, 1-methyl-1-(difluoramino)cyclohexane was used in the hope of obtaining a product with both degradation fragments tied into the same molecule.

This compound was found to react exothermically with concentrated sulfuric acid, giving a colorless homogeneous solution. However, an attempt to distill the product which was isolated after quenching led to decomposition.

The F^{19} NMR spectrum of a freshly prepared solution of 1-methyl-1-(difluoramino)cyclohexane in sulfuric acid consisted of a poorly resolved triplet at -4104 cps (J = 16 cps) relative to external $CFCl_3$, and a singlet at -2159 shown to be due to HF. The triplet cannot be attributed to the expected sulfonic acid  . The results, however, can be explained by fluoride loss and ring expansion as follows:

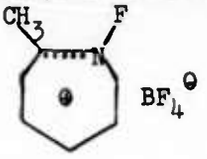


An attempt was made to isolate a salt containing this novel ion by passing gaseous boron trifluoride into a solution of 1-methyl-1-(difluoramino)cyclohexane in sulfur dioxide. Evaporation of the SO_2 left a liquid which still had a slight odor of SO_2. The F^{19} spectrum contained a

*Aerojet-General Report 2099, November 1961, p. 10 (Confidential); Aerojet-General Report 0235-01-13, March 1962, p. 4 (Confidential).

II Technical Discussion, A (cont.)

triplet at -3922 (J = 17 cps), and a singlet at +8524, attributable to $BF_4^{\ominus}$. When pentane was used as the solvent in this preparation, rather than SO_2, a hygroscopic semisolid was isolated, the elemental analysis of which was in moderately good agreement with the theoretical for



This type of rearrangement may be the cause of the general instability of isolated NF_2 groups toward strongly ionizing acids. The stabilizing effect of adjacent NF_2 groups may be attributed to the inductive effect, which would increase the energy of the resulting ion.

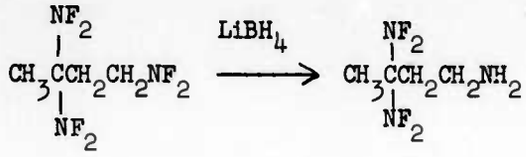
The reduction of 1-methyl-1-(difluoramino)cyclohexane with lithium aluminum hydride in ether gave a 5 to 1 mixture of two amines, as analyzed by gas chromatography. These compounds could not be separated by preparative gas chromatography, but they were separated by fractional recrystallization of the hydrochlorides. The elemental analysis of the lower melting of these salts was consistent with the structure, 1-methyl-1-aminocyclohexane hydrochloride (or an isomer). The analysis of the other salt and the NMR spectra are not yet available. One of these amines could be the ring-expanded secondary amine, inasmuch as similar rearrangements have been reported in the reduction of cyclic nitro compounds*.

A study was also begun of the chemistry of 1,3,3-tris-(difluoramino)butane, which was prepared by the reaction of methyl vinyl ketone with difluoramine in sulfuric acid**. The yield of this adduct was increased to 60% by using a large excess difluoramine, with 100% sulfuric acid as the dehydrating agent. The reaction of 1,3,3-tris(difluoramino)butane with lithium borohydride in tetrahydrofuran gave an almost quantitative yield of 1-amino-3,3-bis(difluoramino)butane, isolated as the hydrochloride.

*G. E. Lee, et al., Chem. and Ind., 1958, 417.

**Aerojet-General Report No. 0235-01-11, July 1961, p. 8 (Confidential).

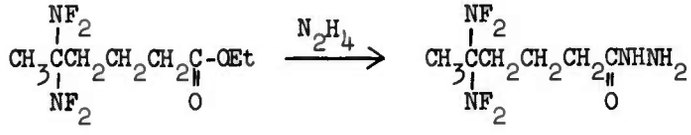
II Technical Discussion, A (cont.)

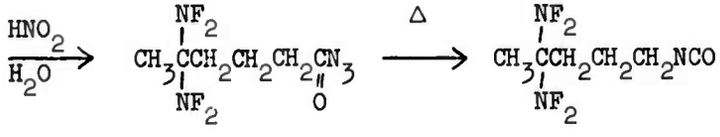


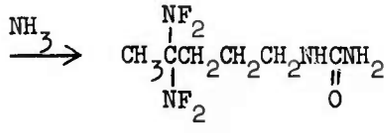
The hydrochloride salt was identified by elemental analysis and by its infrared spectrum in a KBr pellet (Figure 10).

Some unsuccessful attempts were made to dehydrofluorinate 1,3,3-tris(difluoramino)butane to 3,3-bis(difluoramino)butyronitrile. The reaction with sodium methoxide in methanol for 1/2 hour at room temperature resulted in the recovery of only 36% of the starting material, but no other product was found. No reaction took place when gaseous ammonia was bubbled through a pentane solution of the tris(difluoramino)butane.

A new reaction of ethyl 5,5-bis(difluoramino)hexanoate which was investigated was its conversion to the corresponding isocyanate by the Curtius reaction.







II Technical Discussion, A (cont.)

The hydrazide, prepared by heating the ester with methanolic hydrazine, was not characterized, but was treated directly with nitrous acid. Decomposition of this azide in chloroform gave a product which was indicated by its infrared spectrum to be a mixture containing approximately equal amounts of the original ester and the isocyanate. Evidently the preparation of the hydrazide was incomplete. The isocyanate was characterized by converting it to the corresponding urea, a solid derivative, by the addition of gaseous ammonia.

An investigation was also begun of the synthetic usefulness of 5,5,5-trinitro-2,2-bis(difluoramino)pentane*. Hydrolytic degradation of the nitro groups could give 4,4-bis(difluoramino)pentanoic acid, which could not be prepared by direct methods. However, no reaction took place when the general procedure reported by Hamlet, Kaplan and Dacons** was used, and the starting material was recovered. An attempt was also made to convert the trinitromethyl group to a dinitromethyl group by the use of alkaline peroxide. A material was isolated which appeared to contain the desired product on the basis of its infrared spectrum; elemental analysis indicated, however, that the material was impure.

2. Experimental

a. The previously described chromatographic separation of the volatile products of the reactions of 3-hexyne with difluoramine did not give a sample of the initially eluted component uncontaminated by the second component***. However, a trapped mixture of the first two components was resolved using a 1/4 in. by 6 ft column of dioctyl phthalate on Teflon to obtain an analytical sample of the first component.

*Aerojet-General Report No. 0235-01-13, March 1962, p. 9 (Confidential).

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

***Aerojet-General Report No. 0235-01-15, January 1963, p. 4 (Confidential).

II Technical Discussion, A (cont.)

Analysis Calculated for $C_6H_{12}NF_3$: C, 46.5; H, 7.75; N, 9.05; F, 36.8

Found: C, 45.9; H, 7.67; N, 9.05; F, 34.3

The infrared spectrum (Figure 1) is consistent with this structure.

The 60 mc proton NMR spectrum, with TMS as reference (Figure 2), contains a multiplet with its most intense peak at 62 cps. This multiplet may be regarded as a pair of overlapping triplets assignable to the terminal methyls in the structure $CH_3CH_2CF(NF_2)CH_2CH_2CH_3$. The other signals are then assigned to the remaining methylenes in the ethyl and propyl groups. The 56.4 mc F^{19} spectrum (Figure 3) was obtained with $CFCl_3$ as an internal reference. The signal at approximately -942 cps (-16.7 ppm) is assigned to $-NF_2$; the signal at approximately +8194 cps (+145.3 ppm), which is roughly half the intensity of the other, is assigned to $-CF(NF_2)-$. Although the signal-to-noise ratio was too small to show clearly the form of the multiplet, it corresponds, at least roughly, to the quintet which would be expected from coupling to the adjacent methylene protons with possible further splitting from coupling to $-NF_2$. The mass cracking pattern is shown in Table 1.

The high-boiling liquid product which was previously isolated from the reaction of 3-hexyne with difluoramine was purified by a low-temperature crystallization and recrystallization from ether-pentane to give solid N-(1-difluoraminopropyl)propionamide, mp 50 to 51.5°C.

Analysis Calculated for $C_6H_{12}N_2F_2O$: C, 43.4; H, 7.23; N, 16.8; F, 22.9.

Found: C, 43.4; H, 7.65; N, 16.7; F, 22.1.

b. Reaction of 1-Hexyne with Difluoramine

The mixture of volatile products from the reaction of 1-hexyne with difluoramine, catalyzed by $BF_3 \cdot H_3PO_4$, was separated by the same chromatographic procedure used for the 3-hexyne product.

II Technical Discussion, A (cont.)

The first component was identified as 2-fluoro-2-(difluoramino)hexane. The infrared spectrum (Figure 4) is consistent with this structure.

Analysis Calculated for $C_6H_{12}NF_3$: C, 46.5; H, 7.75; N, 9.05; F, 36.8.

Found: C, 45.7; H, 8.24; N, 8.73; F, 34.0.

The proton NMR spectrum (Figure 5) was obtained with a Varian microcell using a 10% solution in CCl_4 with TMS as an internal reference. The irregular triplet at 0.95 ppm is assigned to the terminal methyl, $\underline{CH_3}CH_2$-. The signals at 84 cps and 103 cps are interpreted as a pair of triplets centered on 1.87 ppm and assigned to the other terminal methyl, $-CH_2CF(NF_2)\underline{CH_3}$. The doublet splitting (19 cps) is assumed to result from coupling to the $\underline{CF}$ fluorine and the triplet splitting from the $\underline{NF_2}$ fluorines. The pair of triplets is superimposed on a broader absorption which presumably is due to the chain methylene groups.

The 56.4 mc F^{19} spectrum (Figure 6) was obtained using the same sample with $CFCl_3$ added as an internal reference. The somewhat broadened signal at -1076 cps (-19.1 ppm) is assigned to $-\underline{NF_2}$. The signal at +8220 cps (+145.7 ppm) is apparently a regular sextet with a splitting of approximately 18 cps. It is assigned to $-CH_2\underline{CF}(NF_2)CH_3$.

The mass spectral cracking pattern is shown in Table 2.

The high-boiling product previously isolated* could not be purified by low-temperature recrystallization as was done for the analogous product from 1-hexyne. The previously obtained sample was submitted for elemental analysis:

Analysis Calculated for $C_6H_{12}N_2F_2O$: C, 43.4; H, 7.23; N, 16.8; F, 22.9.

Found: C, 45.3; H, 8.0 ; N, 15.6; F, 20.8.

*Aerojet-General Report No. 0235-01-15, January 1963, p. 12 (Confidential).

II Technical Discussion, A (cont.)

c. 1-Methyl-1-(difluoramino)cyclohexane

Approximately 18 g of difluoramine was refluxed over 2 ml of boron trifluoride-phosphoric acid complex, and 20 g (0.209 moles) of 1-methyl-1-cyclohexene was added dropwise. The mixture was allowed to reflux for 3 hours. Pentane (200 ml) was then added and the unreacted difluoramine was allowed to escape. The catalyst was separated and the pentane solution was dried over sodium sulfate and the solvent was distilled off through a 10 cm packed column. The residue was then vacuum-distilled to give 25.8 g (0.173 moles, 83% yield) of 1-methyl-1-(difluoramino)cyclohexane, bp 44°C, 14 mm.

Analysis Calculated for $C_7H_{13}NF_2$: C, 56.4; H, 8.72; N, 9.4; F, 25.5.

Found: C, 55.9; H, 9.10; N, 9.15; F, 25.2.

The infrared spectrum of 1-methyl-1-(difluoramino)-cyclohexane is shown in Figure 7. The 60 mc proton NMR spectrum (Figure 8) was obtained using a CCl_4 solution with TMS as an internal reference. The triplet at 1.26 ppm is assigned to the methyl group. The splitting indicated a t-alkyl difluoramine. The broad, poorly resolved signal at 1.59 ppm is assigned to the remaining cyclohexane ring protons. The 56.4 mc F^{19} NMR spectrum (Figure 9) was obtained using the same solution with $CFCl_3$ added as an internal reference. The broadened signal at -1250.4 cps (-22.17 ppm) is assigned to $-NF_2$.

d. Reaction of Boron Trifluoride with 1-Methyl-1-(difluoramino)cyclohexane

Boron trifluoride was bubbled through a solution of 1-methyl-1-(difluoramino)cyclohexane (3 g, 0.02 moles) in 15 ml of pentane until the solvent ceased to reflux (approximately 20 min). The pentane was decanted; the viscous oil which remained was dried for 1 hour under vacuum. The product was a white paste at room temperature, and did not solidify upon cooling to -30°C. It crystallized, however, when ether was added. The material was filtered under nitrogen and dried under vacuum.

II Technical Discussion, A (cont.)

Analysis Calculated for $C_7H_{13}NBF_4$: C, 42.5; H, 6.57; N, 7.08; F, 38.4

Found: C, 37.2; H, 6.18; N, 6.41; F, 39.8

The NMR spectrum was obtained with a similarly prepared sample in which SO_2 was used as the solvent. The SO_2 was allowed to evaporate and the sample was not evacuated. The residue was a liquid containing a small amount of SO_2. The F^{19} spectrum, using $CFCl_3$ as an external reference, consisted of a poorly resolved triplet at -3922 cps (-69.54 ppm), J = 17 cps, and a more intense signal at +8524 cps (+151.1 ppm). The latter signal was attributed to $BF_3^{\ominus}$.

e. Reduction of 1-Methyl-1-(difluoramino)cyclohexane

Into a 3-necked flask equipped with a reflux condenser an addition funnel, a thermometer, a magnetic stirrer and a nitrogen bubbler, was added 75 ml of diethyl ether, and 2.28 g (0.060 moles) of lithium aluminum hydride. 1-Methyl-1-(difluoramino)cyclohexane (3 g, 0.02 moles) was added dropwise to the solution with stirring at room temperature. The reaction was slightly exothermic, causing reflux for 1/2 hour. The solution was stirred for 2 days 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 using a 10 cm packed column. Vacuum distillation of the residue gave 1.62 g of colorless liquid, bp 40°C, 7 mm. Gas chromatography showed a 5 to 1 mixture of two components, which could not be resolved sufficiently for preparative separation.

Gaseous hydrogen chloride was bubbled into a pentane solution of the product and the white solid that precipitated was fractionally recrystallized by slowly adding pentane to a methylene chloride solution of the salts. The first fraction was a white solid, mp 173-177°C. The final fraction had a mp of 130 to 131°C.

II Technical Discussion, A (cont.)

Analysis Calculated for $C_7H_{16}NCl$: C, 56.2; H, 10.70; N, 9.36

Found: C, 56.6; H, 10.82; N, 9.71

f. 1,3,3-Tris(difluoramino)butane

To a refluxing mixture of approximately 50 g of difluoramine and 150 ml of 100% sulfuric acid (a solid at the reflux temperature of difluoramine) was added dropwise during a 30 min period, 10 g (0.168 moles) of freshly distilled methyl vinyl ketone. The mixture was allowed to reflux for 3 hours.

Pentane (150 ml) was then added and the unreacted difluoramine was allowed to escape. The pentane layer was separated, dried over sodium sulfate, and diluted with pentane to 200 ml. A 20-ml aliquot was stripped of solvent through a 25-cm platinum spiral column. The residue was then vacuum-distilled to give 2.13 g (0.010 moles, 60% yield) of 1,3,3-tris(difluoramino)-butane, bp 50°, 30 mm.

g. 1-Amino-3,3-bis(difluoramino)butane

A three-necked flask fitted with a reflux condenser (the exit of which was connected to a drying tube), a dropping funnel, a thermometer, and a magnetic stirrer, was loaded with 25 ml of tetrahydrofuran and 1 g of 81% assay lithium borohydride (0.04 moles). 1,3,3-Tris(difluoramino)butane (2.2g, 0.0104 moles) in 7 ml of pentane was added dropwise with stirring. The mixture was stirred at ambient temperature for 3 hours. After 25 ml of water was added, the mixture was extracted with three 30-ml portions of ether, which were combined and dried over sodium sulfate. Gaseous hydrogen chloride was bubbled into the ether solution until precipitation was complete. The ether was poured off and the solid was dried under vacuum to give 2.1 g (0.00995 moles, 96% yield) of 1-amino-3,3-bis(difluoramino)butane hydrochloride.

Analysis Calculated for $C_4H_{10}N_3F_4Cl$: C, 22.6; H, 4.72; N, 19.8.

Found: C, 21.5; H, 4.98; N, 18.8.

II Technical Discussion, A (cont.)

The fluorine analysis and NMR spectrum are not yet available. The infrared spectrum is shown in Figure 10.

h. 4,4-Bis(difluoramino)pentyl isocyanate

A solution of 5.0 g (0.0203 moles) of ethyl 5,5-bis-(difluoramino)hexanoate* and 0.84 g (0.025 moles) of 97% hydrazine in 10 ml of methanol was heated under reflux for 3 hours. The solvent was removed under vacuum and the viscous residue was kept at 0.1 mm Hg for 3 hours. To the residue was added 20 ml of chloroform and 60 ml of water containing 0.022 moles of hydrochloric acid. This mixture was kept at 0 to 3°C and stirred while a solution of potassium nitrite (2.02 g, 0.022 moles, 94% assay) in 5 ml of water was added dropwise over a 15 min period. The chloroform layer was separated and the aqueous layer was washed with 10 ml of ice-cold chloroform. The combined chloroform solutions were washed with two 10-ml portions of ice water and dried at 0°C for 2 hours over sodium sulfate. The solution was then placed in a 200-ml 3-necked flask fitted with a thermometer and a reflux condenser, the exit of which was connected to a drying tube and a wet test meter. The solution was heated at 55°C for 3 hours, during which time 260 ml (0.011 moles) of nitrogen was evolved, mainly during the first hour. The solvent was distilled off through a 10-in. Holzmann column, and the residue was distilled to give 2.0 g of colorless liquid, bp 61°C/0.25 mm. The infrared spectrum showed a strong isocyanate band at 4.4 μ, as well as all of the absorption bands of ethyl 5,5-bis(difluoramino)hexanoate.

i. 4,4-Bis(difluoramino)pentylurea

A 0.5-ml portion of the product of the above reaction was dissolved in 25 ml of methylene chloride, and anhydrous ammonia was bubbled through this solution for 10 min. The addition of pentane resulted in the precipitation of a white solid, mp 89.5°C after a recrystallization from methylene chloride-pentane.

*Aerojet-General Report No. 0235-01-15, January 1963, p. 9 (Confidential).

II Technical Discussion, A (cont.)

Analysis Calculated for $C_6H_{12}N_4F_4O$: C, 31.0; H, 5.18; N, 24.1; F, 32.7.

Found: C, 30.0; H, 5.15; N, 23.4; F, 27.6.

B. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

a. Amides

Several scouting experiments were carried out 2 years ago* in an attempt to fluorinate primary amides to either N,N-difluoro-derivatives or their hydrolysis product, difluoramine. The expected products, however, were not obtained. The fate of amides in these fluorination reactions was not determined at that time and so the fluorination was investigated once again. In the light of the recently obtained evidence for fluoramine, it seemed possible that primary amides might undergo fluorination to give hydrolytically unstable N-fluoro derivatives, which would be decomposed to fluoramine as shown below.

$$RCONH_2 + F_2 \xrightarrow{(H_2O)} \left[RCONHF\right] \longrightarrow RCOOH + \left[NH_2F\right]$$

Because of this possibility, the fluorination of acetamide was attempted in the presence of cyclohexanone, which has been shown to react with fluoramine to give ϵ-caprolactam.**

The fluorination of aqueous acetamide in the presence of an equimolar amount of cyclohexanone did not produce ϵ-caprolactam. Instead, the reaction products were identified as methylamine and ϵ-caprolactone. The formation of methylamine can be rationalized by the Hofmann rearrangement of N-fluoroacetamide:

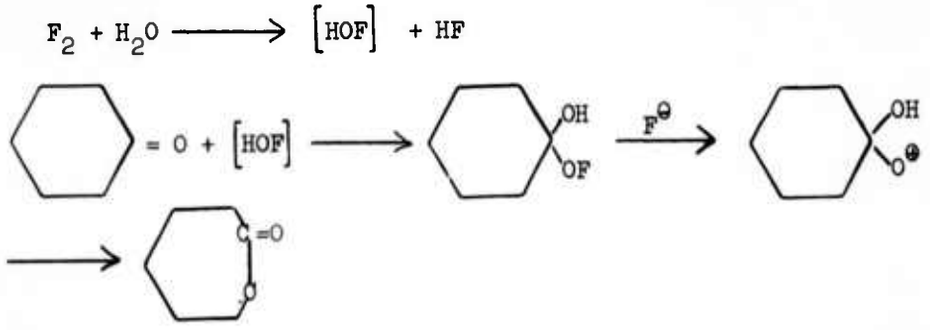
$$CH_3CONH_2 + F_2 \xrightarrow{(H_2O)} CH_3CONHF \xrightarrow{-HF} \left[CH_3\ddot{C}ON:\right] \xrightarrow{H_2O} CH_3NH_2 + CO_2$$

*Aerojet-General Report No. 2099 (Annual Summary), November 1961, p. 21 (Confidential).
**Aerojet-General Report No. 2381 (Annual Summary), October 1962, p. 33 (Confidential).

II Technical Discussion, B (cont.)

An interesting feature of this reaction is that it takes place in an acidic medium, although a base is required when other halogens are used to effect the Hofmann rearrangement.

ϵ-Caprolactone was found to be produced from the fluorination of aqueous cyclohexanone in the absence of acetamide, under either acidic or basic reaction conditions. The formation of lactones from ketones by the action of Caro's acid or related peroxygen compounds is well known*. It is possible that in this reaction the transformation is caused by either hydrogen peroxide or ozone, both of which are known to be produced in low concentration when elementary fluorine reacts with water. On the other hand, it is also possible that the reactive species is hypofluorous acid produced <u>in situ</u> by interaction of fluorine with water. Addition of HOF to the carbonyl function of cyclohexanone, followed by loss of fluoride ion and rearrangement would also account for ϵ-caprolactone formation:



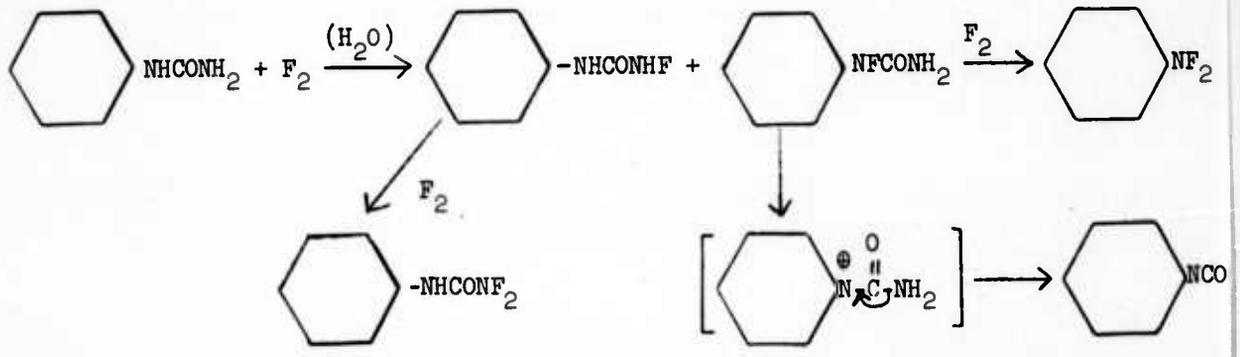
The fluorination of cyclohexanecarboxylic acid amide supplied additional evidence that N-fluoroamides undergo Hofmann rearrangement. In this reaction, in addition to cyclohexylamine, some cyclohexyl isocyanate (the Hofmann rearrangement intermediate) was isolated.

*For a brief review see W. von Doering and L. Speers, <u>J. Am. Chem. Soc.</u>, <u>72</u>, 5515 (1950); R. J. Kennedy and A. M. Stock, <u>J. Org. Chem.</u>, <u>25</u>, 1901 (1960).

II Technical Discussion, B (cont.)

b. Ureas

The direct fluorination of 1,3-dicyclohexylurea gave cyclohexyl isocyanate.* A similar reaction has been observed in the fluorination of cyclohexylurea. The products of this reaction were cyclohexyl isocyanate, difluoraminocyclohexane and N,N-difluorocyclohexylurea:



N,N-Difluorocyclohexylurea was characterized by its elemental analysis, by its infrared spectrum, and by its F^{19} (Figure 11) and proton (Figure 12) NMR spectra.

The fluorination of aqueous thiourea was investigated to determine if there was any analogy between this reaction and that of urea. Fluorine was readily consumed in this fluorination, but the expected N,N-difluorothiourea was not produced. On evaporation of the aqueous fluorination mixture, a white solid (mp 145°C) containing 33% fluorine was isolated. Its F^{19} NMR spectrum (in aqueous solution) consisted of a single peak at +2830 cps from trifluoroacetic acid, suggesting that fluorine was present in the form of bifluoride ion; the F^{19} NMR spectrum of aqueous ammonium bifluoride shows a single sharp peak at +2834 cps from trifluoroacetic acid. On the basis of its F^{19} NMR spectrum, infrared spectrum, and elemental analysis, the compound was tentatively identified as a double bifluoride salt of aminoiminomethyldisulfide, resulting from the oxidative coupling of thiourea:

*Aerojet-General Report No. 0235-01-15, January 1963, p. 17 (Confidential).

II Technical Discussion, B (cont.)

$$NH_2CSNH_2 \xrightarrow[H_2O]{F_2} \left[NH_2C(=NH)\text{-}S\right]_2 \cdot 4HF$$

c. Carbamates

Diethyl tetramethylenedicarbamate was fluorinated under the conditions that were used previously for the lower members of the α,ω dicarbamate series to give 1,4-bis(difluoramino)butane (10% yield), as well as several partially fluorinated intermediates:

$$\left(CH_2CH_2NHCOOC_2H_5\right)_2 + F_2 \xrightarrow{(H_2O)} NF_2(CH_2)_4NF_2$$

1,4-Bis(difluoramino)butane was characterized by its elemental analysis and infrared spectrum (Figure 13).

2. Experimental

a. Fluorination of Acetamide

A solution of 29.5 g (0.5 mole) of acetamide and 49 g (0.5 mole) of cyclohexanone in 850 ml water was fluorinated at 0 to 5°C with elemental fluorine (diluted with nitrogen, 1 to 4) until 22 liters of fluorine was passed into the reaction mixture. The reaction mixture was extracted with five 50-ml portions of methylene chloride. The combined extracts were dried, filtered, and concentrated. The residual liquid was fractionated and 35 g of cyclohexanone was recovered. Further fractionation gave 8 g of a colorless liquid, bp 45 to 47°C/0.1 mm, n_D^{25} 1.4490, which on the basis of its infrared spectrum and its physical properties (reported* bp 96.5 to 97.5°C/15 mm, n_D^{25} 1.4481) was identified as ϵ-caprolactone.

A 10% aliquot of the aqueous solution was evaporated to dryness at 35 to 40°C/0.2 mm. The residual solid was treated with 50 ml of absolute ethanol at 30°C and filtered. On the addition of diethyl ether the ethanolic solution deposited a white solid (1.5 g) which was identified as

*C. S. Marvel and E. R. Birkhimer, Am. Chem. Soc. J., 51, 260 (1929).

II Technical Discussion, B (cont.)

acetamide. The ethanol insoluble portion of the solid was dissolved in 5.0 ml of water. The aqueous solution was made strongly basic by the addition of potassium hydroxide, and the resulting mixture was treated with p-toluenesulfonyl chloride. The reaction mixture was acidified and extracted with 15 ml of methylene chloride. Evaporation of the solvent gave 1.0 g of a white solid which had a melting point of 73 to 75°C when alone or when mixed with an authentic sample of N-methyl-p-toluenesulfonamide.

b. Fluorination of Cyclohexanone

A solution of 98.2 g (1.0 mole) of cyclohexanone in 1200 ml water was fluorinated at 0 to 5°C until 18 liters of fluorine was consumed. The reaction mixture was extracted with seven 50-ml portions of methylene chloride and the combined extracts were dried, filtered, and concentrated. The residual liquid was fractionated to give 75 g of cyclohexanone. The distillation residue, 25 g, was fractionated further to give 10 g of a colorless liquid (bp 42 to 44°C/0.1 mm), which was identified as ϵ-caprolactone on the basis of its infrared spectrum, proton NMR spectrum, and its physical properties. The residual material (bp > 120°C/0.1 mm) solidified on standing. On the basis of its infrared spectrum the material was tentatively identified as a polyester arising from polymerization of ϵ-caprolactone.

c. Fluorination of Cyclohexanecarboxylic Acid Amide

A solution (mainly suspension) of 12.7 g (0.01 mole) of cyclohexanecarboxylic acid amide in 350 ml water was fluorinated at 0 to 5°C until 4.5 liters of fluorine was consumed. The fluorination mixture was filtered and the white solid was washed with n-hexane. The solid amounted to 8.0 g and was identified as starting material. The aqueous filtrate was extracted with five 30-ml portions of n-hexane. The hexane extracts were combined with the washings, and were dried, filtered, and concentrated. The residue was distilled to give 2.0 g of a colorless liquid (bp 28 to 32°C/0.1 mm) which was identified as impure cyclohexyl isocyanate by its infrared spectrum and by converting to the known ethyl cyclohexylcarbamate.

II Technical Discussion, B (cont.)

d. Fluorination of Cyclohexylurea

A suspension of 27.6 g (0.2 mole) of cyclohexylurea in 600 ml water was fluorinated at 0 to 5°C until 18 liters of fluorine was consumed. The reaction mixture was extracted with four 50-ml portions of methylene chloride; the combined extracts were dried, filtered and concentrated. The residual liquid was fractionated to give 5.5 g of a colorless liquid (bp 35 to 42°C/26 mm, n_D^{25} 1.4010), 3.5 g of a colorless liquid (bp 20 to 30°C/0.1 mm), and 9.0 g of a colorless liquid (solidified in the receiver) which had a boiling range of 70 to 80°C/0.1 mm. The lowest boiling product was identified by its infrared spectrum as impure difluoraminocyclohexane. The material of the second fraction was found to be cyclohexyl isocyanate. The crude solid product was recrystallized from n-heptane to white needles (mp 59 to 60°C) and was identified as N,N-difluorocyclohexylurea.

Analysis Calculated for $C_6H_{11}N_2F_2O$: C, 47.18; H, 6.79; N, 15.69; F, 21.33.

Found: C, 46.8; H, 6.9: N, 15.4; F, 22.5.

The 60 mc proton NMR spectrum (Figure 12) was obtained using a carbon tetrachloride solution with TMS added as an internal reference. The weak, broad signal at about 6.4 ppm is assigned to the amide proton - NHCO-. The signal at about 3.6 ppm, which is similar in appearance, is assigned to the proton on the substituted ring carbon, >CHNH-. This signal would be expected to be a very complex multiplet; thus the fact that no form structure is resolved is not surprising. The broad, complicated multiplet to high field (peaks at 108, 87 and 78 cps among others) is assigned to the remaining ring protons.

The 56.4 mc F^{19} NMR spectrum (Figure 11) was obtained using the same sample with Freon-11 added as an internal reference. The spectrum consists of a single, relatively narrow signal at -1850 cps (-32.8 ppm) from Freon-11. It is assigned to the N,N-difluorocyclohexylurea fluorines.

II Technical Discussion, B (cont.)

e. Fluorination of Thiourea

A solution of 36 g (0.5 mole) of thiourea in 600 ml water was fluorinated with elemental fluorine (diluted with nitrogen, 1 to 4) at 0 to 5°C until 20 liters of fluorine was consumed. The reaction mixture was extracted with five 50-ml portions of methylene chloride, followed by five 50-ml portions of diethyl ether, but distillation of the corresponding extracts gave no residue. The aqueous solution was evaporated to dryness at 25 to 35°C/0.2 mm. The white residue was recrystallized from water-ethanol to give 25 g of white solid, mp 144 to 146°C.

Analysis Calculated for $C_2H_{10}N_4F_4S_2$: C, 10.4; H, 4.4; N, 24.3; F, 33.0.

Found: C, 9.8; H, 3.9; N, 24.0; F, 34.0.

f. Fluorination of Diethyl Tetramethylenedicarbamate

A suspension of 70 g (0.3 mole) of diethyl tetramethylenedicarbamate in 650 ml water was fluorinated at 0 to 5°C with elementary fluorine (diluted with nitrogen, 1 to 4) until 27 liters of fluorine was consumed. The reaction mixture was extracted with five 50-ml portions of methylene chloride and the combined extracts were dried, deacidified with solid sodium bicarbonate, filtered, and concentrated. The residual liquid was fractionated to give 16.0 g of a colorless liquid, bp 50 to 51°C/26 mm. The material was found to be 70 to 75% pure 1,4-bis(difluoramino)butane; an analytical sample was separated by gas chromatography.

Analysis Calculated for $C_4H_8N_2F_4$: C, 30.0; H, 5.0; N, 17.5; F, 47.5.

Found: C, 30.5; H, 5.0; N, 17.6; F, 44.3.

The infrared spectrum (Figure 13) of the material is very similar to those of the lower α,ω-bis(difluoramino)alkane homologues, with the exception of an absorption peak in the carbonyl region (5.8 μ), suggesting the presence of a small amount of a foreign material.

II Technical Discussion, B (cont.)

Further fractionation gave 15.0 g of higher boiling liquid, but the mixture was not separated.

C. FLUORAMMONIUM SALTS (A. Remanick)

1. Discussion

It has previously been shown that hydrolysis of ethyl N-fluorocarbamate with concentrated sulfuric acid, followed by reaction of the resulting mixture with cyclohexanone, gave caprolactam. The latter reaction was formulated as the addition of fluoramine to the ketone, followed by Beckmann rearrangement. Furthermore, NMR analysis of the sulfuric acid hydrolysate indicated the presence of the monofluorammonium cation.*

This work has been continued with the aim of isolating fluorammonium salts which are potentially valuable as solid oxidizers. It was found that the reaction of ethyl N-fluorocarbamate with either insufficient or excess quantities of concentrated sulfuric acid, or with oleum, yields (on dilution with ethyl ether) a white, hygroscopic solid, tentatively identified as fluorammonium bisulfate. The F^{19} NMR spectrum in concentrated sulfuric acid was consistent with this structure. Elemental analyses of several preparations indicated 80 to 90% purity. Methods of purification are being investigated.

The isolation of fluorammonium trifluoracetate was attempted by the route shown in the following equation:

$$FNHCO_2Et + \text{excess } H_2SO_4 \longrightarrow FNH_3HSO_4 + EtOSO_3H + H_2SO_4$$

$$FNH_3HSO_4 \xrightarrow[CF_3CO_2H]{Ba(CF_3CO_2)_2} FNH_3CF_3CO_2 + \underline{Ba(EtOSO_3)_2} + \underline{Ba(SO_4)}$$

This metathetical reaction was attempted on the sulfuric acid-fluorocarbamate hydrolysate without isolating fluorammonium bisulfate.

*Aerojet-General Report No. 2381, October 1962, p. 32 (Confidential).

II Technical Discussion, C (cont.)

It was found, however, that the fluorammonium cation coprecipitated with barium sulfate - probably as the bisulfate. This result was unexpected on the basis of the solubility of ammonium bisulfate in trifluoracetic acid.*

The preparation of fluorammonium perchlorate was also attempted by the reaction of anhydrous perchloric acid with ethyl N-fluorocarbamate. Under the conditions employed (70°C, 100% excess $HClO_4$), the reaction was relatively slow as evidenced by slow evolution of carbon dioxide and recovery of starting materials. A trace quantity of an NF containing solid was isolated. More vigorous conditions will be tried in the future.

Because secondary alkyl carbamates are hydrolyzed more easily than primary alkyl carbamates, isopropyl N-fluorocarbamate was prepared by the aqueous fluorination of isopropyl carbamate and was characterized by its infrared spectrum and elemental analysis. The use of this compound as a fluorammonium source has not yet been attempted.

2. Experimental

a. Sulfuric Acid Hydrolysis of Ethyl N-Fluorocarbamate

(1) Excess Ethyl N-Fluorocarbamate

To 4.0 (0.04 mole) of 100% sulfuric acid at 5 to 10°C was added 5.4 g (0.05 mole) of ethyl N-fluorocarbamate. The reaction mixture was heated gradually to 95°C and kept at this temperature for 3.5 hours. Slow gas evolution began at 55 to 60°C, and three gas samples were collected in evacuated infrared gas cells. A sample taken at the beginning of the reaction contained a mixture of carbon dioxide and ethylene. The composition of the second gas sample taken 45 min later was the same. The third gas sample, taken near the end of the reaction, contained silicon tetrafluoride in addition to carbon dioxide and ethylene. During the reaction the mixture became cloudy and a solid was deposited. At the end of the run the reaction mixture was subjected to 0.1 mm vacuum at 60°C, and approximately 1 g of N-fluorocarbamate was removed.

*G. S. Eujioka and G. H. Cady, J. Am. Chem. Soc., 79, 2451 (1957).

II Technical Discussion, C (cont.)

The reaction mixture was cooled to room temperature and a 1 g aliquot of the pasty residue was added to 30 ml of dry diglyme. A white insoluble solid was removed by filtration (N_2 atmosphere) and was washed with five 5-ml portions of diglyme, followed by five 8-ml portions of dry ether. The solid, mp 135 to 145°C, was dried under vacuum.

Analysis Calculated for $NH_3F^{\oplus}HSO_4^{\ominus}$: N, 10.5; F, 14.2

Found: N, 12.2; F, 12.3.

After the material was kept in a closed vial at room temperature for five weeks, a second analysis showed 12.8% nitrogen and 10.6% fluorine.

Another aliquot of the original reaction mixture was diluted with 100% sulfuric acid. The F^{19} NMR spectrum of this solution consisted of a symmetrical quadruplet similar to that of the original product of the reaction of ethyl N-fluorocarbamate with sulfuric acid.

(2) Excess Sulfuric Acid

Ethyl N-fluorocarbamate (0.75 g, 0.007 mole) was reacted with 3.67 g (0.0374 mole) of 100% sulfuric acid at 90°C for 30 min. Carbon dioxide evolution ceased after 15 min at this temperature. The reaction mixture was cooled and half of the solution was poured, with stirring, into 15 ml of dry ether. An oil formed which solidified on standing overnight. The solid was filtered under nitrogen, washed with diethyl ether, and vacuum-dried to yield 0.3 g of white hygroscopic powder.

Analysis Found: N, 8.88%; F, 11.6%.

(3) Oleum

To 4.55 g (0.0416 mole) of ethyl N-fluorocarbamate, 4.8 g (0.060 mole) of 90% oleum was added (with stirring) at 0 to 5°C. The reaction was vigorous and gas evolution started after about half of the oleum

II Technical Discussion, C (cont.)

had been added. After the addition was completed, the mixture was stirred at room temperature. After 2 hours, a small portion of the mixture was removed and added to diethyl ether. An oil formed which solidified after 30 min. The solid was filtered off and washed with diethyl ether.

Analysis Found: N, 8.60; F, 12.1.

The F^{19} NMR spectrum of this material in sulfuric acid was identical to that obtained previously.

The remainder of the original hydrolysis mixture gave 0.77 g of a sticky white solid when quenched with ether after 18 hours.

b. Metathesis of Fluorammonium Bisulfate with Barium Trifluoroacetate

In a 25-ml volumetric flask was placed 3.29 g (0.0308 moles) of ethyl N-fluorocarbamate and 18.44 g (0.188 moles) of 99.8% sulfuric acid. The flask was protected from the moisture by a sulfuric acid bubbler. The reaction mixture was slowly heated to 90°C and maintained at this temperature for 45 min. Then the reaction mixture was cooled to room temperature and diluted to 25 ml with trifluoroacetic acid.

To 18.60 ml of a trifluoroacetic acid-barium trifluoroacetate solution containing 0.147 g of barium/ml was added 3.0 ml of the diluted hydrolysate, with stirring. This amount of barium solution was theoretically sufficient to precipitate all the sulfuric acid and ethyl sulfate present in the hydrolysate. The mixture was centrifuged to remove $BaSO_4$. The supernatant liquid was still cloudy. The precipitate was washed twice with trifluoroacetic acid followed by centrifugation and the washings were combined with the original supernatant solution. The combined, somewhat cloudy, solution was centrifuged again and the clear solution was decanted. Evaporation under vacuum gave a small amount of non-oxidizing oil which solidified on the addition of ether. The solid was found (by analysis) to be barium trifluoroacetate.

II Technical Discussion, C (cont.)

The original solid precipitate was washed with ether and dried under vacuum. This white powder was found to be impure barium sulfate containing some nitrogenous material (0.5% N). A suspension of this material was oxidized to aqueous potassium iodide.

c. Hydrolysis of Ethyl N-Fluorocarbamate with Perchloric Acid

In a 3-necked flask equipped with a dropping funnel, a thermometer, a magnetic stirrer, and a sulfuric acid gas bubbler, was placed 3.06 g of 61% perchloric acid (0.0186 moles of $HClO_4$, 0.0665 moles of H_2O) and 2.0 ml of trifluoracetic acid. The solution was cooled and 13.9 g (0.0665 mole) of trifluoroacetic anhydride was added, with stirring, at a rate which did not allow the temperature to rise above 20°C. To this solution was added 1.0 g (0.0093) of ethyl N-fluorocarbamate, and the resulting solution was evacuated at 30 mm to remove the major portion of trifluoracetic acid. The solution was then heated to 68°C over a 1-hour period. Gas evolution commenced at about 60°C. A gas sample which was removed after 1 hour contained carbon dioxide, trifluoroacetic acid, and a trace of ethylene. Heating at 68°C was continued for an additional 30 min at which time gas evolution had virtually ceased. When the reaction mixture was cooled to room temperature, an oil separated.

The mixture was distilled at 0.1 mm to a pot temperature of 68°C. The infrared spectrum of the distillate indicated perchloric acid, trifluoroacetic acid, and ethyl N-fluorocarbamate. A semisolid pot residue was washed with carbon tetrachloride. This residue separated into two layers on treatment with dry diethyl ether. The viscous bottom layer solidified on standing. The solid was filtered under nitrogen and washed with ether to give about 5 mg of a white, oxidizing solid.

Analysis Calculated for FNH_3ClO_4: N, 10.5%; F, 14.0%.

Found: N, 13.0%; F, 10.3%.

II Technical Discussion, C (cont.)

d. Isopropyl N-Fluorocarbamate

A suspension of 103 g (1.0 mole) of isopropyl carbamate in 500 ml water was fluorinated at 0 to 5°C until 22 liters of fluorine was consumed. The reaction mixture was filtered to remove unreacted starting material and then extracted with methylene chloride. Drying over calcium sulfate and removal of solvent under reduced pressure gave 42 g of an oil which partially solidified on standing. The mixture was filtered and the filter cake was washed with pentane. The solid was identified as isopropyl carbamate. The filtrate was concentrated and the residue was distilled to give 10.3 g of a colorless liquid, bp 46°C/3.5 mm. The crude product was redistilled using a short Vigreaux column to give 5.0 g (middle fraction) of a colorless liquid, bp 57°C/6 mm, n_D^{25} 1.3972.

Analysis Calculated for $C_4H_8FNO_2$: C, 39.6; H, 6.60; N, 11.6; F, 15.7.

Found: C, 40.0; H, 7.32; N, 11.8; F, 14.7.

III. PERSONNEL

The experimental synthesis work was performed by F. J. Gerhart, M. Mascari, A. H. Remanick, E. D. Gilley, V. Grakauskas and K. Baum. Analytical support was provided by H. Nelson, K. Inouye, D. I. Matson, and H. W. Pust.

Report No. 0235-01-16

TABLE 1

MASS SPECTRAL CRACKING PATTERN OF 3-FLUORO-3-(DIFLUORAMINO)HEXANE

M/e	%	Possible Ions
15	18.0	CH_3
19	Negligible	F
20	Negligible	HF
27	83.0	C_2H_3
29	82.0	C_2H_5
31	Negligible	CF
33	9.0	NF
39	25.0	C_3H_3
41	79.0	C_3H_5
43	100.0	C_2F/C_3H_7
45	4.0	CNF
53	8.0	C_4H_5
55	95.0	C_3F
59	10.0	FC_3H_4
61	70.0	C_5H
83	25.0	C_6H_{11}
94	1.0	FC_6H_3
103	4.0	FC_6H_{12}
126	Negligible	FC_6H_2NF
144	Negligible	HC_6FNF_2
146	Negligible	$H_3C_6FNF_2$

CEC 21-130 68 v at 20 μa

Table 1

TABLE 2

MASS SPECTRAL CRACKING PATTERN OF
2-FLUORO-2-(DIFLUORAMINO)HEXANE

M/e	%	Possible Ions
15	18.5	CH_3
19	Negligible	F
20	0.5	HF
27	58.0	C_2H_3
29	48.0	C_2H_5
31	Negligible	CF
33	8.7	NF
41	76.0	C_3H_5
43	100.0	C_2F/C_3H_7
45	Negligible	CNF
52	Negligible	NF_2
55	66.0	C_3F/C_4H_7
57	10.7	C_4H_9
59	10.5	C_2H_2NF
61	41.5	C_5H
69	Negligible	C_3NF
73	5.0	C_6H
83	25.0	C_6H_{11}
93	1.0	FC_6H_2
103	3.0	FC_6H_{12}/FC_4H_3NF
116	Negligible	FC_5H_4NF
129	Negligible	FC_6H_5NF
131	Negligible	FC_6H_7NF
145	Negligible	$FC_6H_2NF_2$

CEC 21-130 68 v at 20 μa

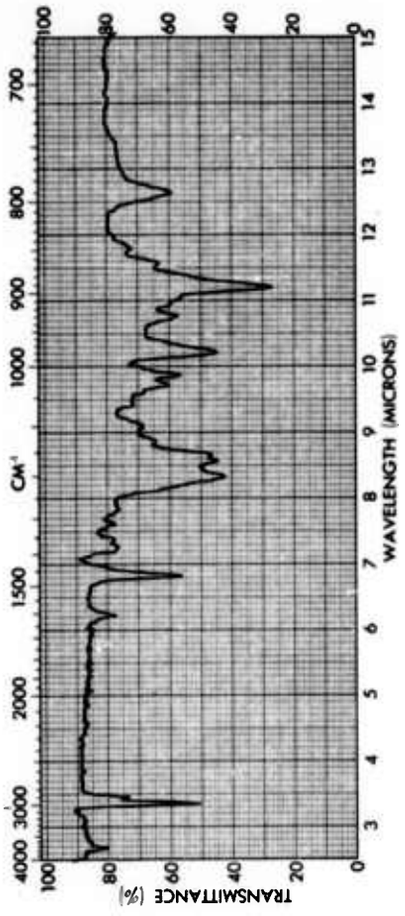


Figure 1 Infrared Spectrum of 3-Fluoro-3-(difluoramino)hexane

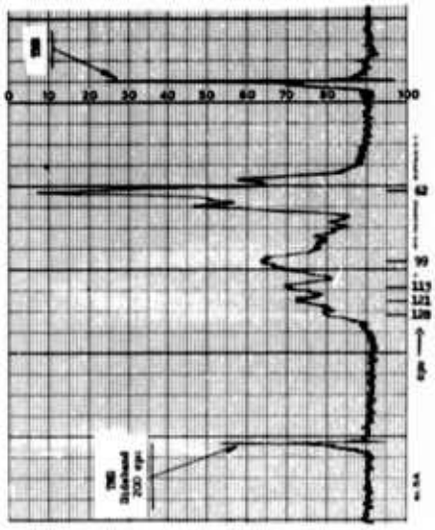


Figure 2 Proton NMR Spectrum of 3-Fluoro-3-(difluoramino)hexane

Figures 1 and 2

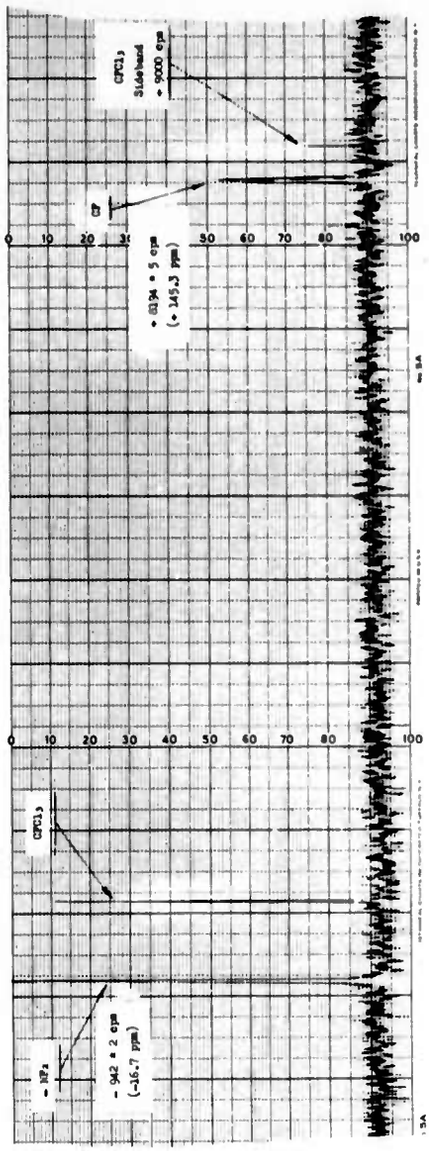


Figure 3 Fluorine NMR Spectrum of 3-Fluoro-3-(difluoramino)hexane

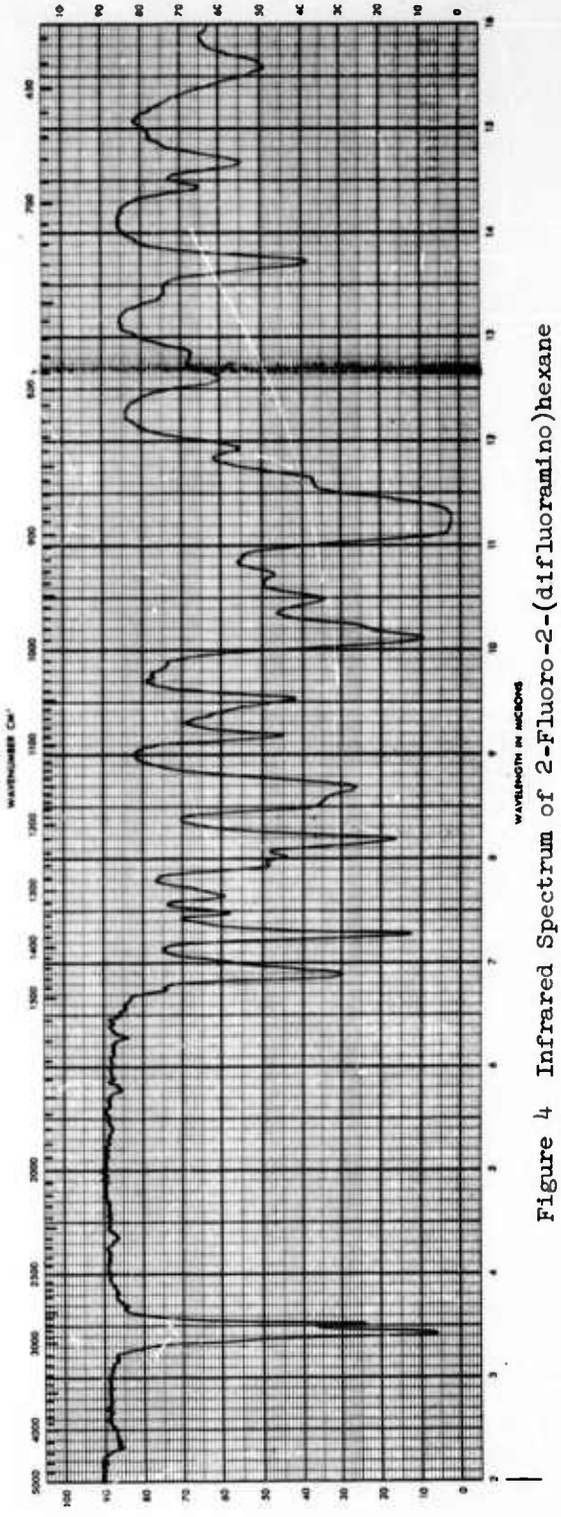


Figure 4 Infrared Spectrum of 2-Fluoro-2-(difluoramino)hexane

Figures 3 and 4

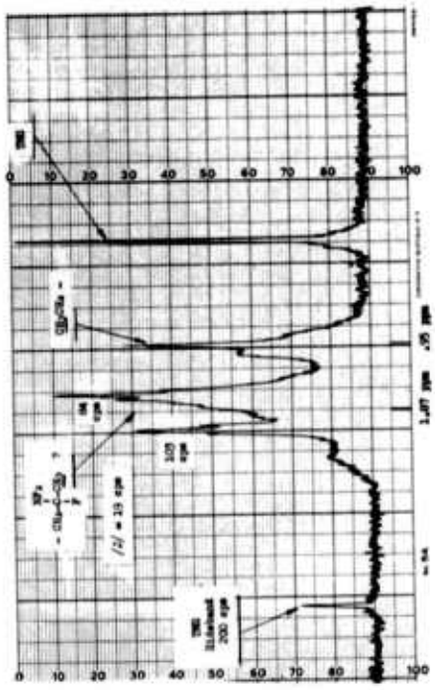


Figure 5 Proton NMR Spectrum of 2-Fluoro-2-(difluoramino)hexane

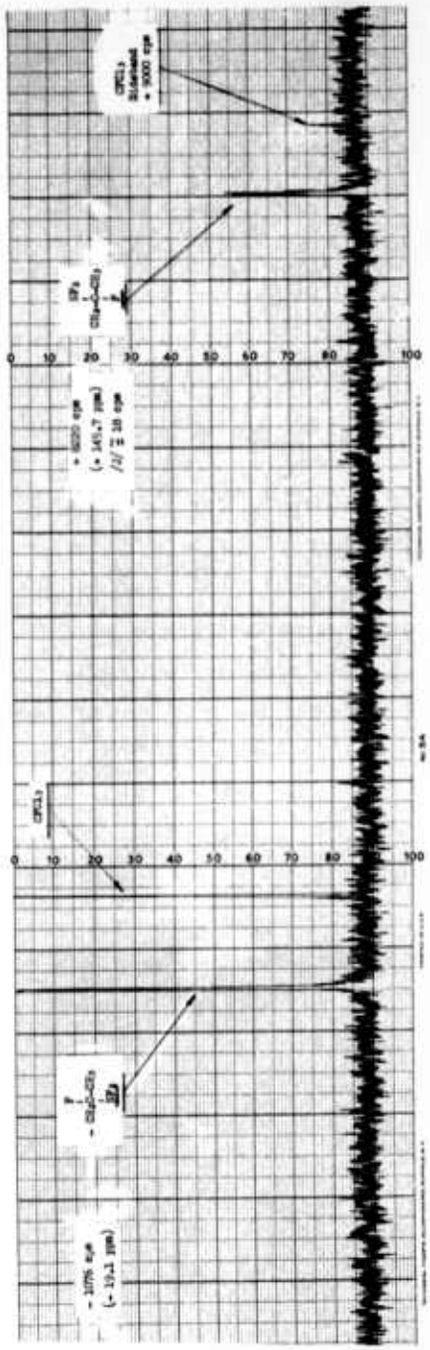


Figure 6 Fluorine NMR Spectrum of 2-Fluoro-2-(difluoramino)hexane

Figures 5 and 6

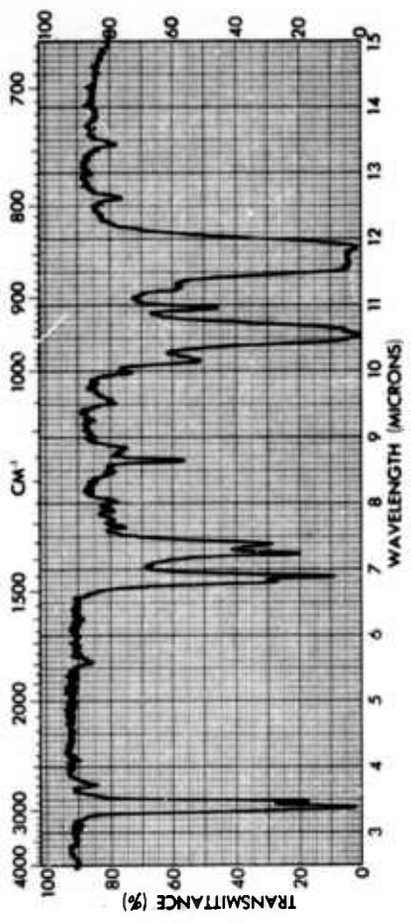


Figure 7 Infrared Spectrum of 1-Methyl-1-(difluoramino)cyclohexane

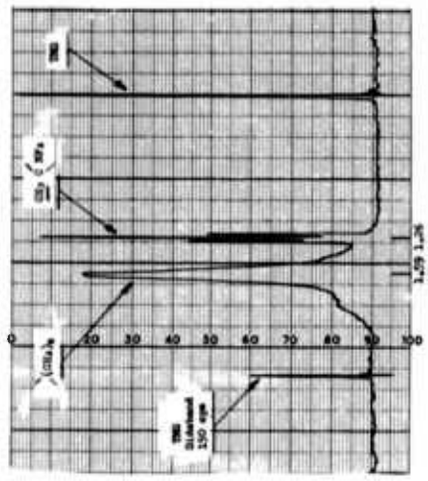


Figure 8 Proton NMR Spectrum of 1-Methyl-1-(difluoramino)cyclohexane

Figures 7 and 8

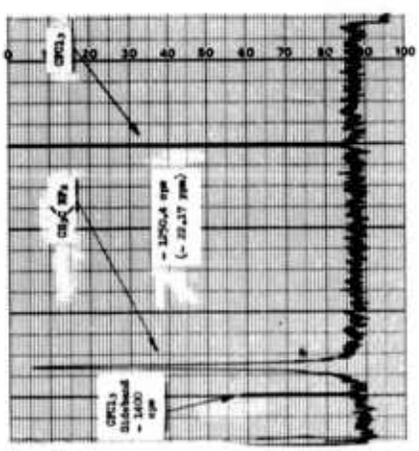


Figure 9 Fluorine NMR Spectrum of 1-Methyl-1-(difluoramino)cyclohexane

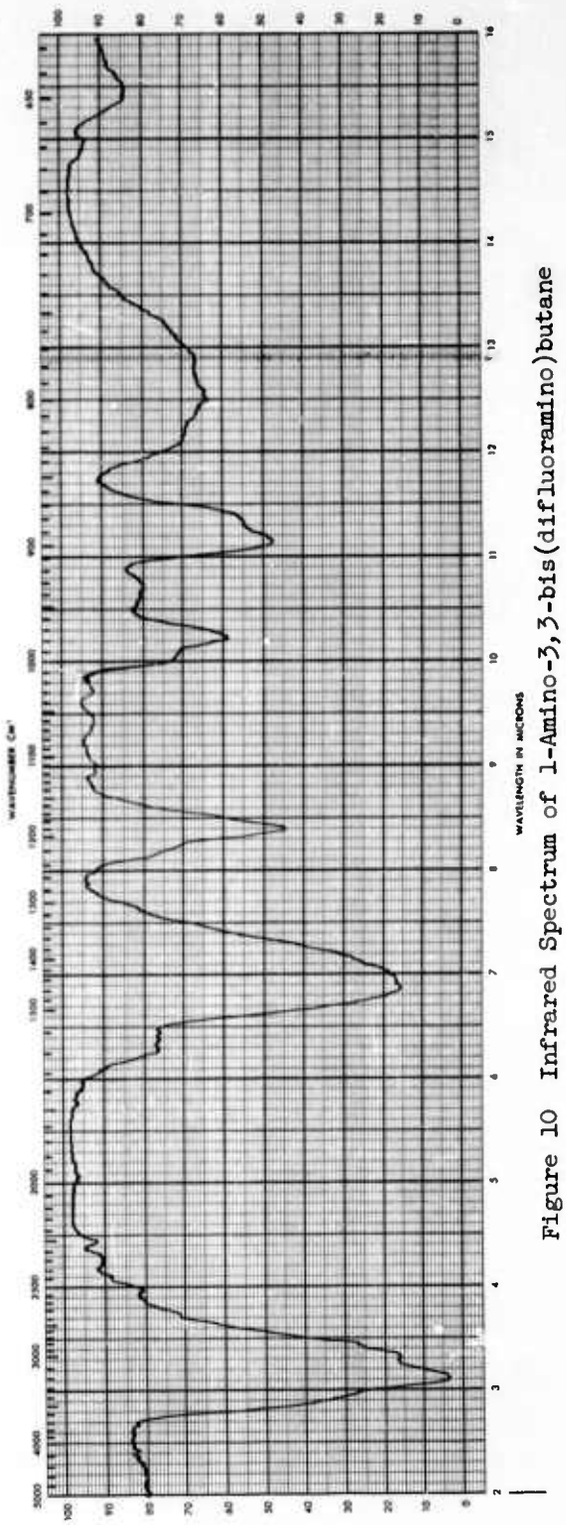


Figure 10 Infrared Spectrum of 1-Amino-3,3-bis(difluoramino)butane

Figures 9 and 10

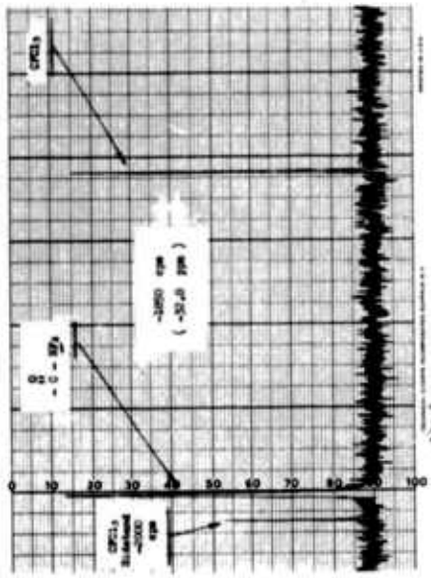


Figure 11 Fluorine NMR Spectrum of N,N-Difluorocyclohexylurea

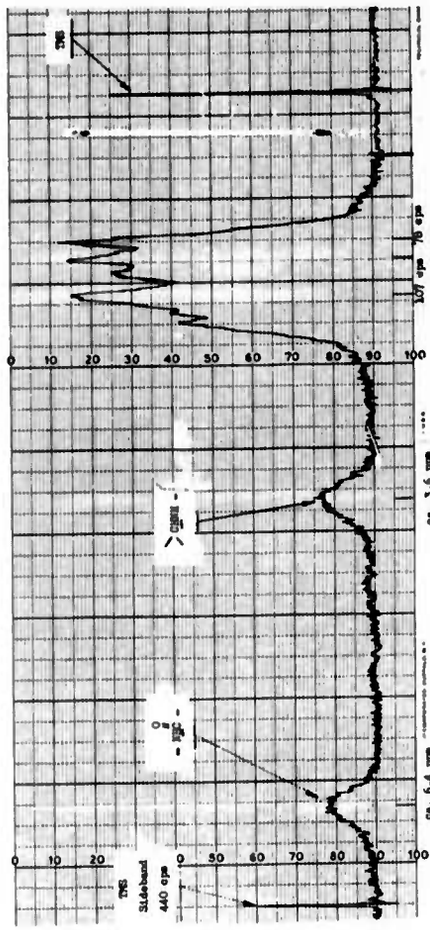
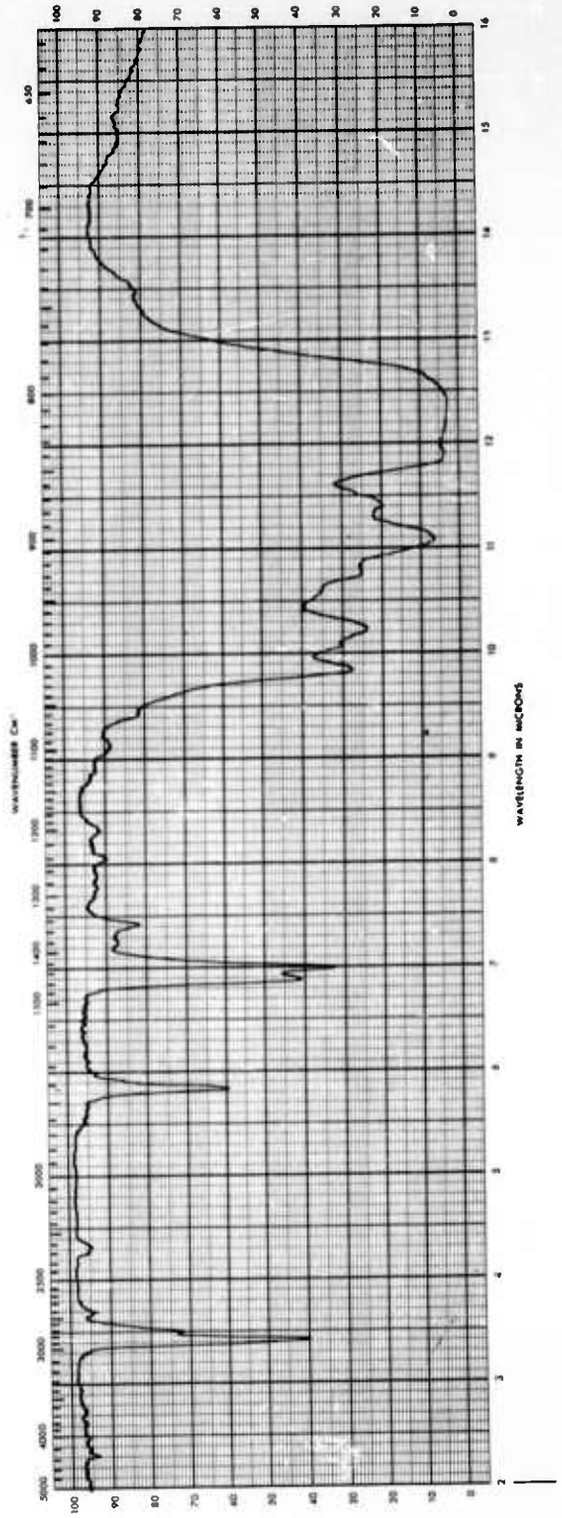


Figure 12 Proton NMR Spectrum of N,N-Difluorocyclohexylurea

Figures 11 and 12



Infrared Spectrum of 1,4-bis(difluoramino)butane

Figure 13

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